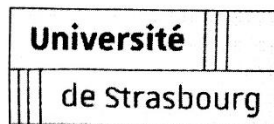




UNIVERSITÀ
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HR EXCELLENCE IN RESEARCH



Da un secolo, oltre.

PhD in Chemical Science

CYCLE XXXVIII

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Biopolymer-Enabled Soft Electronics

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Résumé

1. Introduction

Les dispositifs d'électronique souple visent à associer des fonctions électroniques à la flexibilité mécanique des tissus biologiques, des systèmes portables et des dispositifs ionotroniques émergents.[1,2] Leurs performances dépendent non seulement du transport de charge, de la fidélité du signal, ainsi que de leur capacité d'étirement, de leur adhésion conformable, de leur stabilité en conditions réelles et de leur confort à long terme. Les principaux matériaux utilisés dans ce domaine incluent les élastomères de silicone, les composites conducteurs et les conducteurs organiques mixtes ioniques et électroniques (OMIEC). Ces plateformes offrent de bons niveaux de performance, mais reposent sur des ressources pétrochimiques, sur une soutenabilité limitée et sur des stratégies de dopage complexes.

Les hydrogels représentent une alternative intéressante, car leurs réseaux polymères hydratés reproduisent l'ionoconductivité et la viscoélasticité des tissus mous.[2-5] Toutefois, les hydrogels conventionnels restent sensibles à la déshydratation, au gel de l'eau, à une stabilité mécanique limitée et à des variations de leurs propriétés ioniques en conditions ambiantes.

Les biopolymères offrent une voie prometteuse pour dépasser ces limitations. Des polymères naturels comme l'alginate, la gélatine et le caséinate possèdent des fonctionnalités ioniques intrinsèques, notamment des groupes carboxylate, amine et phosphate, qui leur permettent de former des réseaux par coordination ionique ou par des réactions enzymatiques.[6-8] Ils sont renouvelables, biodégradables et chimiquement riches, ce qui rend possible l'intégration de fonctions multiples sans recourir à des additifs synthétiques. Leur principale faiblesse, à savoir leur instabilité environnementale, peut être atténuée par une conception moléculaire rationnelle, à un contrôle précis de l'architecture du réseau et à l'utilisation de milieux dispersants capables de limiter la déshydratation et le gel.

Cette thèse présente une approche unifiée pour transformer des hydrogels et organohydrogels à base de biopolymères en matériaux fonctionnels pour l'électronique souple. Au travers de cinq projets, des polymères naturels sont conçus pour former des réseaux transparents, ioniquement conducteurs, mécaniquement robustes et stables en conditions réelles, adaptés à des applications de détection de la déformation, de la température et de l'humidité, d'électrolytes polymères gélifiés pour supercondensateurs, et de dispositifs neuromorphiques optoioniques. Chaque projet s'appuie sur le précédent et établit des règles de conception reliant les interactions ion-polymère, l'organisation structurale à l'échelle nanométrique et les performances du dispositif. L'ensemble de ce travail montre que les biopolymères peuvent fonctionner comme des matériaux électroniques actifs plutôt que comme de simples matrices passives, ouvrant de nouvelles perspectives pour une électronique souple écoresponsable.

2. Résultats et discussions

2.1 Organohydrogels alginate-gélatine multiréactifs (Projet 1)

Les organohydrogels alginate-gélatine (AlgGel) ont été conçus en combinant la capacité de coordination ionique de l'alginate avec la thermosensibilité et l'élasticité de la gélatine. L'introduction de glycérol a permis de stabiliser l'hydratation et d'empêcher le gel de l'eau, produisant des matrices transparentes et mécaniquement souples. La réticulation avec des ions de charge et d'affinité différentes (Mn^{2+} , Cu^{2+} , Fe^{3+} , Zr^{4+}) a généré une série de matériaux présentant une structure et des propriétés modulables de manière systématique.

L'ion coordonnant s'est révélé être le principal facteur contrôlant la densité du réseau, la température de transition vitreuse, les propriétés mécaniques et la conductivité ionique. Mn^{2+} et Cu^{2+} ont formé des réseaux extensibles (jusqu'à environ 140 % de déformation), tandis que Fe^{3+} et Zr^{4+} ont produit des structures plus denses et plus rigides (module de Young atteignant $\sim 2,5$ MPa).

L'analyse par calorimétrie différentielle a montré la présence exclusive d'eau non gelable, assurant une stabilité mécanique et ionique en dessous de 0 °C. Ces matériaux ont présenté des réponses réversibles à la température et à l'humidité dans des plages pertinentes pour des applications physiologiques. Leur sensibilité thermique (jusqu'à 0,19 K⁻¹) et leur sensibilité à l'humidité (~0,02 RH⁻¹) proviennent respectivement de la mobilité ionique dépendante de la température et de l'adsorption de vapeur d'eau. Grâce au glycérol, qui stabilise la teneur en eau, les réponses sont restées entièrement réversible et sans dérive pour tous les échantillons réticulés (**Figure 1**).

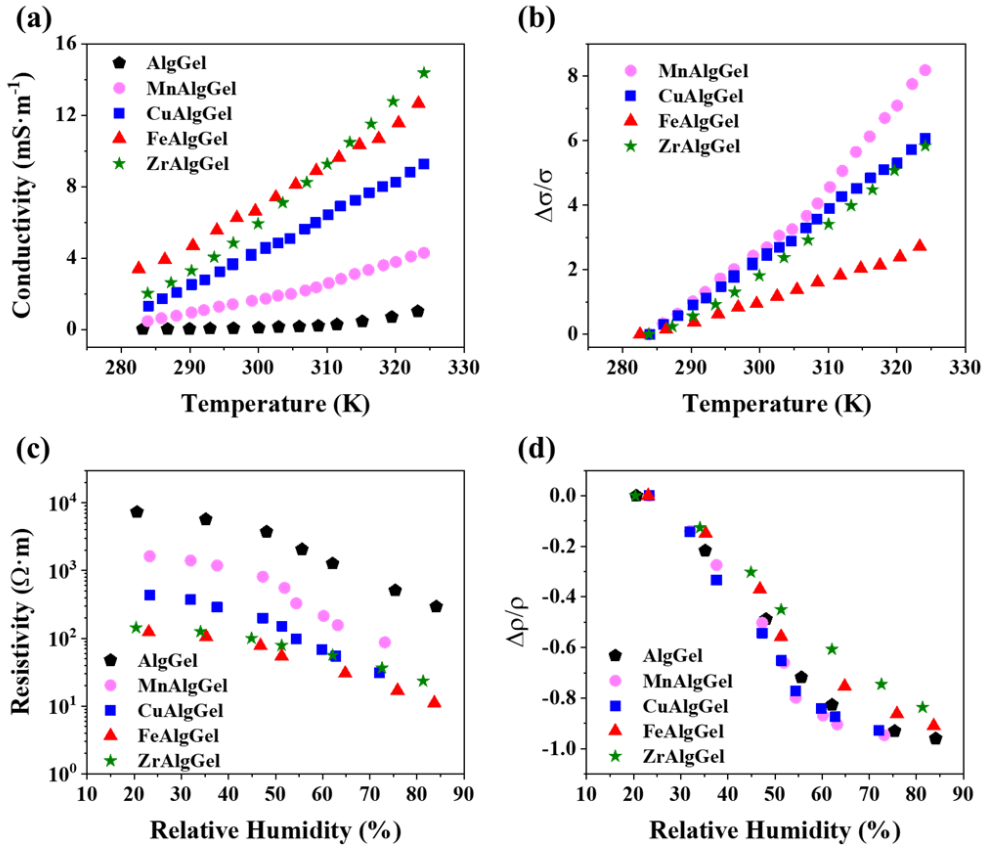


Figure 1. Influence de la température sur (a) la conductivité et (b) la variation relative de conductivité des AlgGel et des MAAlgGel. Influence de l'humidité relative sur (c) la résistivité et (d) la variation relative de résistivité des AlgGel et des MAAlgGel.

Une caractéristique notable est la photo-réactivité observée pour MnAlgGel en présence d'électrodes en cuivre. La jonction MnAlgGel/Cu a produit des photocourants atteignant $9,2 \mu\text{A W}^{-1}$ sous une illumination LED blanche, générés par des champs internes et par une conduction assistée par pièges à l'interface gel/métal. Des expériences d'illumination localisée ont confirmé que le photocourant provient de l'interface métal–gel plutôt que du volume du matériau. Ces résultats montrent que les organohydrogels biopolymères peuvent fonctionner comme conducteurs ioniques photoactifs transparents et sans additifs, une capacité rarement étudiée dans les systèmes hydrogel. Enfin, tous les échantillons MAlgGel ont fonctionné comme capteurs de déformation, avec des facteurs de jauge compris entre 1,7 et 2,3, des valeurs supérieures à celles des capteurs ioniques classiques à base d'hydrogels. CuAlgGel a offert le meilleur compromis entre sensibilité et souplesse, permettant une détection fiable de la flexion du doigt sur plusieurs milliers de cycles.

2.2 Électrolytes polymères gélifiés ioniquement modulables pour supercondensateurs (Projet 2)

L'architecture AlgGel a été adaptée pour développer des électrolytes polymères gélifiés entièrement biopolymériques (GPE) destinés aux supercondensateurs flexibles. Dans ce système, Mn^{2+} et Cu^{2+} assurent la réticulation structurale, tandis que Li^+ est introduit pour moduler la mobilité ionique tout en maintenant une concentration totale en sels constante. Cette stratégie permet de contrôler indépendamment l'architecture du réseau et la densité de porteurs de charge. Les mesures de diffusion des rayons X aux petits angles (SAXS) ont montré que Cu^{2+} induit un compactage polymère plus marqué que Mn^{2+} , en accord avec la hiérarchie d'affinité bien établie pour l'alginate (**Figure 2**).

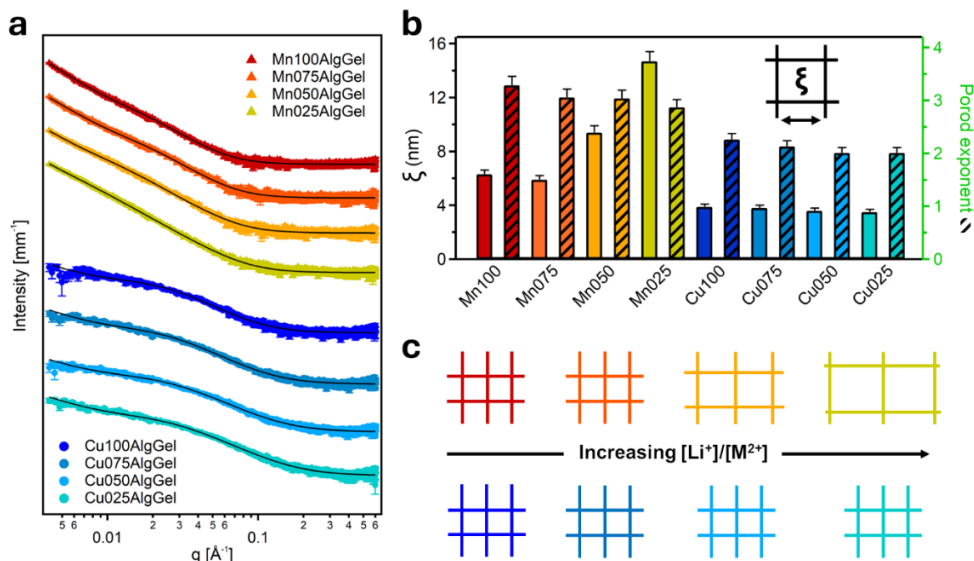


Figure 2. a) Courbes SAXS (en échelle logarithmique et décalées pour plus de clarté) et b) longueurs de corrélation (ξ) et exposants de Porod (barres en pointillés) extraits pour MnXAlgGel et CuXAlgGel. c) Représentation schématique des différences structurales entre les réseaux réticulés par Mn^{2+} et par Cu^{2+} en fonction du rapport $[\text{Li}^+]/[\text{M}^{2+}]$ dans la solution de réticulation. Les MnXAlgGels présentent une augmentation de ξ avec une teneur croissante en Li^+ , indiquant un réseau progressivement plus lâche. À l'inverse, les CuXAlgGels conservent une structure de réseau uniformément compacte.

L'efficacité d'incorporation de Li^+ dépend fortement du cation réticulant: les gels réticulés au Mn^{2+} accueillent nettement plus de Li^+ ($n\text{Li}^+/n\text{M}^{2+}$ pouvant atteindre 2,08) que ceux réticulés au Cu^{2+} (1,28), ce qui reflète des différences de volume libre et de perméabilité du réseau.

La spectroscopie d'impédance électrochimique a montré que la conductivité ionique dépend à la fois de la teneur en Li^+ et de la structure nanométrique. Les gels à base de Mn présentent une rigidité plus faible et une mobilité ionique plus élevée, tandis que les réseaux à base de Cu offrent une meilleure stabilité structurelle à fortes concentrations de sel. Les supercondensateurs assemblés avec des électrodes en carbone activé ont présenté des capacités surfaciques

élevées (jusqu'à $591,8 \text{ mF cm}^{-2}$) et ont conservé leur stabilité électrochimique au-delà de 5000 cycles. Il est notable que les gels conservent leurs performances après six mois de stockage, démontrant une excellente durabilité. Ces résultats montrent que la chimie de coordination des biopolymères peut être transposée en comportements électrochimiques prévisibles, permettant de développer des GPE durables sans polymères synthétiques.

2.3 Organohydrogels de gélatine réticulés enzymatiquement (Projet 3)

Pour compléter la réticulation ionique, les réseaux de gélatine ont été stabilisés par réticulation enzymatique à l'aide d'une transglutaminase microbienne (TG), donnant naissance à des organohydrogels protéiques robustes. La TG catalyse la formation de liaisons ϵ -(γ -glutamyl)lysine, générant des réseaux covalents présentant une stabilité thermique et mécanique améliorée tout en conservant leur biocompatibilité.

Les matériaux obtenus étaient hautement extensibles, résistants, transparents et stables thermiquement jusqu'à environ 90°C . Ils présentaient une double sensibilité à la déformation et à la température. La température modulait principalement la mobilité des protons, issus du caractère acide intrinsèque de la gélatine et constituant les principaux porteurs de charge dans ces réseaux, tandis que la déformation modifiait les chemins disponibles pour la conduction ionique. Les capteurs ont atteint des allongements supérieurs à 400 % (**Figure 3**), des réponses électromécaniques stables et une excellente reproductibilité sur plus de 5000 cycles.

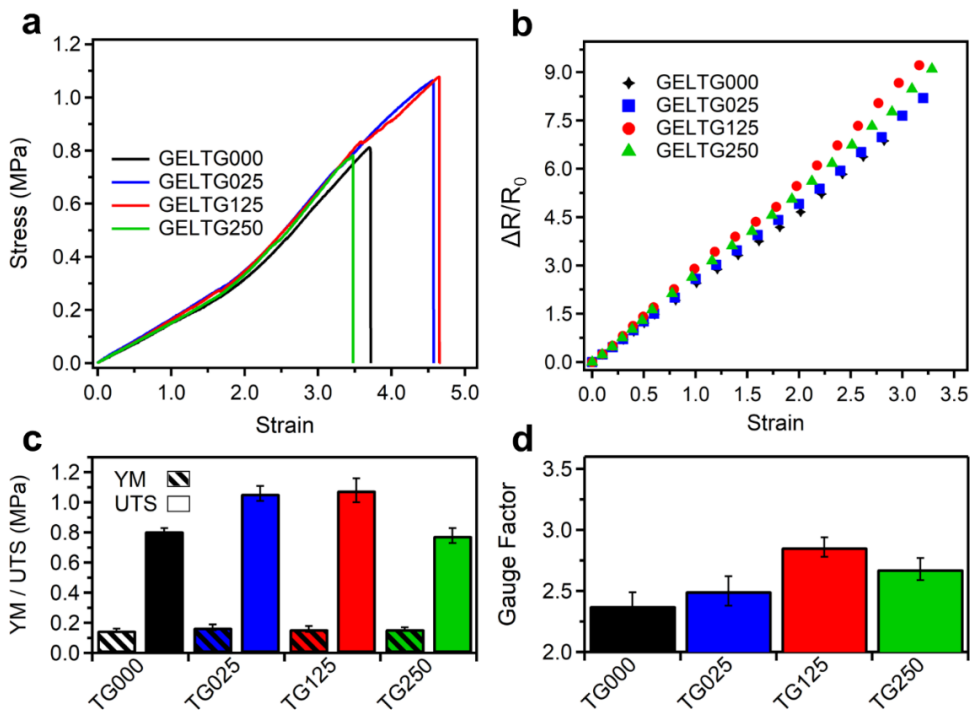


Figure 3. a) Courbes de traction contrainte–déformation montrant l’amélioration de l’extensibilité et de la résistance après réticulation médiée par la TG. b) Variation relative de résistance ($\Delta R/R_0$) en fonction de la déformation, montrant une réponse électromécanique linéaire pour toutes les formulations. c) Valeurs du module de Young (YM) et de la résistance à la rupture (UTS) extraites des essais de traction. d) Valeurs du facteur de jauge dérivées de la zone linéaire de déformation (0–300 %), avec GELTG125 présentant la valeur la plus élevée (2,86).

Ces résultats montrent la réticulation enzymatique comme une stratégie durable pour concevoir des matériaux protéiques robustes destinés à l’électronique souple, sans recourir à des réactifs toxiques. Par rapport aux systèmes AlgGel, les réseaux de gélatine réticulés par TG offrent une meilleure résistance mécanique et une stabilité thermique accrue, permettant une fenêtre de fonctionnement plus large.

2.4 Hydrogels de caséinate réticulés ioniquement : une découverte fortuite (Projet 4)

Le caséinate a été initialement étudié comme simple polymère témoin, mais il a formé de manière inattendue des hydrogels solides et cohésifs lorsqu'il a été exposé à des cations multivalents. Ce résultat imprévu a révélé un mode de gélification ionique jusqu'alors non décrit pour le caséinate de sodium, gouverné par des interactions impliquant les groupements carboxylate et amine. Une évaluation systématique des cations divalents, trivalents et tétravalents a mis en évidence des effets iono-spécifiques marqués sur la compaction du réseau, la porosité, la rigidité mécanique et la conductivité ionique. Les mesures SAXS ont montré des régimes d'organisation nanométrique distincts définissant l'architecture du matériau à différentes échelles (**Figure 4**).

Les hydrogels de caséinate ainsi obtenus ont montré d'excellentes performances électrochimiques en tant qu'électrolytes polymères gélifiés, atteignant des capacitances surfaciques allant jusqu'à 450 mF cm^{-2} et conservant une stabilité opérationnelle sur plus de 5000 cycles. Leurs bonnes propriétés mécaniques, l'absence d'additifs synthétiques et leur conductivité ionique naturellement élevée en font de bons candidats pour des matériaux énergétiques entièrement biosourcés. Notamment, cette étude présente la première démonstration de l'utilisation d'hydrogels de caséinate comme électrolytes dans des dispositifs de stockage d'énergie. Dans l'ensemble, ce projet confirme que la réticulation multivalente permet de transformer des flux résiduels biologiques abondants en matériaux fonctionnels à hautes performances.

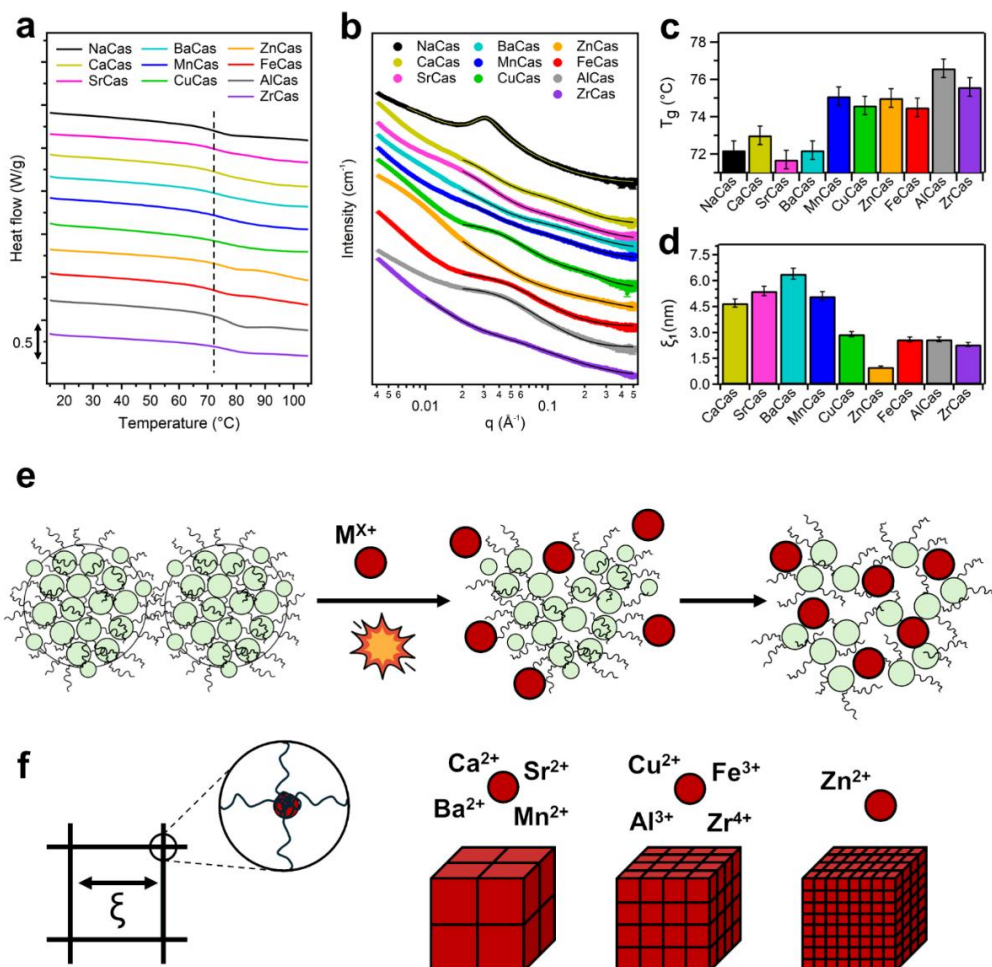


Figure 4. a) Thermogrammes DSC et b) courbes SAXS des gels NaCas et MCas. c) Valeurs de T_g extraites et d) longueurs de corrélation (ξ) pour NaCas et MCas, montrant que la réticulation ionique gouverne l'assemblage des chaînes polymères. e) Illustration schématique de la transition entre des dispersions micellaires et des réseaux réticulés ioniquement via la coordination MX^+ . f) Visualisation conceptuelle de l'influence de l'identité du cation sur le compactage nanostructural et la longueur de corrélation.

2.5 Dispositifs synaptiques optoioniques Biopolymère–MoS₂ (Projet 5)

Le dernier projet associe des biopolymères à un semi-conducteur afin de réaliser des transistors synaptiques optoioniques. Un hydrogel d'alginate de sodium a été utilisé comme réservoir ionique et placé à l'interface avec du MoS₂ monocouche. Sous illumination, les cations mobiles se déplaçaient dans l'hydrogel et modulaient la conductance du canal de MoS₂, ce qui permettait une photoconductivité persistante et l'obtention d'états mémoires multivalués. Le dispositif a reproduit des comportements synaptiques caractéristiques, notamment la potentialisation, la dépression ainsi que des formes de plasticité à court et à long terme, tout en fonctionnant à basse tension et en offrant une programmation optique efficace (**Figure 5**). Ces résultats démontrent que la migration ionique au sein d'un biopolymère peut être exploitée pour contrôler un semi-conducteur, établissant ainsi un lien direct entre transport ionique et transport électronique dans une plateforme entièrement souple, transparente et respectueuse de l'environnement.

Cette approche illustre le potentiel des ionotroniques fondées sur des biopolymères, dans lesquelles des matériaux naturels modulent directement des conducteurs électroniques grâce à des flux ioniques contrôlés.

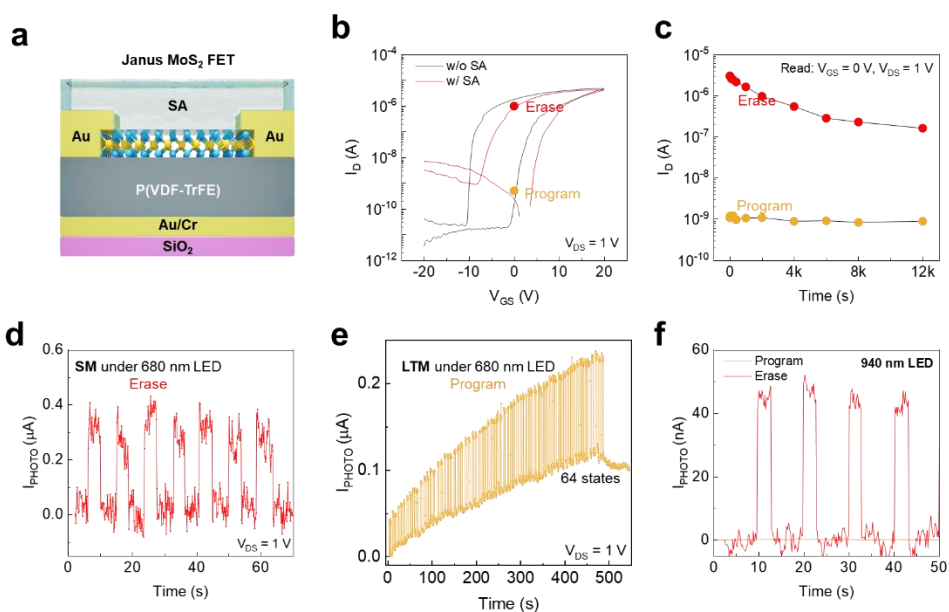


Figure 5. Fonctionnalisation supramoléculaire asymétrique d'un transistor MoS₂ 2D (FET) avec SA et un polymère ferroélectrique. a) Schéma latéral du FET Janus à base de MoS₂ obtenu à l'interface entre SA et le MoS₂ FeFET. b) Courbes de transfert du MoS₂ FeFET (noir) et du FET Janus à base de MoS₂ (rouge) à V_{DS} = 1 V, montrant une hystérèse ferroélectrique maximale de 10 V, indépendante de la présence de SA. c) Propriétés de rétention mémoire du FET Janus à base de MoS₂ sur 12 000 s. Photo-réponse résolue en temps du dispositif Janus MoS₂ à V_{GS} = 0 V et V_{DS} = 1 V, montrant d) une mémoire sensorielle (SM) sous illumination LED 680 nm à l'état ferroélectrique Erase, e) une mémoire à long terme synaptique (LTM) sous illumination LED 680 nm à l'état ferroélectrique Program, et f) une mémoire sensorielle exploitant l'état ferroélectrique Erase sous illumination LED NIR.

3. Conclusion générale

Cette thèse propose un cadre unifié pour la conception de matériaux biopolymères destinés à l'électronique souple, couvrant la détection, le stockage d'énergie et les dispositifs neuromorphiques. Les travaux montrent que l'identité de l'ion gouverne directement la structure et les propriétés mécaniques des réseaux, que le milieu organohydrogel stabilise l'hydratation

ainsi que la mobilité ionique, et que les performances des dispositifs dépendent fortement de l'ingénierie des interfaces gel-électrode ou gel-semi-conducteur. Ces résultats démontrent que les polymères naturels peuvent agir comme matériaux électroniques actifs, offrant des performances proches de celles des systèmes synthétiques tout en introduisant des avantages d'écoresponsabilité. Les stratégies développées ici sont transposables à d'autres biopolymères et architectures, et permettent de développer une électronique souple basée sur des matériaux renouvelables et biodégradables.

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Abstract

This thesis demonstrates how sustainable biopolymers can be engineered into functional materials for soft electronics by controlling their molecular interactions and network structures. Through a combination of coordination and enzymatic crosslinking, natural polymers are transformed into stable, conductive, and responsive gels suitable for sensing, energy storage, and neuromorphic applications. The research progresses from hybrid organohydrogels to gel polymer electrolytes and protein-based sensors, revealing how molecular design dictates mechanical, ionic, and interfacial behavior. The final integration of biopolymer electrolytes with semiconductors yields light-responsive devices that emulate synaptic functions. Together, these studies establish a framework for creating soft, sustainable materials that merge the adaptability of biology with the performance of modern electronics.

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Preface

This thesis presents the research I conducted during my doctoral studies jointly between the Department of Chemistry “Ugo Schiff” at the University of Florence and the Institut de Science et d’Ingénierie Supramoléculaires (ISIS) at the University of Strasbourg. The work lies at the cross-road between chemistry, materials science, and soft electronics, and aims to establish biopolymer-based hydrogels and organohydrogels as a sustainable platform for functional devices in sensing, energy storage, and neuromorphic applications. The thesis is the result of a research path that began during my Master’s degree, where I investigated ionic crosslinking in alginate systems. Those studies provided the conceptual and methodological foundations for this work and led so far to three scientific papers, reported in *Appendix III*, that explored how ion identity and coordination strength govern alginate structure, porosity, and mechanics. These papers established the design principles later expanded throughout the PhD.

Chapter 1 provides the Introduction to this thesis, offering to the reader the theoretical and scientific framework of this work. It begins with an overview of soft electronics, their material requirements, and the motivation for developing biopolymer-based approaches. It then discusses the intrinsic limitations of natural polymers and presents the three model systems (alginate, gelatin, and caseinate) together with their structural, chemical, and functional characteristics. The chapter concludes with the research roadmap, which connects the early Master’s work on alginate to the five PhD projects, defining the logic and continuity of the research progression.

Chapter 2 reports the Research Projects of this thesis work. It is sub-divided into five main projects, each corresponding to a self-contained study that evolved chronologically and conceptually from the previous one. The first project introduces multiresponsive alginate/gelatin organohydrogels, combining alginate’s ionic coordination with gelatin’s elasticity to yield transparent, stretchable, and thermoresponsive materials. This chapter

establishes the structure–function relationships that underpin all subsequent work. The second project translates this platform into gel polymer electrolytes (GPEs) for supercapacitors, correlating $\text{Li}^+/\text{M}^{2+}$ composition ($\text{M} = \text{Cu}, \text{Mn}$), nanoscale structure from SAXS, and electrochemical performance. The third project introduces enzymatically crosslinked gelatin networks, using microbial transglutaminase as a biocompatible covalent crosslinker to obtain stretchable, thermally stable, and robust protein-based sensors. The fourth project presents the serendipitous discovery of ionic caseinate hydrogels, in which sodium caseinate forms cohesive networks through multivalent cations; here, the systematic comparison of di-, tri-, and tetravalent crosslinkers reveals ion-specific effects on structure, stiffness, and ionic transport, leading to exceptional capacitance and durability in gel-electrolyte devices. The fifth and final project explores optoionic MoS_2 memory devices, integrating biopolymers with semiconducting MoS_2 to create light-responsive synaptic transistors that bridge ionic conduction and electronic transport.

Each project includes a conceptual overview, an experimental section, and results and discussion subdivided into thematic subsections, followed by a concise conclusion summarizing the key findings. Figures are systematically numbered and accompanied by extended captions that highlight structure–function correlations. Additional datasets, analyses, and characterizations are presented in the *Supporting Information* to ensure full transparency and reproducibility.

Chapter 3 reports the Conclusions, synthesizes the conceptual and experimental advances achieved throughout the thesis. It emphasizes the unifying design principles that emerge from this work: the crosslinking ion defines structure and mechanics, the medium controls hydration and mobility, and the interfacial configuration determines device performance. It also discusses short- and long-term perspectives of this work and related research.

Chapter 4, Supporting Information (SI), gathers all additional data associated with the five projects, including extended figures (coded as P#_S), detailed procedures, spectra, SAXS fitting parameters, and complete data tables. Each

section mirrors the numbering of the main text, ensuring direct correspondence between the results and their underlying datasets.

Chapter 5, Bibliography, compiles all bibliographic references cited throughout the thesis, formatted consistently following the style adopted in the main chapters to allow direct cross-referencing between citations and reference entries.

The Appendices complement the main chapters with additional materials. **Appendix I** presents the characterization methods used across all projects, describing the spectroscopic, thermal, scattering, and electrochemical techniques applied, together with instrumental details and data analysis procedures. **Appendix II** collects all other publications mentioned within the thesis (Publisher’s Main Text PDF) that are scientifically related to the presented projects developed during the doctoral period. **Appendix III** contains the three research papers (Publisher’s Main Text PDF) derived from my Master’s thesis work on alginate crosslinking, which form the methodological and conceptual foundation of this PhD.

Throughout the thesis, figures and tables follow a consistent hierarchical scheme to ensure clarity and traceability. Each project (P) uses a dedicated code (for example P1_1 or P2_S4), with “S” identifying *Supporting* figures. All images were defined and formatted using a unified visual logic (consistent color palettes and layout) to highlight correlations between structure, chemistry, and performance across chapters. This system allows the reader to navigate between datasets and interpretations seamlessly while maintaining visual and conceptual continuity throughout the work.

Together, the structure of this thesis ensures continuity from molecular coordination chemistry to device-level realization, while maintaining a unified scientific and visual narrative. It is designed so that each chapter can stand on its own yet contributes to a coherent demonstration of how sustainable biopolymers can evolve into active materials for next-generation soft electronic technologies.

The manuscripts and publications resulting from this doctoral research are listed below:

- **P. Tordi**; A. Tamayo; Y. Jeong; M. Bonini; P. Samorì, Multiresponsive Ionic Conductive Alginate/Gelatin Organohydrogels with Tunable Functions, *Advanced Functional Materials*, **2024**, 34 (52), 2410663. (Featured in *Hot Topic: Organic Electronics*)
- **P. Tordi**; F. Ridi; P. Samorì; M. Bonini, Cation–Alginate Complexes and Their Hydrogels: A Powerful Toolkit for the Development of Next-Generation Sustainable Functional Materials, *Advanced Functional Materials*, **2025**, 35 (9), 2416390.
- **P. Tordi**; V. Montes-García; A. Tamayo; M. Bonini; P. Samorì; A. Ciesielski, Ionically Tunable Gel Electrolytes Based on Gelatin–Alginate Biopolymers for High-Performance Supercapacitors, *Small*, **2025**, 21 (33), 2503937. (Featured in *Hot Topic: Batteries and Supercapacitors*)
- Y. Jeong*; **P. Tordi***; A. Tamayo; B. Han; M. Bonini; P. Samorì, Mimicking Synaptic Plasticity: Optoionic MoS₂ Memory Powered by Biopolymer Hydrogels as a Dynamic Cation Reservoir, *Advanced Functional Materials*, **2025**, 35 (50), e09607. (*Equal contribution)
- **P. Tordi**; A. Tamayo; Y. Jeong; B. Han; T. Al Kayal; A. Cavallo; M. Bonini; P. Samorì, Fully Bio-Based Gelatin Organohydrogels via Enzymatic Crosslinking for Sustainable Soft Strain and Temperature Sensing, *Advanced Functional Materials*, **2025**, e20762. (Featured in *Hot Topic: Wearable Sensors*)
- **P. Tordi**; V. Montes-García; V. Losasso; P. Samorì; M. Bonini, Ion-Directed Assembly of Protein Hydrogels: Sodium Caseinate as a Versatile Platform for Tunable Soft Materials, ready for submission.

The manuscripts originating from my Master’s research, which provided the methodological and conceptual foundation for this thesis, are listed below:

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- **P. Tordi**; F. Ridi; M. Bonini, A Green and Sustainable Approach for the Preparation of Cu-Containing Alginate Fibers, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2023**, 677, 132396.
 - **P. Tordi**; F. Ridi; M. Bonini, A Bioinspired and Sustainable Route for the Preparation of Ag-Crosslinked Alginate Fibers Decorated with Silver Nanoparticles, *Carbohydrate Polymers*, **2024**, 326, 121586.
 - **P. Tordi**; R. Gelli; S. Tamantini; M. Bonini, Alginate Crosslinking Beyond Calcium: Unlocking the Potential of a Range of Divalent Cations for Fiber Formation, *International Journal of Biological Macromolecules*, **2025**, 306, 141196.

1. Introduction

1.1 The Soft Electronics Landscape

Soft electronics redefine device architectures to match the mechanical softness of skin, biological tissue, and soft robotic systems.^[1,2] By enabling conformal contact, stretchability, and long-term biointegration, they open applications ranging from physiological monitoring and therapy to skin-interfaced and implantable systems, soft robotics, and emerging neuromorphic or ionotronic platforms that process information through both ions and electrons (**Figure 1**).^[2–4]

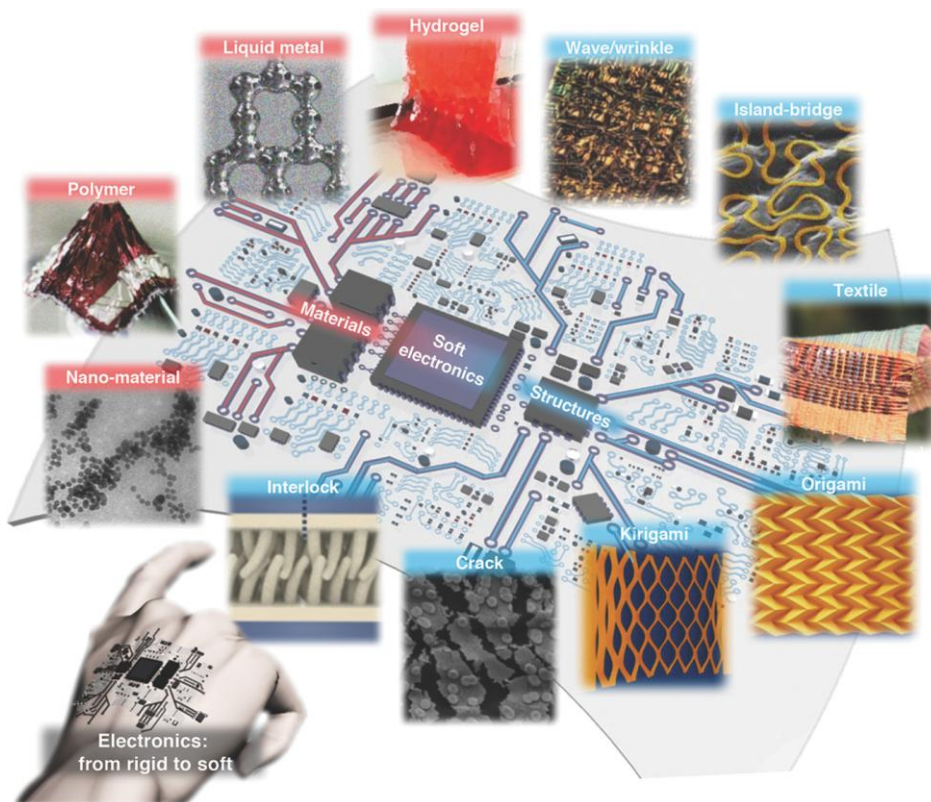


Figure 1. Strategies for soft electronics, combining material innovations (polymers, nanomaterials, hydrogels, liquid metals) and structural designs (wrinkles, island–bridge, textiles, origami, kirigami, cracks, interlocks) to achieve flexible and biointegrated devices. Reproduced with permission from^[2].

In this context, mechanical compliance, interfacial comfort, and signal fidelity under large, repeated strains are as critical as traditional performance metrics. Recent advances highlight the rapid maturation of biointegrated wearables and implants, while also underscoring the need for materials that remain stable, comfortable, and functional at the body interface over extended timescales.

The current material palette for soft electronics is dominated by elastomers, conductive composites, and organic mixed ionic–electronic conductors (OMIECs). Among them, OMIEC-based platforms such as PEDOT:PSS have proven highly effective at coupling ionic fluxes in biofluids to electronic signals, making them indispensable in electrochemical transistors and other low-impedance interfaces.^[5,6] However, their reliance on petrochemical feedstocks, complex doping and processing steps, and opaque fillers often limit scalability, transparency, and environmental sustainability. State-of-the-art reviews emphasize both the unique capabilities of OMIECs and organic electrochemical transistors (OECTs) as well as the ongoing challenges of achieving softness, stability, manufacturability, and ecological responsibility within a single material system.^[5,7,8]

Hydrogels occupy a unique niche within this landscape.^[9–11] Their hydrated polymer networks replicate the ion transport pathways of biological tissues while maintaining high deformability, making them excellent candidates for soft electronic devices (see **Figure 2**).^[2] Yet, conventional hydrogels are not without drawbacks: they are prone to dehydration, freezing, and drift under ambient conditions. To overcome these limitations, the organohydrogel concept has emerged.^[12,13] By partially replacing water with low-volatility, hygroscopic cosolvents, organohydrogels stabilize hydration and mechanical integrity without compromising ionic conduction. This approach has led to a new class of materials with antifreezing properties, self-healing capability, and long-lived responsiveness, extending the operational stability of hydrogel-based devices in real-world environments.

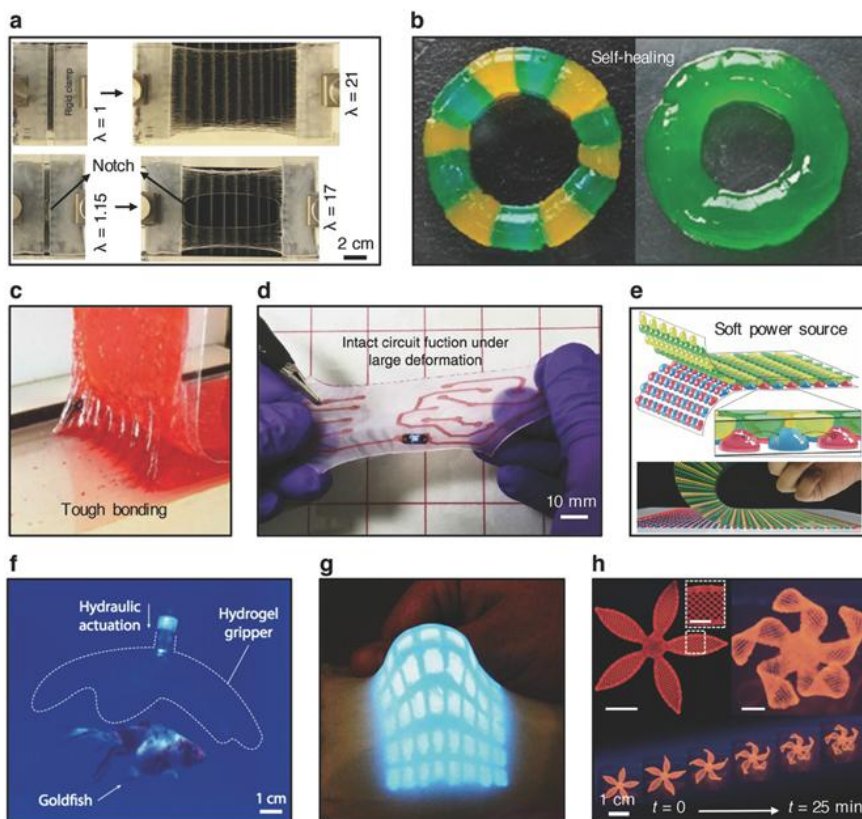


Figure 2. Hydrogels in soft electronics, showcasing their versatility across different functions: stretchable and notch-insensitive networks (a), self-healing gels (b), and tough bonding to smooth surfaces (c) enable robust mechanical performance; hydrogel-based circuits (d) and artificial electronic organs (e) illustrate their potential in bioinspired electronics; while soft actuators (f), electroluminescent displays (g), and 4D-printed biomimetic structures (h) highlight their application in actuation, sensing, and adaptive devices. Reproduced with permission from^[2].

Within this broader framework, biopolymer-based hydrogels and organohydrogels present a particularly promising route. Unlike synthetic analogues, they combine functionality with renewability, biocompatibility, and chemical richness. Their backbones (bearing carboxylate, amine, hydroxyl, and phosphate groups) allow ionic coordination, enzymatic stabilization, and hybrid network design, enabling multifunctional properties without the need for opaque or non-sustainable fillers. Recent surveys of hydrogel-based sensors and bioelectronics underscore a shift toward transparent, filler-free, and long-

term stable systems—precisely the space where biopolymer-based architectures can excel by merging sustainability with performance.

1.2 Aim of the Thesis

As highlighted in the previous section, soft electronics demand materials that are mechanically compliant, ionically conductive, environmentally stable, and scalable, yet most current solutions still rely on synthetic polymers, petrochemical feedstocks, or filler-based composites. Biopolymer-based hydrogels and organohydrogels stand out as a compelling alternative: they unite functionality with sustainability, offering intrinsic biocompatibility, chemical versatility, and renewable origins. However, their translation into robust, device-ready systems remains limited by challenges such as weak mechanical stability, dehydration, and insufficient control over ionic transport.

The overarching aim of this thesis is therefore to establish biopolymer-based hydrogels and organohydrogels as a robust platform for soft electronics, bridging the gap between sustainable materials design and functional device performance. The central hypothesis is that rational molecular and network engineering can transform abundant natural polymers into conductors, sensors, and electrolytes competitive with synthetic counterparts, without the need for electronic fillers or environmentally detrimental additives.

This objective unfolds across four complementary levels:

- Fundamental understanding: mapping the interactions between biopolymers and multivalent ions to uncover how coordination chemistry dictates network structure, ionic mobility, and macroscopic response.
- Material innovation: developing hybrid and modified architectures—through blending, organohydrogel formation, or enzymatic crosslinking—that overcome the intrinsic weaknesses of native biopolymers, such as poor stability, dehydration, or mechanical fragility.

-
- Device translation: demonstrating that the resulting gels can be seamlessly integrated into real devices, including strain and humidity sensors, gel polymer electrolytes for supercapacitors, and emerging neuromorphic systems.
 - Design principles: extracting generalizable rules that link chemistry, processing, and performance, providing a transferable framework for the future development of soft, bio-based electronic materials.

The work presented in this thesis builds directly on this context. It operationalizes the idea that soft electronics can be constructed from abundant natural polymers, using rational design principles to transform them into robust, multifunctional conductors, sensors, and electrolytes. The following chapters trace this journey, from ion–polymer design rules to hybrid protein–polysaccharide networks, and finally to device-level demonstrations in sensing, gel electrolytes, and neuromorphic interfaces, establishing a transferable framework for sustainable soft electronics.

By uniting sustainability with functional performance, this thesis aims not only to expand the chemical space of soft conductors but also to illustrate the potential of biopolymers as the foundation of next-generation wearable, biointegrated, and environmentally responsible electronic technologies.

1.3 Intrinsic Limitations

While biopolymers provide a sustainable and versatile foundation for soft electronics, their native forms are not without critical shortcomings. The very features that make them appealing (hydration, flexibility, and responsiveness) also render them fragile and environmentally unstable when directly implemented in devices.

The first limitation lies in mechanical integrity. Hydrated biopolymer networks are often weak, deforming or fracturing under modest stress. When devices are subjected to repeated stretching or bending, these gels are prone to fatigue,

irreversible damage, or even dissolution, which restricts their long-term usability.

Equally problematic is their environmental sensitivity. High water content makes biopolymer hydrogels vulnerable to dehydration, leading to shrinkage, brittleness, and diminished ionic mobility. At low temperatures, water crystallization can induce catastrophic structural collapse, whereas excessive swelling in humid or aqueous environments compromises dimensional stability. Such fluctuations not only degrade mechanical robustness but also destabilize the electrical properties of the material.

The ionic conductivity of native biopolymer gels is also highly environment-dependent. Temperature, humidity, or ion concentration shifts can drastically reconfigure transport pathways within the network, resulting in erratic device performance outside of tightly controlled laboratory conditions. Finally, limited durability under cyclic stress further undermines their reliability: crack formation, water expulsion, and gradual network rearrangement often culminate in progressive loss of functionality.

Overcoming these challenges requires more than simply selecting an appropriate polymer. It demands a deliberate engineering approach in which molecular interactions, crosslinking mechanisms, and network architectures are tuned to reinforce stability, regulate hydration, and decouple ionic transport from environmental fluctuations. By addressing these intrinsic weaknesses, biopolymers can be transformed from fragile natural matrices into robust, multifunctional materials capable of reliable and long-term integration in soft electronics.

1.4 Biopolymers Selected for This Thesis

Having discussed the general opportunities and limitations of biopolymers, the focus now shifts to the three systems that I have selected as the foundation of this thesis: **alginate, gelatin, and caseinate**. These materials were selected not because they represent the entire spectrum of natural polymers, but because

they each offer distinctive and appealing features that align with the aims of this work.

Alginate provides a well-established platform for exploring ionic crosslinking, with a predictable structure and rich coordination chemistry. Gelatin brings elasticity, biocompatibility, and the possibility of enzymatic stabilization, features that make it particularly attractive for soft and biointegrated devices. Caseinate, derived from dairy byproducts, offers an unconventional yet promising matrix capable of forming ionic networks through multivalent coordination—an opportunity that remains largely unexplored.

These three biopolymers will be presented in the following paragraphs, where their origins, structures, and properties are introduced to set the stage for the material innovations and device concepts developed in the subsequent chapters.

1.4.1 Alginate

This section originates from the publication:

P. Tordi; F. Ridi; P. Samorì; M. Bonini, “Cation–Alginate Complexes and Their Hydrogels: A Powerful Toolkit for the Development of Next-Generation Sustainable Functional Materials,” *Advanced Functional Materials*, 2025, 35 (9), 2416390.
(<https://doi.org/10.1002/adfm.202416390>)

Alginate is an anionic polysaccharide obtained primarily from brown algae of the *Phaeophyceae* family through alkaline extraction, a process first reported by Stanford in 1881. Its occurrence is not limited to algae, as certain bacterial species also produce alginate as part of their extracellular polymeric substances. The material is certified as safe by the U.S. Food and Drug Administration and is already exploited on an industrial scale as a food additive and thickener, as well as in biomedical and cosmetic formulations.^[14]

Its molecular structure has been extensively characterized by ¹H- and ¹³C-NMR spectroscopy, which revealed that alginate is composed of (1→4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues. The relative abundance and sequential arrangement of M and G residues vary according to the extraction source, leading to homopolymeric blocks of consecutive

mannuronates (MM) or guluronates (GG), as well as heteropolymeric MG or GM sequences (see **Figure 3**).^[14,15] This block structure critically determines alginate's macroscopic properties, with G-blocks favoring tight coordination with multivalent cations and M-blocks imparting flexibility and reduced packing regularity. Commercial alginates typically contain 14–31% guluronic residues, and their molecular weight ranges between 30 and 400 kDa, producing significant variation in solution viscosity. Moreover, pH strongly influences viscosity: protonation of carboxylate groups around pH 3.5 promotes interchain hydrogen bonding, increasing viscosity and rigidity.^[14]

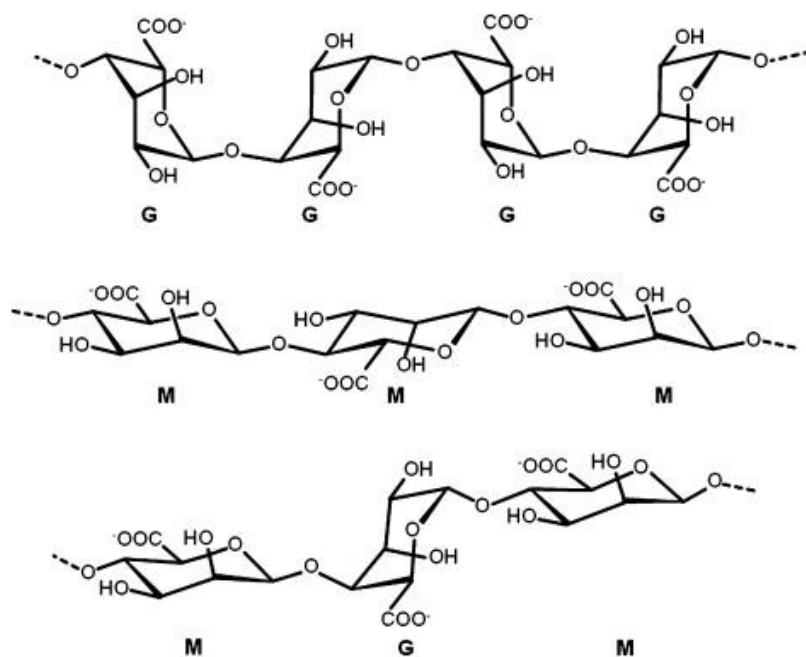


Figure 3. Chemical structure of alginate, showing homopolymeric G blocks (guluronate), M blocks (mannuronate), and heteropolymeric MG sequences. Reproduced with permission from^[15]

The defining feature of alginate is its remarkable ability to form complexes with a broad spectrum of cations. The carboxylate groups distributed along the chain serve as primary coordination sites, and depending on the ion's size, charge density, and hydration shell, different binding modes can be established.

Coordination can occur through monodentate binding, where one oxygen of the carboxylate coordinates the cation, or bidentate chelation, where both oxygens of a single carboxylate group engage the ion.^[14] In other cases, a cation may act as a bridge between carboxylates on different residues or chains, producing intermolecular junctions that generate extended networks. The most iconic motif is the so-called “*egg-box*” structure, formed when divalent cations, particularly calcium, fit cooperatively into cavities created by consecutive guluronate residues, resulting in buckled-chain arrangements that stabilize large-scale gel networks.^[14]

Divalent ions represent the most thoroughly studied group of alginate crosslinkers. Calcium is the archetype, yielding stable, biocompatible gels that are used extensively in drug delivery, food encapsulation, and tissue engineering. Strontium forms even stronger interactions, likely due to its larger ionic radius and increased number of coordination sites, and this property is coupled with its intrinsic osteogenic activity, making Sr^{2+} -alginate particularly relevant for bone regeneration scaffolds. Barium, by contrast, coordinates not only guluronate but also mannuronate residues, generating highly stable yet less homogeneous gels.^[14] Transition-metal cations add new layers of functionality: copper binds strongly to carboxylates and produces hydrogels with antimicrobial activity and high rigidity, while manganese forms weaker complexes but imparts paramagnetic properties that enable magnetic resonance imaging applications and, in hybrid organohydrogels, photoresponsivity. Zinc generates medium-strength gels that resist biofouling and release ions dynamically, making them promising in antimicrobial coatings.^[14] The affinity scale for divalent ions, established through titration and rheological studies, follows the order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Co}^{2+} \approx \text{Ni}^{2+} \approx \text{Zn}^{2+} > \text{Mn}^{2+}$. Importantly, this sequence of binding strength does not always translate directly into the stiffness or toughness of the gels, since the specific coordination geometry and the interplay with the M/G sequence also shape supramolecular packing and mechanics.^[14]

Complexation with trivalent cations, such as Fe^{3+} , Al^{3+} , or Cr^{3+} , drives even greater network compaction. These ions typically form octahedral complexes involving multiple carboxylates from different chains, leading to predominantly intermolecular junctions that anisotropically reinforce the network. For example, Fe^{3+} crosslinking can be accompanied by partial protonation of the alginate backbone, further tightening the structure. Rare-earth ions such as Nd^{3+} , Eu^{3+} , and Tb^{3+} add unique photophysical properties, including fluorescence, while Gd^{3+} confers MRI contrast. However, the inclusion of trivalent ions often comes at the expense of long-term biocompatibility, necessitating careful evaluation of application-specific risks.^[14] Tetravalent cations, although less explored, form some of the most robust complexes. In particular, zirconium generates dense, highly crosslinked matrices through symmetrical coordination of multiple carboxylates, yielding hydrogels of exceptional mechanical strength and chemical stability. These systems are being explored for advanced applications in catalysis, flame retardancy, and ion-conducting membranes.^[14]

The supramolecular assembly of alginate is thus governed by a subtle balance between polymer sequence and ion identity. Guluronate-rich alginates tend to form rigid, tightly packed “*egg-box*” networks, while mannuronate-rich analogues yield softer, more hydrated gels with greater flexibility. The valency, radius, and hydration energy of the crosslinking ion tune this balance, allowing the design of materials ranging from soft, responsive scaffolds suitable for drug delivery to stiff, load-bearing matrices appropriate for environmental remediation or electrochemical devices. Furthermore, ion-exchange equilibria make alginate gels inherently dynamic: weaker cations can be replaced by stronger ones, altering the gel structure over time or enabling controlled release applications.

This interplay between molecular coordination and macroscopic function explains alginate’s versatility across scientific and industrial domains. Calcium- and strontium-alginate hydrogels are used in food encapsulation and regenerative medicine; barium-alginate capsules enable immunisolated cell

transplantation; copper- and zinc-alginate gels serve as antimicrobial coatings; and zirconium- or iron-alginate complexes underpin developments in flame retardants, catalysis, and sustainable energy devices. In the context of soft electronics, alginate provides a sustainable platform for ion-conductive networks, and its performance can be tuned by combining different cations or by hybridizing with other polymers, as explored in this thesis.

In conclusion, alginate exemplifies how a simple, renewable polysaccharide can yield a broad spectrum of functional materials through the strategic use of ionic coordination. Its intrinsic block structure encodes sequence-dependent binding preferences, while the choice of crosslinking ion defines the geometry, stability, and functionality of the resulting hydrogel. These attributes make alginate both a model system for fundamental studies of biopolymer–ion interactions and a practical material for the development of sustainable, multifunctional platforms in fields spanning from biomedicine, environmental remediation, energy storage to soft electronics.

1.4.2 Gelatin

Gelatin is a collagen-derived biopolymer that has gained broad interest due to its biocompatibility, biodegradability, low cost, and intrinsic thermo-responsiveness.^[16–18] As a denatured form of collagen, it is typically obtained from animal byproducts (skin, bones, cartilage) through acid or alkaline hydrolysis, leading to two major types: type A (acid-pretreated, isoelectric point ~pH 6–9) and type B (alkali-pretreated, isoelectric point ~pH 4–5).^[19] The amino acid composition of gelatin is dominated by glycine, proline, and hydroxyproline, which govern its conformational transitions and mechanical behavior (see **Figure 4**).^[16–19] Unlike polysaccharides such as alginate, gelatin contains a wide range of ionizable side chains (lysine, arginine, aspartate, glutamate, histidine) that offer multiple functionalization and crosslinking opportunities.

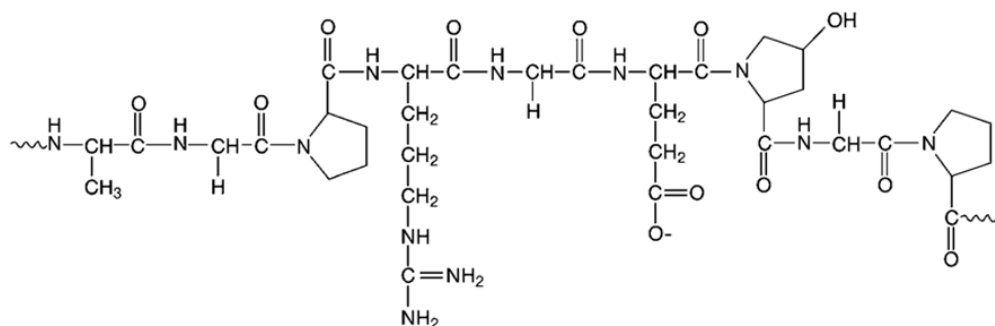


Figure 4. Representative peptide sequence of gelatin, showing the typical amino acid residues forming its polypeptide backbone. Reproduced with permission from^[20]

Gelatin exhibits desirable physicochemical properties, including excellent film-forming ability, emulsification, and water retention, as well as its unique capacity to form thermo-reversible gels upon cooling below $\sim 30\text{--}35\text{ }^{\circ}\text{C}$. This sol–gel transition arises from partial reformation of collagen-like triple helices, stabilized by hydrogen bonding and hydrophobic interactions. However, physically crosslinked gelatin gels are typically weak and unstable under hydrated or physiological conditions, undergoing dissolution or loss of mechanical integrity at body temperature. These limitations have prompted the widespread development of covalently crosslinked gelatin hydrogels.

Chemical and enzymatic crosslinking strategies have been explored extensively. Aldehyde-based reagents (e.g., glutaraldehyde), carbodiimides (e.g., EDC/NHS), and natural crosslinkers (e.g., genipin) provide permanent networks but often raise biocompatibility concerns due to cytotoxic residues.^[21–24] In contrast, enzymatic approaches (most notably microbial transglutaminase (TG)) have emerged as powerful and bio-safe alternatives. TG catalyzes the formation of ϵ -(γ -glutamyl)lysine isopeptide bonds between neighboring polypeptide chains, producing robust, permanent, and non-toxic hydrogels under mild aqueous conditions.^[25–28] Such networks overcome the poor stability of physical gels while preserving biocompatibility, enabling applications in tissue engineering, drug delivery, and food technology.

Beyond homopolymeric systems, gelatin is frequently employed as a component of composite or interpenetrating network (IPN) hydrogels to tailor properties such as stiffness, degradation rate, and cell-adhesion capacity. Gelatin inherently presents arginine–glycine–aspartic acid (RGD) sequences, which mimic extracellular matrix (ECM) cues and promote cell attachment, proliferation, and differentiation.^[29,30] This property makes gelatin-based hydrogels especially attractive as scaffolds for regenerative medicine and as bioinks for 3D bioprinting.^[30,31] In addition, gelatin’s functional groups allow facile conjugation with nanomaterials, synthetic polymers, and ionic liquids, leading to hybrid systems with enhanced mechanical, conductive, or responsive behavior.

In summary, gelatin represents a versatile hydrogel matrix whose properties can be finely tuned through physical, chemical, or enzymatic crosslinking. While its unmodified form suffers from poor mechanical robustness and thermal stability, advances in crosslinking chemistries (particularly enzymatic stabilization with transglutaminase) have positioned gelatin as a sustainable and multifunctional building block for applications spanning biomedicine, environmental remediation, packaging, and soft electronics.

1.4.3 Caseinate

The transition towards sustainable economy hinges on the valorization of renewable and underutilized resources. Among industrial byproducts, dairy waste (particularly sodium caseinate, the water-soluble salt of casein proteins) offers an abundant yet underexploited polymeric matrix enriched with carboxylate and amine functionalities capable of coordinating multivalent cations and forming supramolecular networks (see **Figure 5**).^[32–37]

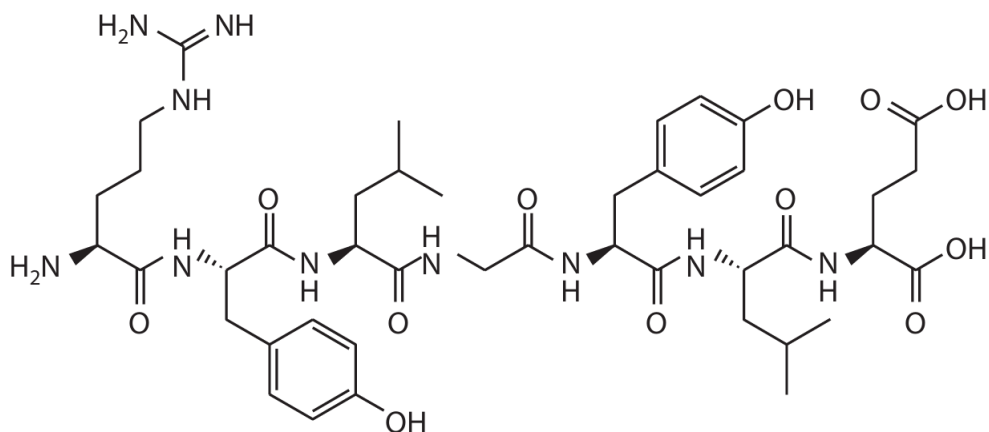


Figure 5. Representative molecular structure of casein, showing the polypeptide backbone and typical side-chain functionalities such as carboxylate, amide, and hydroxyl groups derived from its amino acid composition. Reproduced with permission from^[34].

Caseins are amphipathic phosphoproteins with highly flexible and open conformations, in contrast to the compact, globular structures of whey proteins. Their sequences contain both polar and hydrophobic domains, with clusters of phosphoseryl residues that strongly interact with Ca^{2+} and other multivalent cations, enabling the formation of micellar structures in milk.^[38–40] This intrinsic amphiphilicity and ion-binding capacity confer caseinate with remarkable emulsifying and stabilizing properties, making it a longstanding component in food formulations and a promising platform for functional materials design.

Despite these advantages, structuring sodium caseinate into robust, water-insoluble materials has remained challenging. Traditional strategies include enzymatic crosslinking via microbial transglutaminase (TG) and ionic complexation under dilute conditions.^[41–45] As discussed in the previous chapter, TG efficiently catalyzes the formation of ϵ -(γ -glutamyl)lysine isopeptide bonds between glutamine and lysine residues, producing high-molecular-weight aggregates and covalently crosslinked networks. Casein is an excellent substrate for TG due to its open tertiary structure and accessibility of reactive residues.^[46] The resulting covalent networks exhibit enhanced gelation, water retention, and stability compared to native caseinate, and have

been explored in applications ranging from dairy product stabilization and restructured meats to enzyme-induced gels. Importantly, TG-crosslinked caseinate gels can be formed under mild, aqueous, and food-safe conditions, offering a sustainable alternative to chemical crosslinkers.

Parallel efforts have explored ionic crosslinking of sodium caseinate with divalent and multivalent cations. These interactions are mediated by carboxylate and phosphoseryl clusters, yielding supramolecular aggregates that resemble the calcium phosphate–stabilized micelles of native milk. However, under typical conditions these assemblies remain weak and water-soluble, lacking the mechanical integrity required for functional hydrogels. As a result, ionic complexation has so far provided valuable mechanistic insight into protein–ion interactions, but has not yielded stable, water-insoluble networks with practical utility.

In recent years, caseinate has begun to attract renewed attention in the context of functional biomaterials. TG-induced crosslinking enables the design of elastic, thermally stable gels, while combining enzymatic and ionic approaches offers opportunities to further tune mechanical properties, degradation behavior, and bioactivity. Moreover, the abundance of reactive groups in caseinate provides a versatile platform for hybrid materials incorporating nanoparticles, synthetic polymers, or bioactive molecules. Nevertheless, compared to alginate or gelatin, caseinate remains underrepresented in the field of ionically crosslinked hydrogels, underscoring the need for systematic studies to fully exploit its unique chemical versatility and sustainability potential.

1.5 Research Roadmap

This thesis presents a research journey that originates from the physico-chemical understanding of alginate crosslinking (initially developed during my Master’s degree in Chemical Sciences) and gradually evolves toward the creation of sustainable soft materials for energy storage, sensing, and neuromorphic electronics. The early foundation was established through three

studies, reported in Appendix III, which explored the interaction of alginate with different metal cations and unveiled how ion identity governs network formation, porosity, and macroscopic performance. The first work described a green, sustainable route for producing copper-containing alginate fibers through in situ ion reduction; the second introduced a bioinspired method to form Ag^+ -crosslinked fibers decorated with silver nanoparticles using natural reducing agents; and the third expanded the understanding of alginate crosslinking beyond calcium, systematically examining the influence of Sr^{2+} , Ba^{2+} , Mn^{2+} , Cu^{2+} , and Zn^{2+} on fiber morphology and mechanics. Together, these studies provided the methodological and conceptual framework (centered on ionic coordination chemistry and extrusion-based processing) that guided the subsequent doctoral research.

Building on these principles, I initially focused my PhD activity on alginate/gelatin organohydrogels as programmable soft matrices (**Project 1**). By coupling alginate's ionic coordination with gelatin's elasticity, robust, transparent, and elastic networks were obtained, whose properties could be precisely tuned through the choice of crosslinking ion and solvent composition. The organohydrogel environment stabilized hydration and prevented freezing, revealing a key design rule: the ion defines structure and mechanics, while the medium determines mobility and stability.

In the second stage, this platform was adapted into gel polymer electrolytes for energy storage (**Project 2**). By introducing Li^+ and varying the crosslinking ion between Cu^{2+} and Mn^{2+} , it became possible to correlate nanoscale organization (probed by SAXS) with ionic conductivity and electrochemical behavior. Cu-based gels delivered high capacitance and power, whereas Mn-based systems ensured long-term durability, establishing a direct connection between ion coordination chemistry and device performance.

The next stage introduced enzymatic crosslinking as a complementary stabilization route (**Project 3**). Gelatin was crosslinked by microbial transglutaminase to yield covalently reinforced, stretchable, and thermoresponsive networks. These materials retained the biocompatibility and

dynamic response typical of protein hydrogels, while gaining mechanical robustness and long-term stability, demonstrating that enzymatic chemistry can offer a sustainable alternative to purely ionic crosslinking.

An unexpected yet crucial development emerged with the discovery of ionic gelation in sodium caseinate (**Project 4**). Originally explored as a control system, caseinate unexpectedly formed strong and cohesive hydrogels upon exposure to multivalent cations, revealing a serendipitous mechanism of ionic network formation. Systematic investigation across di-, tri-, and tetravalent ions showed pronounced ion-specific effects on structure, stiffness, and charge transport. These caseinate hydrogels, entirely free of added salts or fillers, exhibited remarkable capacitance and cycling stability when used as gel polymer electrolytes. This finding expanded the conceptual framework of the thesis, proving that the design rules derived from polysaccharides can be successfully translated to protein systems and that even unanticipated phenomena can open new directions in sustainable soft electronics.

In the final stage, the research transitioned from ionic conductors to hybrid optoionic devices (**Project 5**). By interfacing a sodium-alginate reservoir layer with MoS₂, a synaptic transistor was realized in which light-driven cation migration within the biopolymer modulates the semiconductor's conductance. The resulting device exhibited multilevel memory states and persistent photoconductivity, marking the convergence of ionic transport, optical excitation, and electronic functionality in a fully biopolymer-based framework. Taken together, these stages define a unifying strategy for biopolymer-enabled soft electronics, in which molecular coordination controls network structure, hybrid crosslinking ensures stability, and interfacial engineering bridges ionic and electronic domains. Starting from the fundamental understanding of alginate coordination chemistry gained during the Master's work and culminating in the serendipitous discovery of ionic caseinate, this thesis charts a continuous path from molecular design to device-level realization, demonstrating how sustainable biopolymers can evolve into active components of advanced electronic and energy-storage technologies.

2. Projects

2.1 Project 1. Multiresponsive Alginate/Gelatin organohydrogels with tunable functions

This section originates from the publication:

P. Tordi; A. Tamayo; Y. Jeong; M. Bonini; P. Samorì, “Multiresponsive Ionic Conductive Alginate/Gelatin Organohydrogels with Tunable Functions,” Advanced Functional Materials, 2024, 34 (52), 2410663.

(<https://doi.org/10.1002/adfm.202410663>)

2.1.1 Introduction

The development of multifunctional materials for soft electronics increasingly depends on strategies that combine structural compliance with reliable ionic transport. Within this context, alginate–gelatin (AlgGel) organohydrogels provide a natural convergence of two complementary chemistries: alginate’s ability to form ion-coordinated networks and gelatin’s elasticity and thermoresponsiveness. When combined, these biopolymers generate transparent, stretchable matrices whose performance can be programmed through the choice of crosslinking ions.

Previous studies have largely confined alginate hydrogels to calcium-based coordination, producing mechanically stable but functionally limited gels. To expand this space, we systematically explored a broader ionic library (divalent (Mn^{2+} , Cu^{2+}), trivalent (Fe^{3+}), and tetravalent (Zr^{4+}) cations) introduced into AlgGel organohydrogels. This strategy not only diversifies the accessible mechanical regimes but also tunes optical and electrical responses, offering a controllable link between molecular coordination and macroscopic behavior.

The resulting materials combine several critical features for wearable and biointegrated electronics: transparency for unobtrusive interfacing, compliance to accommodate deformation, and stable ionic conductivity under ambient

conditions. Beyond conventional functions, these gels also exhibit distinct photoresponsivity, a property that emerges from the interplay of gelatin chromophores with ion-mediated charge transfer. Such responsiveness is rare among hydrogels and underscores the untapped multifunctionality of biopolymer-based systems.

This chapter therefore establishes AlgGel organohydrogels as a versatile platform in which ion choice becomes a design knob for tailoring stretchability, sensitivity, and optical/electrical coupling. By situating ionic coordination at the heart of material design, the work bridges fundamental biopolymer chemistry with device-relevant functionalities, laying the foundation for their integration into sustainable soft-electronic sensors.

2.1.2 Preparation

Gelatin (1.36 g) was dissolved in deionized water (11.3 mL) at 50 °C under gentle stirring for 10 min. A sodium alginate solution (4 % w/v; 3.80 g) was then added, and the mixture was maintained at 50 °C for an additional 10 min to ensure homogenization. The hot sol was cast into a 9-cm diameter Petri dish, allowed to cool at room temperature for 20 min, and subsequently placed at 4 °C for 10 min to complete gelation.

Crosslinking was performed by immersing the hydrogel in 20 mL of a 0.5 M aqueous metal salt solution (MnCl_2 , pH $\approx$ 4.9; CuCl_2 , pH $\approx$ 3.1; FeCl_3 and ZrCl_4 , pH $\approx$ 0) for 1 h. Gels were then rinsed in 200 mL of deionized water for 1 h to remove excess ions. The samples were cut into 6-cm squares and equilibrated in 30 mL of 25 % (w/v) glycerol solution for 3 h, followed by overnight drying in a fume hood. Dried gels were trimmed into strips of 4.5×1.0 cm.

Samples were denoted MAlgGel, where M = Mn, Cu, Fe, or Zr. A non-crosslinked AlgGel control was prepared using the same protocol without the crosslinking and washing steps. Unless otherwise specified, all processing was

carried out at room temperature using deionized water, with careful handling to preserve uniform thickness.

2.1.3 Compositional, structural, optical, and electrical properties of AlgGel and MAlgGel

The compositional, structural, and optical properties of alginate–gelatin organohydrogels (MAlgGels) crosslinked with selected multivalent cations were systematically analyzed to establish how ionic coordination governs their macroscopic behavior. As summarized in **Table P1_S1** and **Figure P1_S1 (SI)**, the incorporation of crosslinking ions yields gels of comparable thickness ($\approx 800\ \mu\text{m}$), consistently higher than that of the non-crosslinked AlgGel reference. Importantly, ionic coordination confers enhanced robustness: while AlgGel collapses upon dehydration, crosslinked samples maintain structural integrity, reflecting the denser packing of their polymer networks (**Figure P1_S2, SI**). Optical characterization highlights that all MAlgGels retain high transparency in the visible region (**Figure P1_1b,c**), confirming their potential for transparent bioelectronics.

Neither the identity nor the valency of the coordinating ion significantly influences the glycerol uptake during equilibration, which remains between 58 wt% and 64 wt% (**Table P1_S1, SI**). Similarly, thermogravimetric analysis (TGA; **Figure P1_S3, SI**) reveals a nearly constant water content of $\approx 14\ \text{wt}\%$ across all samples. In contrast, the effective polymer content varies with ion type, as a direct consequence of different network collapse during the final drying step. This variation in polymer density strongly affects the materials' light responsiveness, as later discussed.

Low-temperature differential scanning calorimetry (LT-DSC; **Figure P1_S4a, SI**) shows the absence of crystallization or melting peaks, confirming that only non-freezable water is present in the gels.^[47,48] This feature ensures flexibility below $0\ ^\circ\text{C}$ and extends their applicability beyond the operating limits of conventional hydrogels.

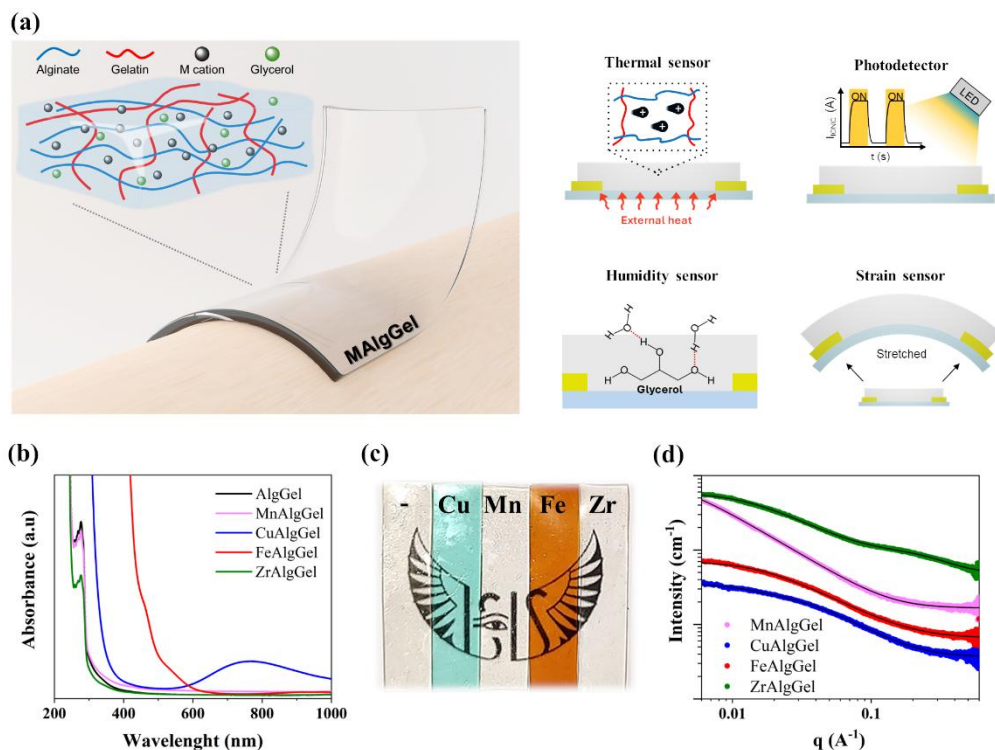


Figure P1_1. a) Three-dimensional cartoon of the multi-responsive alginate/gelatin organohydrogel crosslinked with a metal cation (MAAlgGel), placed on human skin. The scheme shows the potential applications of MAAlgGel, as thermal sensor, photodetector, humidity sensor and strain sensor. b) UV-Vis spectra, (c) optical image of the prepared MAAlgGel samples placed on top of a printed ISIS Strasbourg logo, and (d) Small angle X-ray scattering curves. Samples' coding: - = AlgGel = black; Mn = MnAlgGel = pink; Cu = CuAlgGel = blue; Fe = FeAlgGel = red; Zr = ZrAlgGel = green. SAXS curves were offset for clarity

TGA profiles (**Figure P1_S5, SI**) indicate that glycerol addition reduces the degradation onset of the uncrosslinked AlgGel matrix to ≈ 150 °C; however, crosslinking reverses this trend, with MAAlgGels exhibiting improved stability and degradation onsets around 170 °C (**Table P1_S2, SI**). DSC thermograms (**Figure P1_S4b, SI**) further reveal that glycerol plasticizes the system, lowering the glass transition temperature (T_g) and enhancing chain mobility. Notably, AlgGel displays two transitions (41.7 °C and 57.1 °C), reflecting facile chain rearrangements in the absence of crosslinking. By contrast, MnAlgGel and CuAlgGel each exhibit a single T_g near 42.5 °C, suggesting that coordination restricts polymer mobility. FeAlgGel and ZrAlgGel present

markedly higher T_g values (52.5 °C and 62.8 °C, respectively), consistent with reduced segmental freedom due to protonation effects in the acidic Fe^{3+} and Zr^{4+} crosslinking baths. These thermal signatures correlate directly with the enhanced rigidity of FeAlgGel and ZrAlgGel.

The strength of polymer–ion interactions is further captured by SAXS-derived correlation lengths (ξ , **Figure P1_1d** and **Table P1_S3, SI**), which quantify the nanoscale packing of the networks. Shorter ξ values correspond to denser networks and are observed in Fe^{3+} - and Zr^{4+} -crosslinked gels, consistent with their higher T_g and mechanical rigidity. Conversely, MnAlgGel and CuAlgGel show larger ξ values, indicative of more open structures.

Elemental analysis by ICP-AES (**Table P1_S1, SI**) shows that the absolute ion uptake remains modest (0.4–1.5 mmol g⁻¹), yet sufficient to impart marked changes in conductivity and mechanical stability. Conductivity measurements confirm strong ion-specific effects: AlgGel displays the lowest conductivity ($0.17 \pm 0.06 \text{ mS m}^{-1}$), while crosslinked gels show progressively higher values depending on cation type. MnAlgGel reaches $1.3 \pm 0.3 \text{ mS m}^{-1}$, CuAlgGel $3.7 \pm 0.5 \text{ mS m}^{-1}$, FeAlgGel $6.0 \pm 1.4 \text{ mS m}^{-1}$, and ZrAlgGel $6.1 \pm 0.9 \text{ mS m}^{-1}$ (**Table P1_S4, SI**). While glycerol content contributes to baseline conductivity, the hierarchy arises primarily from the specific electrostatic interactions between MX^+ and the protein–polysaccharide backbone, modulated by ion charge and size.^[49]

Altogether, the conductivity values of MAlgGels ($1\text{--}10 \text{ mS m}^{-1}$) compare favorably with state-of-the-art ionic conductive hydrogel sensors ($1\text{--}1000 \text{ mS m}^{-1}$).^[50–53] These findings demonstrate that subtle changes in ionic coordination translate into profound differences in packing, stability, and conductivity—establishing MAlgGels as tunable, multifunctional soft conductors.

2.1.4 Sensitivity of AlgGel and MAlgGel organohydrogels to temperature and RH

Temperature-dependent ionic conductivity was evaluated between 283 K and 323 K, a range relevant to skin-interfaced wearables.^[54–56] Samples were contacted with two copper electrodes on a temperature-controlled stage, and conductivity (σ) was extracted while heating and cooling.

As shown in **Figure P1_2a** conductivity increased with temperature for all gels, consistent with an ion-transport mechanism governed by the balance between ion–matrix interactions and medium viscosity. At lower temperatures, protons and metal counterions interact via dipole–dipole forces with carboxylate and hydroxyl groups on alginate/gelatin, limiting mobility. As temperature rises, these interactions weaken and the water–glycerol mixture becomes less viscous, jointly enhancing ionic mobility and σ .

Thermal sensitivity, obtained from the slope of $\Delta\sigma/\sigma$ versus T (**Figure P1_2b**, **Table P1_S4**, **SI**), distinguished the crosslinkers: MnAlgGel $\sim 0.19\text{ K}^{-1}$, CuAlgGel $\sim 0.16\text{ K}^{-1}$, and ZrAlgGel $\sim 0.13\text{ K}^{-1}$, while FeAlgGel exhibited the lowest sensitivity ($\sim 0.06\text{ K}^{-1}$). The reduced response of FeAlgGel is consistent with stronger ion–polymer interactions that more effectively hinder ion motion; correspondingly, its long-distance SAXS correlation length is the smallest among the series ($\xi_1 \approx 6.3\text{ nm}$), indicating a denser network. MnAlgGel showed a change in thermal sensitivity above $\sim 307\text{ K}$, attributable to the gelatin phase transition within the composite;^[57] despite gelatin’s bi-modal thermoresponsiveness, Mn^{2+} crosslinking maintained structural integrity over the full temperature window.

The uncrosslinked AlgGel control displayed a nonlinear temperature dependence with high apparent sensitivity ($> 0.2\text{ K}^{-1}$) and an onset of melting near $\sim 300\text{ K}$, accompanied by a sharp conductivity increase. Owing to this nonlinearity and the change in physicochemical state across the region of interest, AlgGel is not suitable as a temperature-sensing platform.

Crosslinked samples exhibited high reversibility over multiple heat–cool cycles within 283–323 K (**Figure P1_S6, SI**), whereas AlgGel did not recover its original behavior after melting.

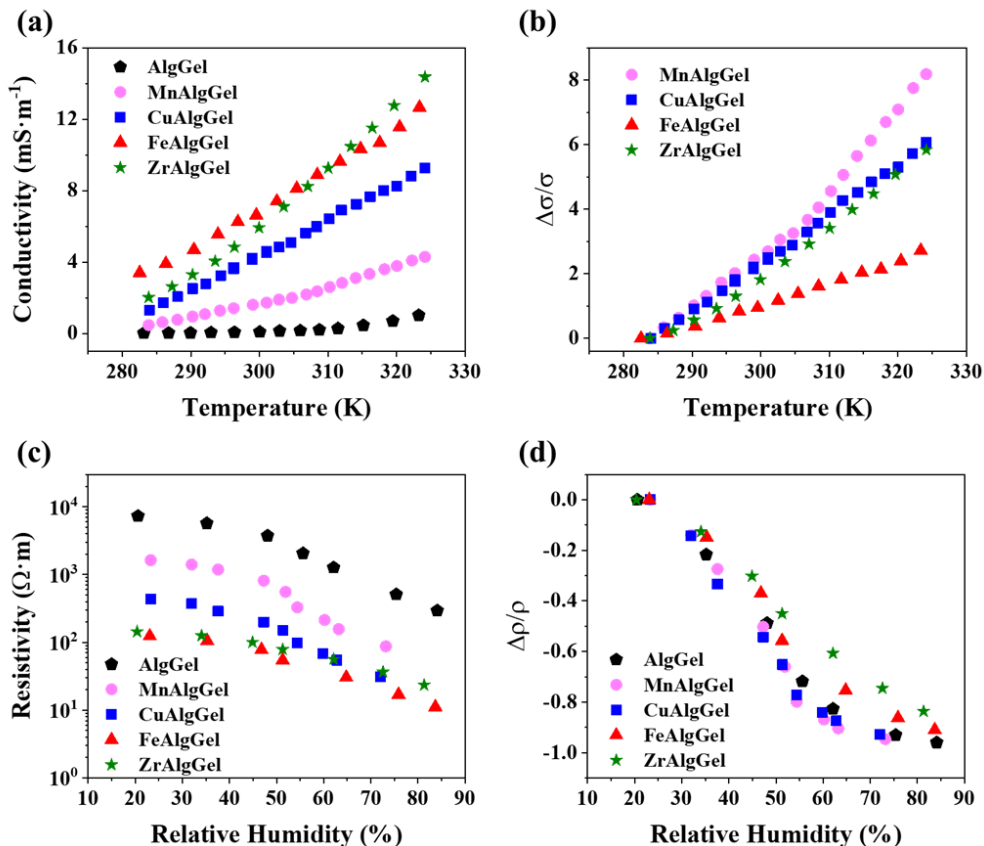


Figure P1_2. The influence of the temperature on (a) conductivity and (b) relative change of conductivity of AlgGel and the MAlgGels. The influence of relative humidity on (c) resistivity and (d) relative change of resistivity of AlgGel and the MAlgGels.

The organohydrogels reversibly absorb water owing to the hydrophilicity of both the alginate–gelatin matrix and glycerol (≈ 60 wt%), making them suitable for wearable humidity sensing.^[58–60] Resistivity was measured while cycling the ambient relative humidity (RH) between 20% and 80% in a controlled chamber (**Figure P1_2c**); the humidity sensitivity was taken as the slope of the $\Delta\rho/\rho$ vs RH response in the linear regime (**Figure P1_2d, Table P1_S4, SI**).

Across the series, AlgGel, MnAlgGel, and CuAlgGel displayed essentially identical sensitivities of $\approx 0.020 \text{ RH}(\%)^{-1}$ from 20% to 60% RH, followed by a response plateau above $\sim 60\%$ RH. In contrast, FeAlgGel and ZrAlgGel maintained comparable linear sensitivities of $\sim 0.018 \text{ RH}(\%)^{-1}$ and $\sim 0.015 \text{ RH}(\%)^{-1}$, respectively, over broader ranges (20–70% RH for FeAlgGel; 20–80% RH for ZrAlgGel). The extended linear windows are attributed to differences in water retention and matrix rigidity, consistent with the slightly higher glycerol content (by $\sim 3 \text{ wt}\%$) and higher stiffness of FeAlgGel and ZrAlgGel relative to the M^{2+} -crosslinked gels.

Overall, the crosslinked samples cluster within $0.022\text{--}0.015 \text{ RH}(\%)^{-1}$, indicating that glycerol chiefly governs the sensing process by imparting high hydrophilicity while the chosen cation tunes linear range and mechanical support. The working mechanism involves water uptake that promotes proton/ion transport, with proton generation (H_3O^+) and hopping along hydrogen-bonded pathways across glycerol-rich domains, leading to increased conductivity with RH.^[61] The crosslinked gels exhibited fully reversible responses over multiple humidity cycles across 20–80% RH (**Figure P1_S7, SI**), confirming robustness for wearable operation.

2.1.5 Photodetection with MAlGgel organohydrogels

A schematic of the MAlGgel photodetector under white-LED illumination is shown in the inset of **Figure P1_3a**. In all experiments, the illuminated area was kept constant at 3.14 cm^2 (circular spot with $r = 1 \text{ cm}$). Polycarbonate substrates (transparent and mechanically flexible, thus relevant for wearable e-skin applications) were used to fabricate the devices. Bottom-contact electrodes of Al, Au, or Cu were patterned on the substrate, and the gels served as the active channel.

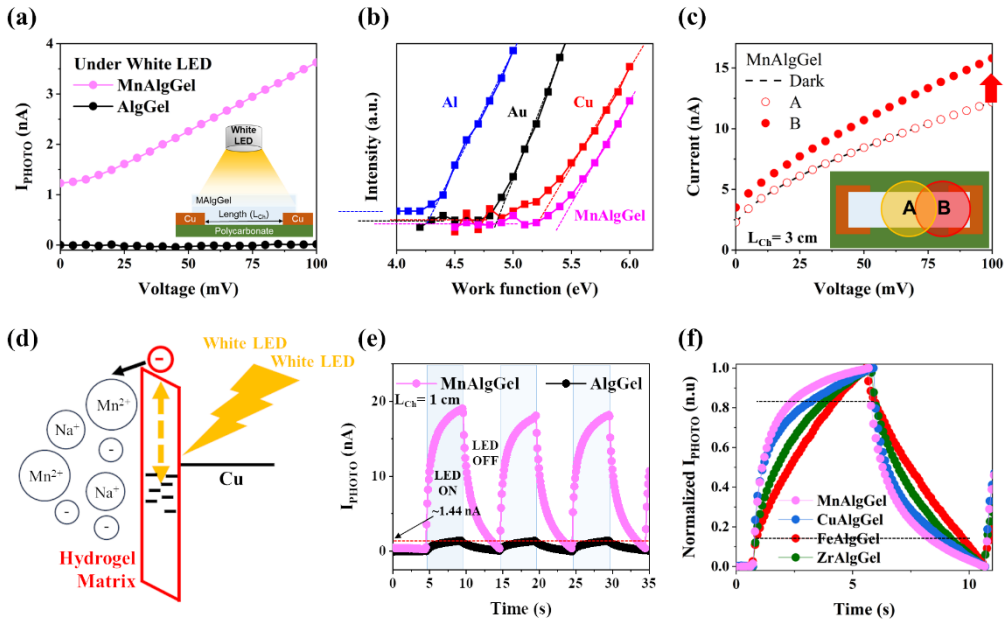


Figure P1_3. Photoresponse of MnAlGgel and AlgGel upon exposure to white LED. Schematic inset image displaying a side-view of MAlGgel photodetector. b) Secondary-electron cutoff of Al (blue circles), Au (black), Cu (red), and MnAlGgel (pink). c) Current vs. voltage characteristics of the MnAlGgel photodetector with a channel length of 3 cm, receiving the photons focused on the local area: a center of hydrogel (Position A) and a metal/hydrogel interface (Position B). d) Band diagram of the MnAlGgel/Cu interface. e) Time-resolved photoresponse of the MnAlGgel and AlgGel photodetector with a channel length of 1 cm. f) Normalized I_{PHOTO} vs. time plots of MAlGgel. All the illuminated area by the LED in this experiment was fixed as a circle with a 1 cm radius.

Among the tested electrode metals, only MnAlGgel/Cu devices exhibited a clear photocurrent response under LED illumination (**Figure P1_3a**), whereas

the Al- and Au-based counterparts showed negligible activity (**Figure P1_S8a–c, SI**). Since all three metals can support ionic conduction in conventional electrolytes,^[62,63] the superior performance of Cu contacts suggests an interfacial effect, specifically efficient electron injection at the MnAlgGel/Cu junction that facilitates enhanced ionic conduction in the hydrogel.

To probe this mechanism, photoelectron yield spectroscopy in air (PYSA) was employed to measure the secondary-electron cutoff (**Figure P1_3b**). The distinct work functions of Al, Au, and Cu yield variable built-in electric fields at the hydrogel/metal interface. The Cu contact provides the most favorable alignment, whereas Al induces the strongest barrier to injection, thereby suppressing photocurrent. Detailed PYSA spectra are provided in **Figures P1_S8d–f and P1_S9 (SI)**.

The critical role of the metal/gel junction was further confirmed by position-dependent illumination (**Figure P1_3c, inset**). When the LED spot was centered on the hydrogel channel (Position A, excluding the interface), the current matched the dark baseline. In contrast, irradiation at Position B (including the Cu/hydrogel interface) generated a reproducible photocurrent (I_{PHOTO}) with a ~30% increase in ionic current. This interfacial dependence is consistent with previous reports on built-in field-assisted photocurrent in ionically conductive systems.^[64,65] The corresponding band diagram of the MnAlgGel/Cu interface, highlighting trap-mediated photoresponse, is shown in **Figure P1_3d**.

The influence of ionic crosslinking was evident when comparing crosslinked and uncrosslinked matrices. MnAlgGel exhibited the highest I_{PHOTO} among all MAlgGel variants (**Figure P1_3a,e; Figure P1_S10, SI**), outperforming AlgGel by more than an order of magnitude. This enhancement correlates with the higher polymer content of MnAlgGel (**Table P1_S1, SI**), which increases the density of electron-trapping sites within the gel. For $L_{\text{Ch}} = 3$ cm, MnAlgGel devices delivered $I_{\text{PHOTO}} > 3.5$ nA, whereas AlgGel showed no detectable response. Even at a shorter channel length ($L_{\text{Ch}} = 1$ cm), AlgGel reached only

~1.4 nA, while MnAlgGel maintained a ~15× larger response (**Figure P1_3e**; Photoresponsivity = 9.2 $\mu\text{A W}^{-1}$, **Table P1_S4, SI**).

Device stability was evaluated by re-measuring photocurrent after one week of ambient storage. As shown in **Figure P1_S11 (SI)**, MnAlgGel retained its I_{PHOTO} with negligible decay, underscoring the role of Mn^{2+} ions in stabilizing the gel matrix and sustaining ionic conduction.

Finally, photoswitching dynamics were benchmarked across the MAlgGel series (**Figure P1_3f**). MnAlgGel exhibited the fastest response, with rise and fall times of 2.23 s and 3.13 s, respectively, compared to >3.0 s rise and >3.5 s fall for other cation-crosslinked gels. Switching times were extracted between 10% and 90% of normalized I_{PHOTO} (dashed line in **Figure P1_3f**), and all values are summarized in **Table P1_S4 (SI)**. The superior responsivity and switching kinetics of MnAlgGel highlight its unique suitability as a transparent, flexible, and filler-free photoactive hydrogel platform.

2.1.6 Mechanical properties and strain sensitivity

The mechanical behavior of MAlgGel organohydrogels strongly depends on the identity of the coordinating cation. As shown in **Figure P1_4b**, all crosslinked samples display reduced stretchability compared to the uncrosslinked AlgGel reference, reflecting the higher rigidity imparted by ionic coordination. Among the MAlgGels, CuAlgGel and MnAlgGel sustain the largest elongations (~140%), whereas FeAlgGel and ZrAlgGel are markedly more rigid, with maximum stretchabilities of ~45% and ~55%, respectively. This increased rigidity is attributed to protonation of alginate chains during crosslinking in the acidic Fe^{3+} and Zr^{4+} baths. The resulting tightening of the network imparts linear stress–strain responses, in contrast to AlgGel, whose curves resemble those reported for gelatin in the literature.^[66] CuAlgGel shows a similarly linear response, while the weaker Mn^{2+} –alginate interaction fails to fully linearize the mechanical trace.

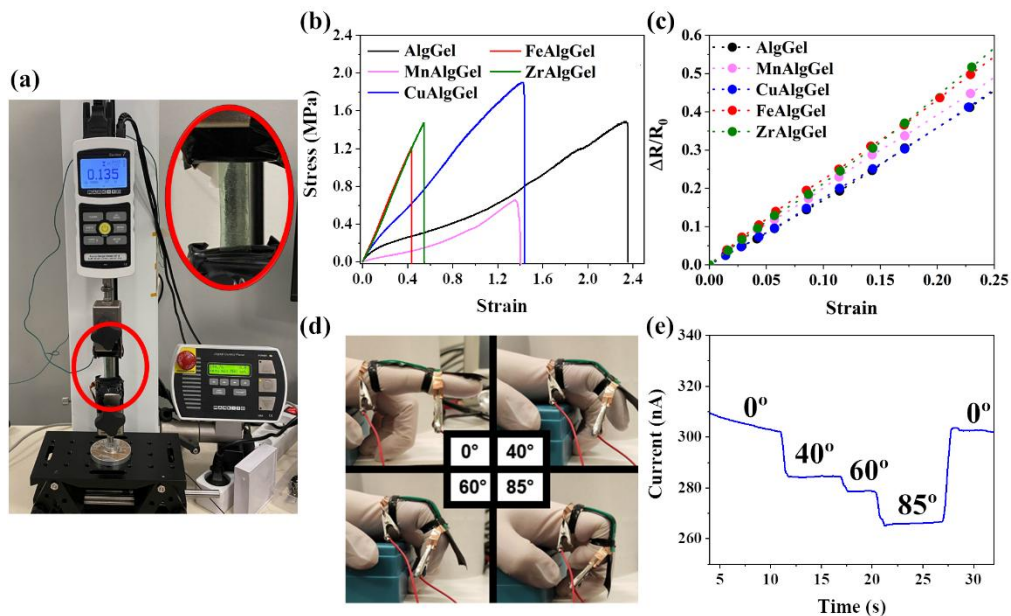


Figure P1_4. a) Photograph of the experimental setup for the samples connected using two copper electrodes. b) Stress vs. strain curves and (c) $\Delta R/R_0$ vs. strain of AlgGel (black), MnAlgGel (pink), CuAlgGel (blue), FeAlgGel (red) and ZrAlgGel (green). Images of the finger bending steps for the strain sensing test (d) and related electrical response (e).

The Young's modulus (YM) was determined from the slope of the stress–strain curve in the 0–0.04 strain window (**Figure P1_S12, SI**). As summarized in **Table P1_S4 (SI)**, YM follows the trend $\text{Mn}^{2+} < \text{Cu}^{2+} \approx \text{Zr}^{4+} < \text{Fe}^{3+}$, consistent with the long-distance correlation lengths (ξ_l) extracted from SAXS (see **Section 3** and **Table P1_S3, SI**). Ultimate tensile strength (UTS) values are also listed in **Table P1_S4 (SI)**: CuAlgGel exhibits the highest UTS (1.88 ± 0.04 MPa), while MnAlgGel remains the weakest (0.64 ± 0.02 MPa). These findings align with the divalent ion–alginate affinity scale reported previously.^[67–69]

Stretching the organohydrogels alters the ionic pathways, producing pronounced changes in conductivity and thereby enabling motion-sensing functionality. To evaluate electromechanical sensitivity, the relative resistance change ($\Delta R/R_0$) was measured under strain up to 0.25. As shown in **Figure P1_4c**, all samples exhibit $\Delta R/R_0 \approx 50\%$ in this window. Importantly, strain

alone does not reflect the absolute stress applied, underscoring the need to also consider mechanical parameters.

The gauge factor (GF) was calculated according to Eq. 1:^[70]

$$GF = (\Delta R/R_0)/\varepsilon \quad (\text{Eq. 1})$$

where $\Delta R/R_0$ is the relative resistance change and ε is the applied strain. GF values were extracted in two strain windows (0–0.04 (GF₁) and 0–0.25 (GF₂)) to verify linearity across low and moderate strains. Results are summarized in **Table P1_S4 (SI)**. The AlgGel reference exhibited large fluctuations at very low strains, consistent with its nonlinear stress–strain behavior (**Figure P1_S12, SI**). By contrast, CuAlgGel, FeAlgGel, and ZrAlgGel provided stable and reproducible responses. The highest GFs were recorded for Fe³⁺- and Zr⁴⁺-crosslinked gels (2.15 ± 0.07 and 2.27 ± 0.18 , respectively). Overall, the GFs of MAlgGels (1.7–2.3) are comparable to, or even exceed, those of typical ionic-conductive hydrogel strain sensors reported in the literature (0.5–1.7).^[51,53,71]

From an application standpoint, CuAlgGel offers the best compromise between sensitivity and compliance, making it suitable for detecting small, stress-limited deformations. To demonstrate this, CuAlgGel was applied to monitor finger bending (**Figure P1_4d**), where the electrical response scaled with bending angle (**Figure P1_4e**). Durability tests confirmed that the response was preserved over 2500 stretch–release cycles (**Figure P1_S13, SI**). Notably, these devices operated reliably at a low bias voltage (0.2 V), highlighting their potential for real-time, low-power motion monitoring.

2.1.7 Conclusion

This chapter established a reproducible, fully aqueous route to alginate–gelatin organohydrogels that remain transparent and compliant while delivering stable ionic conduction. Crosslinking alginate with transition-metal ions generated robust film architectures, while gelatin imparted thermoresponsiveness and

skin-compatibility. The water–glycerol medium further stabilized hydration and conductivity without resorting to opaque electronic fillers.

The findings can be organized around three interdependent design knobs:

- **Crosslinker identity** set the network baseline. Mn^{2+} and Cu^{2+} yielded extensible gels (up to ≈ 140 % strain), while Fe^{3+} and Zr^{4+} produced denser networks with higher rigidity (Young’s modulus ≈ 2.5 MPa) and elevated glass-transition temperatures (> 50 °C). Conductivity followed the hierarchy $\text{Mn} < \text{Cu} < \text{Fe} \approx \text{Zr}$, spanning from ≈ 0.2 to 6.1 mS m^{-1} .
- **Organohydrogel chemistry** governed hydration and ion mobility. Glycerol uptake stabilized water content at ≈ 14 wt% and suppressed freezing, enabling reversible operation between -10 °C and $+50$ °C. As a result, the gels exhibited clean, repeatable temperature and humidity responses, with sensitivities of $\approx 0.02 \text{ RH}^{-1}$ and $\approx 0.15\text{--}0.20 \text{ K}^{-1}$ depending on crosslinker.
- **Metal/gel interfaces** determined photoresponsivity. Only Cu–MnAlgGel junctions exhibited stable photocurrents under visible illumination, with responsivities up to $9.2 \mu\text{A W}^{-1}$ and switching times below 3 s. This performance was directly linked to the trap landscape defined by polymer fraction and ion coordination.

Together, these insights define a compact rule set: choose the ion to define structure and mechanics, choose the medium to tune ionic mobility and environmental response, and engineer the contact to control interfacial injection and light coupling.

This framework not only rationalizes the multifunctionality of AlgGel organohydrogels but also provides transferable principles for the design of sustainable, transparent, and filler-free soft-electronic elements. The next sections apply this logic to gel electrolytes, strain sensors, and optically addressable interfaces built directly on this coordination–organohydrogel–interface triad.

2.2 Project 2. Ionically Tunable Gel Electrolytes Based on Gelatin-Alginate Biopolymers for High-Performance Supercapacitors

This section originates from the publication:

P. Tordi; V. Montes-García; A. Tamayo; M. Bonini; P. Samorì; A. Ciesielski, “Ionically Tunable Gel Electrolytes Based on Gelatin–Alginate Biopolymers for High-Performance Supercapacitors,” Small, 2025, 21 (33), 2503937.

(<https://doi.org/10.1002/sml.202503937>)

2.2.1 Introduction

Gel polymer electrolytes (GPEs) are central to the development of safe and flexible energy storage devices, as they combine the mechanical compliance of solids with the ionic transport of liquids. However, most current GPEs rely on synthetic matrices or volatile solvents, which compromise durability, sustainability, and long-term stability. Organohydrogels have emerged as a promising alternative by incorporating humectant phases that suppress dehydration and enhance handling. Yet, their reduced water content often limits ion mobility unless both the polymer network and ionic environment are deliberately engineered.

In this chapter, the alginate–gelatin organohydrogel architecture introduced previously is translated into a fully biopolymeric GPE. Prior work in this thesis demonstrated that AlgGel organohydrogels are transparent, compliant, and ionically programmable: altering the crosslinking cation reorganizes the nanoscale network and predictably shifts mechanical and transport properties. Here, these principles are repurposed from sensing to energy storage, establishing a sustainable electrolyte platform that avoids synthetic polymers such as PVA.

The strategy rests on two design elements. First, alginate’s coordination chemistry follows a well-established affinity ladder (e.g., stronger binding with Cu^{2+} than with Mn^{2+}), enabling the crosslinker to define network packing, correlation length, and chain mobility. Second, controlled incorporation of Li^+

introduces an independent handle over charge carrier density and viscosity-coupled transport, allowing ionic conduction to be tuned without sacrificing transparency or processing simplicity. Together, $\text{Cu}^{2+}/\text{Mn}^{2+}$ crosslinking sets the framework, Li^+ modulates mobility, and SAXS provides structural insights linking nanoscale organization to bulk transport and device performance.

This project therefore extends the design rule set developed earlier (ion choice defines structure and mechanics; the medium stabilizes hydration and conduction; interfaces govern device behavior) to the realm of supercapacitor electrolytes. By systematically varying the $[\text{Li}^+]/[\text{M}^{2+}]$ ratio at fixed total salt, we demonstrate how nanoscale structure and ion composition co-determine bulk resistance, interfacial kinetics, and long-term cycling stability. The result is a green, ionically tunable GPE that translates biopolymer coordination chemistry into practical electrochemical performance.

2.2.2 Preparation of Gelatin–Alginate Gel Polymer Electrolytes

To prepare the gel polymer electrolytes, 1.36 g of gelatin was dissolved in 11.3 mL of water under gentle stirring at 50 °C for 10 minutes. A 4% (w/v) alginate solution (3.80 g) was then added, and the mixture was stirred at 50 °C for an additional 10 minutes. Aliquots of 6 mL were poured into polystyrene molds (2×6 cm), allowed to cool at room temperature for 10 minutes, and then refrigerated at 4 °C for another 10 minutes. The gels were subsequently immersed in 50 mL of an aqueous solution containing MCl_2 ($\text{M} = \text{Mn}$ or Cu) and LiCl for 1 hour. The specific concentrations of MCl_2 and LiCl used for crosslinking are provided in **Table P2_S1 (SI)**.

After crosslinking, the gels were transferred to a glycerol:water solution (1:4 v/v) containing the same salt concentrations (**Table P2_S1, SI**) and incubated for 1.5 hours, followed by immersion in a fresh glycerol:water solution (1:4 v/v) for an additional 1.5 hours to remove excess salts. The samples were then dried overnight under a fume hood and equilibrated at 40% relative humidity (RH).

The resulting gels were denoted MXAlgGel, where M indicates the metal ion (Mn or Cu) and X the molar concentration: 100 (1.00 M), 075 (0.75 M), 050 (0.50 M), or 025 (0.25 M). The LiCl concentration was adjusted to maintain a constant total salt concentration of 1 M (see **Table P2_S1, SI**). LiAlgGel was prepared as a reference to isolate the role of the metal ion, while AlgGel (without added salts) served as a blank control.

All samples were stored in hermetically sealed Petri dishes under dark conditions until use. Results labeled as “6-month-old samples” were obtained from specimens stored under these conditions. Before characterization, samples were cut into disks (1 cm diameter) or strips (1 cm width), depending on the intended measurement.

2.2.3 General properties of AlgGel-based gel polymer electrolytes

Figure P2_1a illustrates the synthetic pathway used to prepare alginate–gelatin (AlgGel)-based organohydrogels. The process begins with the dissolution of gelatin in water at 50 °C, followed by incorporation of a 4% (w/v) alginate solution under continuous stirring (see Experimental Section for details). The resulting mixture is cast into molds, cooled, and subsequently crosslinked in mixed salt baths containing MCl_2 ($M = \text{Mn or Cu}$) and LiCl. After equilibration in a glycerol–water solution, the materials are dried at room temperature to yield MXAlgGel samples, where X denotes the molar concentration of MCl_2 : 100 (1.00 M), 075 (0.75 M), 050 (0.50 M), or 025 (0.25 M). In all cases, the LiCl content was adjusted to maintain a constant total salt concentration of 1 M (**Table P2_S1, SI**). This controlled ionic environment enables systematic modulation of the $[Li^+]/[M^{2+}]$ ratio in the crosslinking solution, thereby providing a reproducible framework to study the effect of ion composition on the physicochemical and electrochemical properties of the gels.

Two reference systems were also prepared: LiAlgGel (1.00 M LiCl only) to isolate the role of divalent ions, and AlgGel (no added salts) as a blank control. Importantly, all formulations exhibited comparable thickness, as confirmed in

Figure P2_S1 and **Table P2_S3** (SI), ensuring reliable comparisons of their properties.

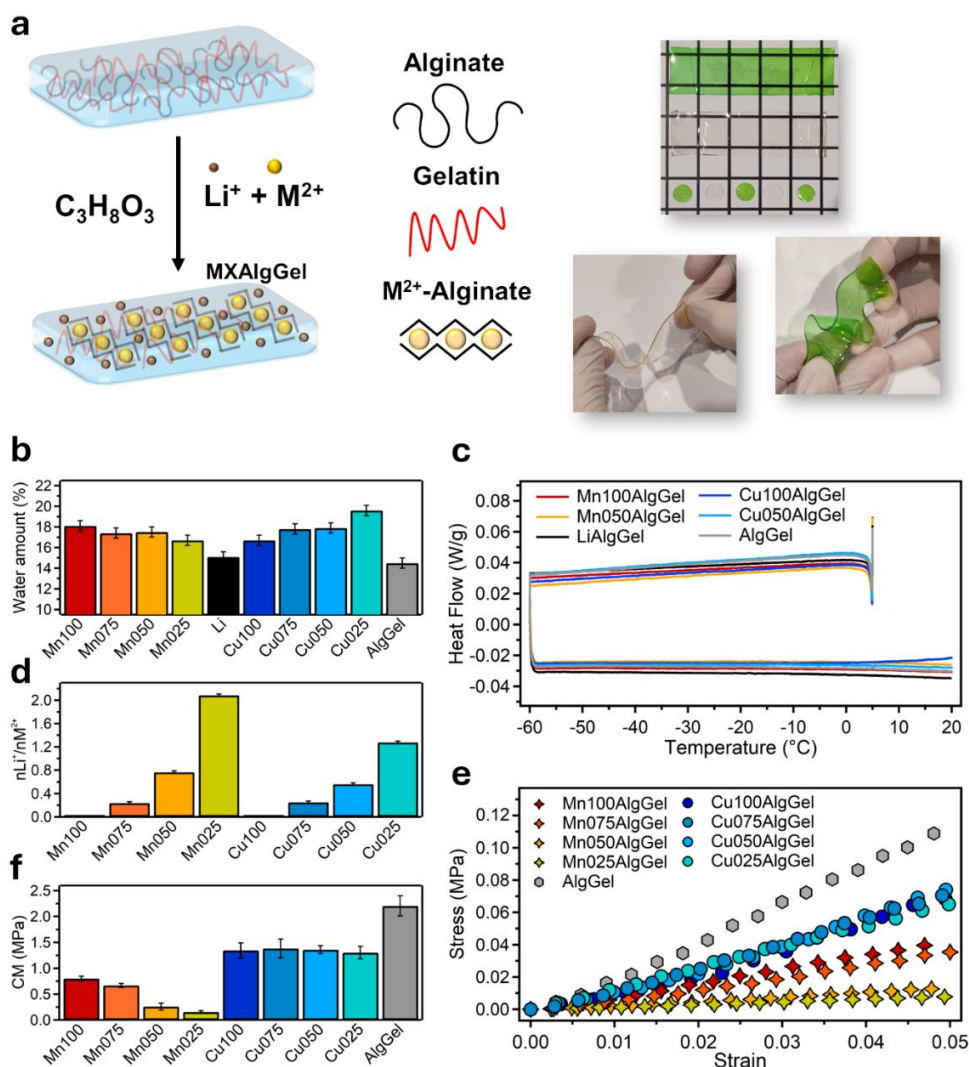


Figure P2_1. a) Schematic representation of the preparation process for AlgGel-based organohydrogels and their visual appearance. b) Water content, and c) freezable water evaluation through DSC analysis. d) Experimental Li⁺ over M²⁺ molar ratio (nLi⁺/nM²⁺) for the AlgGel-based organohydrogels. e) Stress-strain curves, and f) compressive modulus (CM) values of Cu100AlgGel, Cu075AlgGel, Cu050AlgGel, Cu025AlgGel, Mn100AlgGel, Mn075AlgGel, Mn050AlgGel, Mn025AlgGel and AlgGel.

The incorporation of Mn^{2+} and Cu^{2+} ions into alginate significantly alters the polymer matrix by reducing chain mobility and rendering the gels water-insoluble. Qualitatively, Mn^{2+} -crosslinked hydrogels appear softer than their Cu^{2+} counterparts, consistent with the stronger affinity of Cu^{2+} for alginate.^[14] Moreover, MnXAlgGel and LiAlgGel samples exhibit similar mechanical consistency, in contrast to the distinctly rigid Cu^{2+} -crosslinked gels. The hydrogels also display characteristic optical properties: Mn^{2+} -crosslinked samples remain transparent, while Cu^{2+} -crosslinked ones exhibit a green coloration (**Figure P2_1a**; **Figure P2_S1d**, SI).

Compositional analysis (**Table P2_S3**) shows that the organohydrogels contain ≈ 60 wt% glycerol, ≈ 20 wt% polymer (gelatin + alginate), and ≈ 20 wt% water (**Figure P2_1b**), with ions homogeneously distributed throughout the matrix. Thermogravimetric analysis (**Figure P2_S2**, SI) confirms these values. The absence of phase separation, combined with the plasticizing effect of glycerol, preserves structural integrity for several months (**Figure P2_S1d–f**; **Table P2_S2**, SI). Differential scanning calorimetry (**Figure P2_1c**) reveals no detectable phase transitions upon heating or cooling, demonstrating that the confined water is predominantly non-freezable.^[72] This feature ensures flexibility and ionic mobility even at subzero temperatures.

The composition of the crosslinking solution directly dictates the ionic uptake of the gels. As summarized in **Table P2_S4** (SI) and illustrated in **Figure P2_1d**, the amount of incorporated Li^+ scales with its concentration in the crosslinking bath, though incorporation efficiencies differ markedly between Mn^{2+} - and Cu^{2+} -crosslinked systems. The experimental molar ratio ($n\text{Li}^+/n\text{M}^{2+}$) reaches 2.08 in Mn025AlgGel but only 1.28 in Cu025AlgGel, highlighting the higher permeability of Mn^{2+} -crosslinked frameworks to Li^+ ions. This trend correlates with the nanoscale structural features observed by SAXS (discussed later).

The compressive behavior of the gels is shown in **Figure P2_1e,f**. AlgGel, with the lowest water content due to the absence of hygroscopic ions, displays the highest compressive modulus. Mn^{2+} -crosslinked gels progressively soften as

Li⁺ content increases, while Cu²⁺-crosslinked networks maintain their mechanical robustness across all formulations, underscoring their suitability for applications requiring both stability and adaptability.

2.2.4 Nanoscale assembly of AlgGel-based gel polymer electrolytes

The structural characteristics of alginate–gelatin gels crosslinked with Cu²⁺ or Mn²⁺ ions, in combination with Li⁺, provide critical insights into their suitability as gel polymer electrolytes (GPEs) for energy storage. Small-angle X-ray scattering (SAXS) was employed to probe how these ions dictate nanoscale organization, thereby linking internal structure to mechanical and functional behavior. SAXS curves (**Figure P2_2a**) were fitted using the following Lorentzian–Porod equation:^[73–76]

$$I(q) = \frac{A}{q^n} + \frac{B}{1+(q\xi)^m} + bkg \quad (\text{Eq. 2})$$

where A is the Porod scaling factor, n the Porod exponent, B the Lorentzian scale factor, m the Lorentzian exponent, ξ the correlation length, and bkg the background. Fitting results are summarized in **Table P2_S5 (SI)**, while extracted correlation lengths and Porod exponents are plotted in **Figure P2_2b**. Both Cu²⁺ and Mn²⁺ crosslink alginate primarily through interactions with carboxylate groups, yet with markedly different binding strengths. Cu²⁺ forms stronger, more localized interactions,^[72,77] producing denser and more rigid networks, whereas Mn²⁺ binding is weaker and more easily perturbed by Li⁺ incorporation. This contrast is evident in the SAXS results: Cu²⁺-crosslinked gels maintain consistently short correlation lengths ($\xi = 3.5\text{--}3.9$ nm) across all nLi⁺/nCu²⁺ ratios, reflecting a structurally resilient network. In contrast, Mn²⁺-crosslinked gels show a pronounced increase in ξ from 6.3 nm to 14.7 nm as nLi⁺/nMn²⁺ rises, indicative of progressive disruption of Mn²⁺ crosslinking by Li⁺ and the formation of more open networks (**Figure P2_2c**). This effect can

be attributed to competitive ion exchange,^[14] which destabilizes Mn^{2+} junctions but leaves Cu^{2+} frameworks largely unaffected.

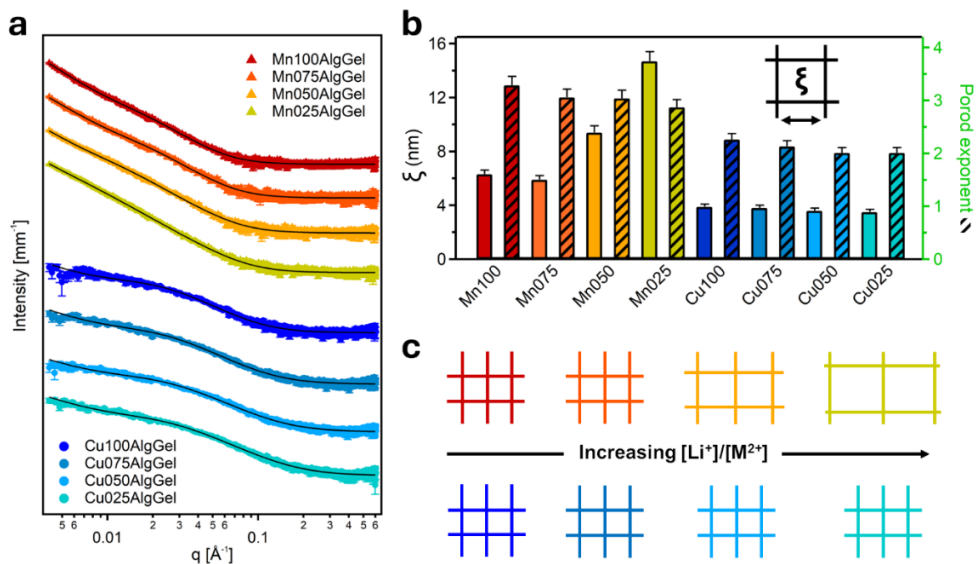


Figure P2_2. a) SAXS curves (in log scale and offset for clarity) and b) extracted correlation lengths (ξ) and Porod exponents (dashed bars) for MnXAlgGel and CuXAlgGel. c) Schematic representation of the structural differences between Mn^{2+} - and Cu^{2+} -crosslinked networks as a function of $[\text{Li}^+]/[\text{M}^{2+}]$ ratio in the crosslinking solution. MnXAlgGels show increasing ξ with higher Li^+ content, indicating a progressively looser network. In contrast, CuXAlgGels maintain a consistently compact network structure.

The Porod exponent (n) provides additional evidence. In Mn^{2+} -crosslinked gels, n decreases from 3.29 to 2.87 with increasing $n\text{Li}^+/n\text{Mn}^{2+}$, signaling a transition from compact, mass-fractal-like to more open structures.^[73–76] By contrast, Cu^{2+} -crosslinked gels display lower and relatively constant values (2.26–2.01), characteristic of a surface-fractal-like morphology. This subtle difference emphasizes the rigidity imparted by Cu^{2+} , which yields networks resistant to deformation despite their less compact nanoscale appearance.

This interplay between rigidity and flexibility underpins distinct electrochemical advantages. Cu^{2+} -crosslinked gels provide highly organized, robust networks that support stable ion transport pathways, making them strong candidates for durable electrolyte frameworks in solid-state devices. Mn^{2+} -

crosslinked gels, on the other hand, form looser, more porous structures as Li^+ content increases, which enhances ionic mobility but may compromise long-term mechanical resilience.

By tuning the $\text{Cu}^{2+}/\text{Mn}^{2+}/\text{Li}^+$ ratios, these systems can be engineered to balance stability with conductivity. Importantly, this dual-ion crosslinking approach (combined with SAXS as a structural diagnostic) offers a rare ability to deliberately tailor nanoscale architecture in fully biopolymer-based GPEs. Such structural control directly links internal organization to electrochemical performance, a crucial yet often overlooked factor in designing next-generation sustainable gel polymer electrolytes. This versatility underscores the potential of AlgGel-based organohydrogels as next-generation GPEs, with SAXS offering a crucial framework for understanding and optimizing their performance. To further evaluate their suitability for energy storage, thermal stability was first assessed by thermogravimetric analysis (TGA). As shown in **Figure P2_S2** and **Table P2_S3 (SI)**, all samples exhibited thermal degradation onset near 190 °C, except for Cu-rich formulations (Cu075–Cu100), which degraded slightly earlier (~180 °C) due to the catalytic effect of Cu^{2+} on decomposition.^[14,78] These values confirm that, despite their biopolymeric nature, gelatin–alginate gels retain sufficient thermal tolerance for practical energy storage, where organohydrogel electrolytes are typically required to operate below ~80 °C.^[79–81]

2.2.5 Electrochemical performance of AlgGel-based GPEs

Building on these physicochemical characteristics, the electrochemical performance of AlgGel-based organohydrogels was evaluated in symmetric supercapacitors. Coin cells were assembled using activated carbon as both electrodes, with the various gel formulations serving as electrolytes (see Experimental Section for details).

· Ionic transport and impedance

Electrochemical impedance spectroscopy (EIS) was employed to probe ionic transport properties (**Figures P2_3a and P2_S3, SI**).

A key parameter extracted from EIS is the bulk resistance (R_b), corresponding to the high-frequency intercept in Nyquist plots. R_b reflects intrinsic ionic transport through the gel matrix; lower values indicate higher ionic conductivity and reduced ohmic loss. As the gels are electronically insulating, the conductivity values obtained from EIS (**Table P2_S6, SI**) refer exclusively to ionic transport.

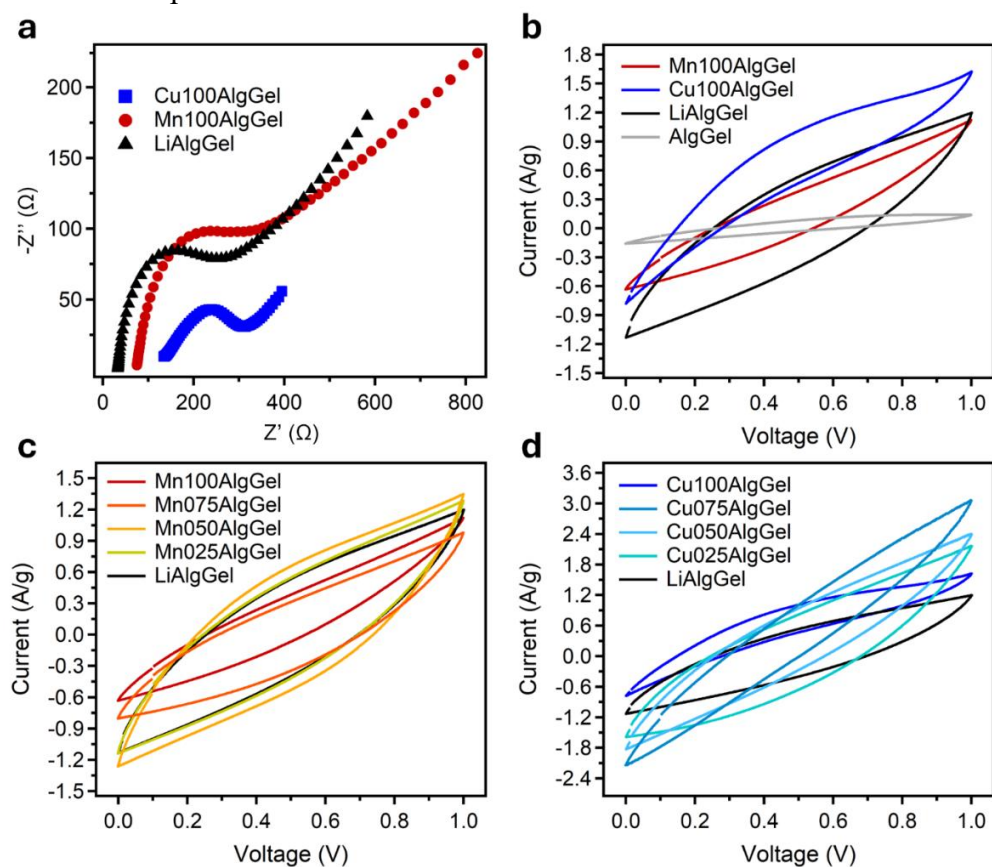


Figure P2_3. a) Nyquist plot showing the impedance behavior for Cu100AlgGel, Mn100AlgGel, and LiAlgGel in supercapacitors. A comparison with AlgGel is provided in **Figure P2_S3a (SI)**. b) CV curves of gels with single cationic species at 10 mV/s in supercapacitors. CV curves at 10 mV/s of c) MnXAlgGels and d) CuXAlgGels in supercapacitors. The CV curves for other scan rates are reported in **Figure P2_S4, P2_S5 and P2_S6 (SI)**.

Elevated R_b generally signifies hindered ion mobility, arising from poor dissociation, high viscosity, or excessive crosslinking density. Another important parameter is the charge transfer resistance (R_{ct}), which quantifies interfacial kinetics at the electrode–electrolyte junction. Lower R_{ct} values denote more efficient ion exchange and faster charge/discharge capability—key requirements for high-power devices.

The results highlight a complementary relationship between bulk and interfacial behavior. Cu100AlgGel displayed the highest R_b (119.0 Ω , **Table P2_S6, SI**) due to its dense, tightly packed Cu^{2+} –alginate network revealed by SAXS ($\xi = 3.9$ nm). By contrast, Mn100AlgGel exhibited a lower R_b (73.3 Ω), consistent with its more open network ($\xi = 6.3$ nm), which promotes faster bulk ion transport. However, the trend reversed for R_{ct} : Cu100AlgGel showed a lower R_{ct} (239.9 Ω) than Mn100AlgGel (296.4 Ω), reflecting the ability of strong Cu^{2+} –alginate coordination to form stable and cohesive electrode–electrolyte interfaces, whereas weaker Mn^{2+} –polymer interactions lead to less defined interfaces. These findings confirm that R_b and R_{ct} probe distinct aspects of electrochemical behavior (bulk ionic conduction and interfacial kinetics) and must be considered independently when evaluating GPE performance.

LiAlgGel, with its highly porous and disordered framework, achieved the lowest R_b (32.7 Ω), indicating excellent ionic mobility. Notably, even modest incorporation of Li^+ into Mn^{2+} - or Cu^{2+} -crosslinked systems (Mn075AlgGel and Cu075AlgGel) substantially decreased R_b , as seen in their Nyquist plots (**Figure P2_S3b,c, SI**), aligning their impedance characteristics with those of LiAlgGel.

· *Cyclic voltammetry*

Cyclic voltammetry (CV) further illustrated the electrochemical trends (**Figure P2_3b**). The loop area, which scales with capacitance, was largest for LiAlgGel, reflecting its high ionic mobility and charge storage capacity. Cu100AlgGel and Mn100AlgGel, by contrast, displayed narrower loops due to the restricted ion mobility imposed by strong M^{2+} –polymer coordination,

despite their structural robustness. AlgGel, lacking crosslinking ions, showed negligible electrochemical activity.

The influence of Li^+ incorporation is highlighted in **Figure P2_3c,d**. In Mn^{2+} -crosslinked systems, progressively increasing the $n\text{Li}^+/n\text{Mn}^{2+}$ ratio expanded the CV loop area, demonstrating that Li^+ disrupts Mn^{2+} crosslinking, enhances ion mobility, and increases capacitance, albeit at the cost of reduced rigidity. In Cu^{2+} -crosslinked systems, Li^+ addition produced a synergistic effect: Li^+ ions enhanced transport while Cu^{2+} ions preserved structural integrity. This dual contribution led to steadily larger CV loops, with Cu050AlgGel surpassing even LiAlgGel in capacitance, underscoring its promise for high-performance energy storage.

· Charge–discharge behavior

The galvanostatic charge–discharge (GCD) profiles recorded at a current density of 0.2 mA/cm^2 (**Figure P2_4a,b**) provide further insight into the electrochemical behavior of Mn^{2+} - and Cu^{2+} -crosslinked organohydrogel electrolytes, highlighting differences in charge storage capacity, ionic transport, and stability. GCD curves acquired at higher current densities (*i.e.*, 0.5 mA/cm^2 , 1.0 mA/cm^2 , 2.0 mA/cm^2) and comparisons between AlgGel, Mn100AlgGel, Cu100AlgGel and LiAlgGel references are reported in **Figure P2_S7**, **P2_S8** and **P2_S9** (SI).

For MnXAlgGel, a progressive enhancement in charge storage is observed with increasing $n\text{Li}^+/n\text{Mn}^{2+}$ ratios. Among these, Mn050AlgGel displays the longest discharge time, confirming its optimal balance between structural integrity and enhanced ion mobility. This trend is consistent with CV results, where Mn050AlgGel exhibited the largest electrochemical response. In contrast, Mn100AlgGel shows a markedly shorter discharge duration, reflecting high internal resistance and limited ion accessibility within its rigid Mn^{2+} -dominated framework. The systematic progression from Mn100 $\rightarrow$ Mn025 formulations underscores the role of Li^+ in progressively disrupting Mn^{2+} crosslinks, thereby improving charge storage efficiency—fully corroborating the EIS and SAXS analyses.

The CuXAlgGel series reveals a distinct behavior. Cu050AlgGel exhibits the longest discharge time and highest capacitance, in agreement with its superior CV response (**Figure P2_3d**). This performance reflects the synergistic effect of Cu^{2+} and Li^+ : Cu^{2+} provides structural robustness while Li^+ enhances ionic mobility, together optimizing transport and storage. By contrast, Cu100AlgGel and Cu075AlgGel struggle to sustain stable charge–discharge up to 1 V, indicating elevated internal resistance arising from overly strong Cu^{2+} –polymer interactions, which hinder ion motion. This observation is consistent with EIS, where Cu100AlgGel exhibited the highest R_b .

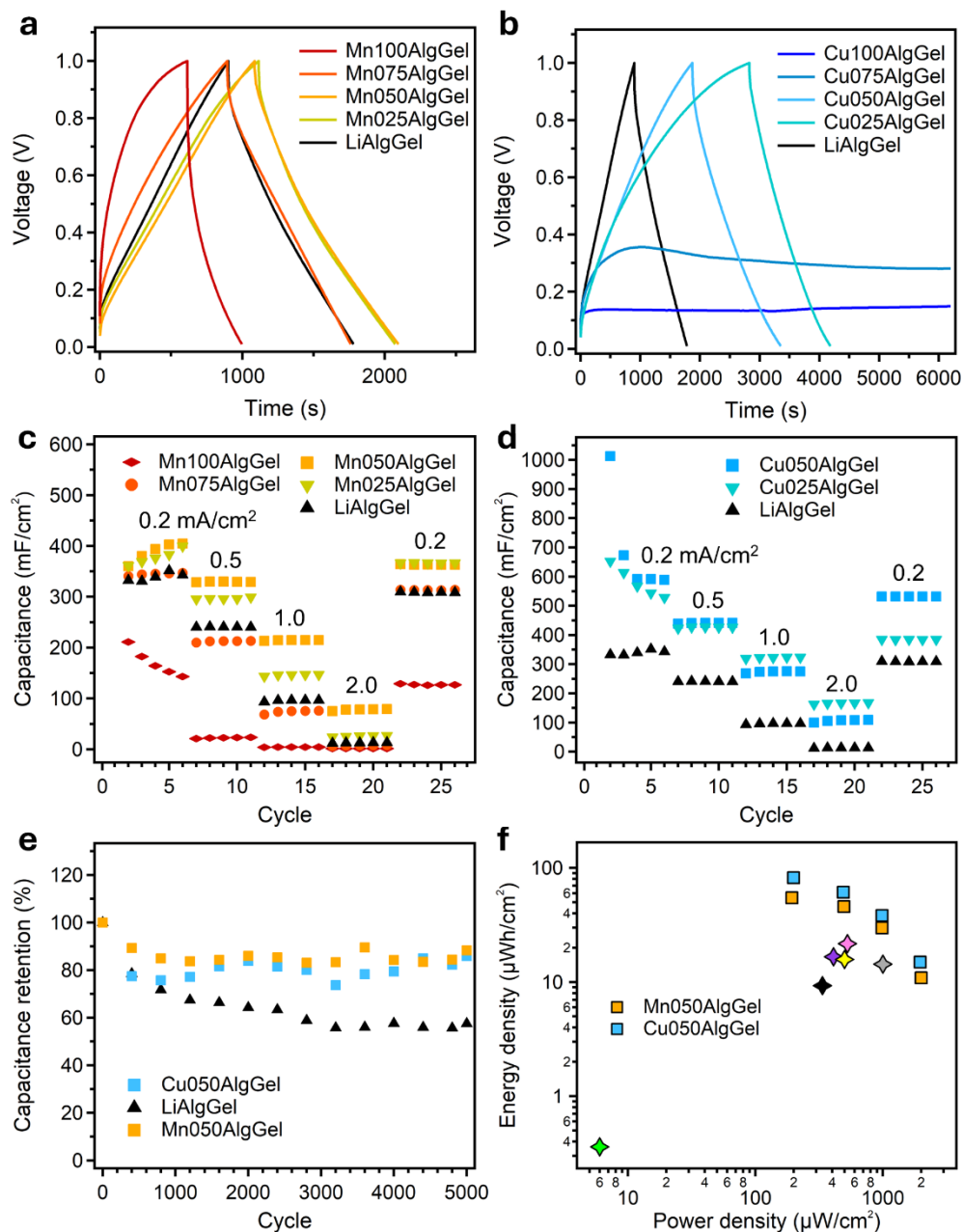


Figure P2_4. GCD curves of a) MnXAlgGels and b) CuXAlgGels along with LiAlgGel. (current density = 0.2 mA/cm²). other current densities can be seen in **Figure P2_S7** and **P2_S8, SI**). In panel c) and d) the areal capacitances of MnXAlgGels and CuXAlgGels (respectively) along with LiAlgGel, at different current densities (*i.e.*, 0.2 mA/cm², 0.5 mA/cm², 1.0 mA/cm², 2.0 mA/cm²). e) Capacitance retention over cycling of Mn050AlgGel, Cu050AlgGel and LiAlgGel over 5000 charge/discharge cycles. f) Ragone plot comparing the

energy and power densities of Mn050AlgGel and Cu050AlgGel with state-of-the-art references from **Table P2_S9 (SI)**.

LiAlgGel, despite its open structure and excellent ionic mobility, delivers shorter discharge times compared to Mn050AlgGel and Cu050AlgGel. This finding reinforces the notion that while Li^+ facilitates transport, the absence of divalent crosslinking compromises structural stability, leading to reduced capacitance retention and weaker long-term performance.

· *Capacitance and cycling stability*

The areal capacitance of AlgGel-based organohydrogels, extracted from GCD measurements, is summarized in **Figure P2_4c,d** and **Table P2_S7 (SI)**. The results highlight the strong influence of crosslinking composition on ionic transport and charge storage performance.

For Mn^{2+} -crosslinked gels (**Figure P2_4c**), capacitance systematically increases with higher $n\text{Li}^+/n\text{Mn}^{2+}$ ratios, reaching a maximum in Mn050AlgGel (394.2 mF cm^{-2} at 0.2 mA cm^{-2}). This formulation achieves the best compromise between structural stability and enhanced ionic mobility, consistent with earlier SAXS and EIS analyses.

For Cu-crosslinked gels (**Figure P2_4d**), the optimal composition is Cu050AlgGel, which delivers an exceptional capacitance of 591.8 mF cm^{-2} at 0.2 mA cm^{-2} . This value not only surpasses all Mn-based gels but also exceeds LiAlgGel, underscoring the synergistic effect of Cu^{2+} maintaining structural rigidity while Li^+ promotes efficient ion transport. SAXS and mechanical data corroborate this finding, showing that the compact Cu^{2+} network remains stable even with increasing Li^+ incorporation, thereby supporting robust ionic pathways.

· *Cycling stability and durability*

The ionic composition of Mn050AlgGel and Cu050AlgGel remained stable after extended cycling, as confirmed by XPS survey spectra (**Figures P2_S10a, P2_S11a, SI**) and elemental analysis (**Table P2_S8, SI**), which showed no significant variation in atomic ratios. High-resolution Mn 2p and Cu 2p spectra (**Figures P2_S10c,d and P2_S11c,d, SI**) further verified the retention of Cu^{2+}

oxidation states and revealed the presence of partially oxidized Mn^{3+} , most likely resulting from surface oxidation of Mn^{2+} during sample handling or XPS acquisition. Importantly, these spectral features remained unchanged after 5000 charge/discharge cycles, underscoring the redox stability of the gels. Their macroscopic appearance also remained intact (**Figures P2_S10b, P2_S11b, SI**), confirming that the materials preserve their structural integrity under prolonged operation.

The superior electrochemical performance of these gels can thus be attributed to the intrinsic chemical and physical stability of the ionically crosslinked biopolymer networks. Benchmarking against state-of-the-art systems (**Table P2_S9, SI; Figure P2_4f**), Cu050AlgGel and Mn050AlgGel clearly outperform most reported organohydrogel electrolytes in terms of capacitance, energy density, and power density. Cu050AlgGel achieved the highest areal capacitance (591.8 mF cm^{-2} , 59.2 F g^{-1}) and energy density ($82.2 \text{ } \mu\text{Wh cm}^{-2}$, 8.2 Wh kg^{-1}), surpassing conventional hydrogel-based electrolytes. Mn050AlgGel followed closely with capacitance of 394.2 mF cm^{-2} (39.4 F g^{-1}) and energy density of $54.8 \text{ } \mu\text{Wh cm}^{-2}$ (5.5 Wh kg^{-1}).

Both gels also demonstrated excellent power performance, with Cu050AlgGel delivering $1957.8 \text{ } \mu\text{W cm}^{-2}$ (196.5 W kg^{-1}) and Mn050AlgGel $1994.9 \text{ } \mu\text{W cm}^{-2}$ (192.7 W kg^{-1}). Such values highlight their potential for high-power applications requiring rapid charge/discharge cycles. Durability was equally impressive: Mn050AlgGel retained 88.3% of its capacitance after 5000 cycles, while Cu050AlgGel maintained 85.9%.

· Device-level benchmarks

Comparison against state-of-the-art organohydrogel electrolytes (**Figure P2_4f; Table P2_S9, SI**) underscores the competitiveness of the present system. Cu050AlgGel achieves the highest values, with an areal capacitance of 591.8 mF cm^{-2} (59.2 F g^{-1}), energy density of $82.2 \text{ } \mu\text{Wh cm}^{-2}$ (8.2 Wh kg^{-1}), and power density of $1958 \text{ } \mu\text{W cm}^{-2}$ (196.5 W kg^{-1}). Mn050AlgGel follows with 394.2 mF cm^{-2} (39.4 F g^{-1}), $54.8 \text{ } \mu\text{Wh cm}^{-2}$ (5.5 Wh kg^{-1}), and $1995 \text{ } \mu\text{W cm}^{-2}$ (192.7 W kg^{-1}). These values place both systems above or on par with most

reported biopolymer-based GPEs, particularly in terms of energy–power balance and long-term durability.^[80,82–96] The superior stability of Mn050AlgGel (88.3% retention) and Cu050AlgGel (85.9%) contrasts with the weaker retention of LiAlgGel, reinforcing the importance of divalent cation crosslinking in ensuring extended operational life.

2.2.6 Conclusion

This study demonstrates the successful development of gelatin–alginate organohydrogels as gel polymer electrolytes (GPEs) for high-performance supercapacitors. By combining divalent metal crosslinking with controlled Li^+ incorporation, the gels were systematically tuned in terms of mechanical properties, nanoscale structure, and electrochemical behavior.

SAXS analysis revealed how crosslinker identity dictates nanoscale organization and thereby governs both ionic transport and stability. Mn^{2+} -crosslinked gels form flexible, Li^+ -responsive networks in which progressive disruption of crosslinking enhances mobility and capacitance, though at the expense of rigidity. Cu^{2+} -crosslinked gels, by contrast, maintain compact and resilient networks that preserve mechanical strength, while Li^+ incorporation selectively enhances ion conduction. This complementary behavior highlights Li^+ as a versatile tuning knob: in Mn-based gels it unlocks ionic mobility, while in Cu-based gels it synergizes with robust crosslinking to maximize performance.

The electrochemical data converge on a clear design principle: Li^+ incorporation enhances ionic transport, while divalent crosslinking preserves mechanical and structural stability. Among the tested systems, Mn050AlgGel provided the best compromise between mobility and stability, whereas Cu050AlgGel maximized absolute capacitance and energy density. The resulting devices demonstrated high capacitance, favorable energy–power figures, and excellent cycling stability, confirming that ionically tunable network design is an effective strategy for durable, sustainable electrolytes.

More broadly, this work contributes a transferable design framework:

- Crosslinker identity sets the balance between rigidity and flexibility.
- Li^+ incorporation tunes mobility without compromising biopolymeric integrity.
- Nanoscale architecture, revealed by scattering, provides predictive rules for electrochemical performance.

This framework can be extended to other soft electrochemical systems (such as batteries, sensors, and neuromorphic devices) bridging sustainable biopolymer chemistry with application-specific engineering in next-generation flexible electronics.

2.3 Project 3. Fully Bio-based Gelatin Organohydrogels via Enzymatic Crosslinking for Sustainable Soft Strain and Temperature Sensing

This section originates from the publication:

P. Tordi; A. Tamayo; Y. Jeong; B. Han; T. Al Kayal; A. Cavallo; M. Bonini; P. Samorì, “Fully Bio-Based Gelatin Organohydrogels via Enzymatic Crosslinking for Sustainable Soft Strain and Temperature Sensing,” Advanced Functional Materials, 2025, e20762, in press.

(<https://doi.org/10.1002/adfm.202520762>)

2.3.1 Introduction

In the previous chapters, we showed how ionic crosslinking of polysaccharides and protein–polysaccharide hybrids enables tunable soft conductors. By varying crosslinking ions, network organization and ionic conductivity could be programmed systematically, establishing design rules that connect molecular interactions to functional performance.

Here, we extend this framework by focusing on proteins as structural backbones. Unlike polysaccharides, proteins present diverse reactive groups (carboxylates, amines, and hydroxyls) distributed along flexible chains, offering unique opportunities for crosslinking and functionalization. A particularly attractive route is enzymatic stabilization with microbial transglutaminase (TG), which catalyzes covalent ϵ -(γ -glutamyl)lysine bonds between protein chains under mild, aqueous conditions. This strategy yields permanent, biocompatible networks without toxic reagents or harsh processing. Despite its widespread use in food technology, TG remains largely unexplored in soft electronics, where robust and sustainable hydrogel platforms are urgently needed.

In this chapter, we introduce gelatin–TG organohydrogels (GELTG) as a fully bio-based and transparent material platform. Gelatin provides a protein backbone rich in reactive sites, glycerol ensures plasticity and moisture retention, and TG confers covalent stability against mechanical and environmental stress. The resulting gels are stretchable, reproducible, and

display reliable strain and temperature sensitivity—all achieved without conductive fillers or synthetic additives.

By incorporating enzymatic crosslinking, we add a complementary dimension to the design space. Ionic coordination offers tunability and dynamic response, while enzymatic chemistry ensures long-term stability and robustness. Together, these approaches create a versatile toolkit for soft electronics, which we later unify in hybrid systems such as caseinate-based ionic hydrogels, where protein backbones and ionic crosslinks converge to yield multifunctional, sustainable materials.

2.3.2 Preparation of GELTG Organohydrogels

GELTG organohydrogels were prepared through a reproducible one-pot enzymatic crosslinking process. A 20 % (w/v) gelatin stock solution was first obtained by dissolving gelatin in a glycerol:water mixture (1:2 v/v) at 60 °C under continuous stirring until fully homogenized. To this solution (5 mL), 1 mL of microbial transglutaminase (TG) solution was added at controlled concentrations of 0.000, 0.025, 0.125, or 0.250 g mL⁻¹ in deionized water. The resulting mixture (6 mL) was cast into a rectangular PMMA mold (9.5 × 3.0 cm) and incubated at 60 °C for 2 h to allow enzymatic crosslinking.

After incubation, the gels were cooled to room temperature, carefully demolded, and cut into rectangular strips (4.5 × 1.0 cm). Samples were coded GELTGXXX, where XXX denotes enzyme concentration: 000 (blank, no enzyme), 025, 125, or 250. Thickness was consistently ~630 μm across all formulations, as measured with a Mitutoyo digimatic micrometer (**Table P3_S1, SI**), confirming reproducibility of the method.

The protocol is readily scalable: as shown in **Figure P3_S1 (SI)**, the same procedure applied to larger PMMA molds (25 × 15 cm) produced macroscopically uniform hydrogel sheets suitable for device integration. This simple, aqueous-based preparation underscores the accessibility of TG-assisted

gelatin organohydrogels, achieved without additional reagents, synthetic fillers, or harsh conditions.

2.3.3 General Properties of GELTG Organohydrogels

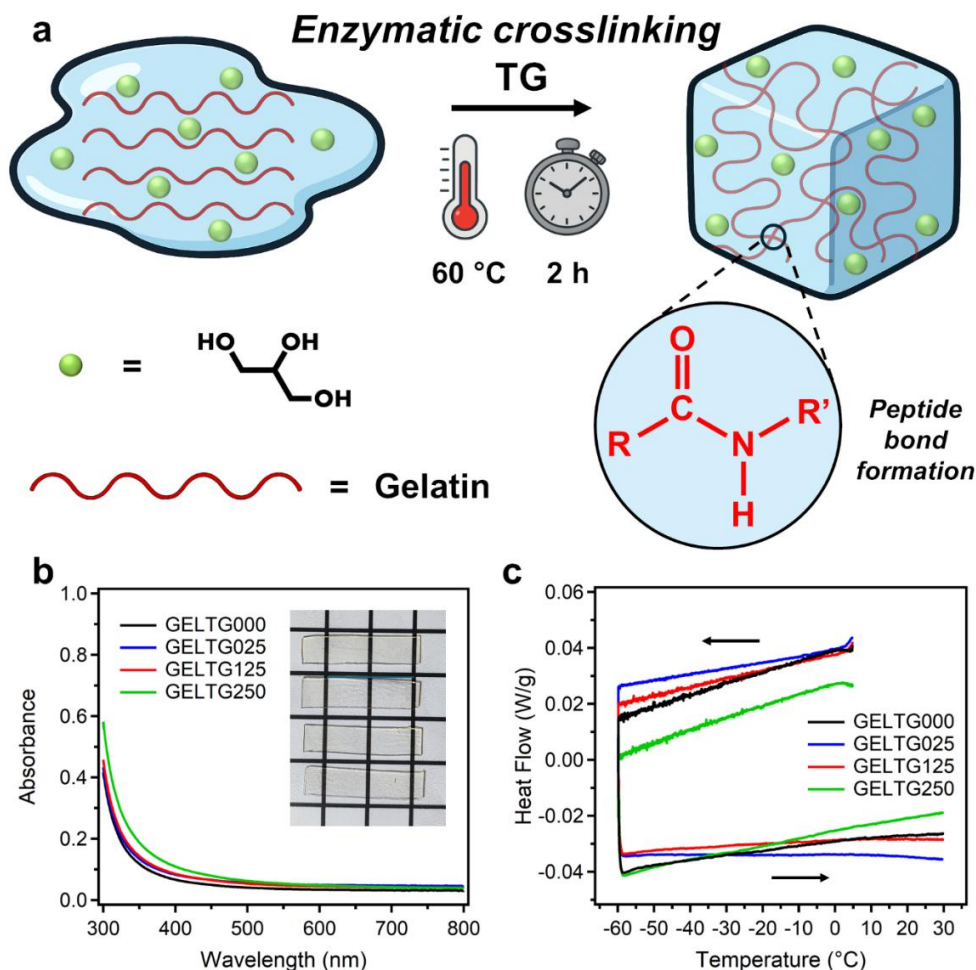


Figure P3_1. Fabrication and basic characterization of TG-crosslinked gelatin organohydrogels. a) Schematic of the enzymatic crosslinking process using microbial transglutaminase (TG) b) UV-vis spectra of GELTG samples (GELTG000-GELTG250) showing high transparency across the visible range. Inset: photographs of gels over a black-white grid. c) Differential scanning calorimetry (DSC) curves, indicating absence of water freezing/ice melting transitions and confirming that all water in the organohydrogels is non-freezable due to strong gelatin-glycerol interactions (Exo-up).

To establish a robust, fully bio-based soft material, organohydrogels were prepared from gelatin, glycerol, and microbial transglutaminase (TG) under mild thermal conditions. As shown in **Figure P3_1a**, TG catalyzes covalent ϵ -(γ -glutamyl)lysine bonds between glutamine and lysine residues of gelatin, producing a permanent enzymatically crosslinked network. Glycerol served both as a plasticizer and a humectant, enhancing elasticity while stabilizing water content. The entire process was completed in a single step at 60 °C using only edible, water-dispersible components, providing a simple and scalable route to sustainable soft materials.

To probe the effect of enzymatic crosslinking, samples were coded according to TG concentration. The uncrosslinked control (GELTG000) was compared with GELTG025, GELTG125, and GELTG250, prepared with TG solutions of 0.025, 0.125, and 0.250 g mL⁻¹, respectively. All formulations exhibited a consistent thickness of ~630 μ m after demolding (**Table P3_S1, SI**), ensuring reliable comparison across the series.

· Optical properties

All GELTGXXX samples displayed high optical transparency across the visible spectrum (**Figure P3_1b**). Below 400 nm, a progressive increase in absorbance was observed, indicative of enhanced UV-shielding capacity. This attenuation, combined with the transparency in the visible range, suggests that these gels may provide partial protection from UV irradiation while remaining optically suitable for transparent bioelectronics or dermal applications. Inset photographs in Figure 1b confirm this behavior, showing the homogeneous and colorless appearance of the gels when overlaid on a black–white grid.

· Thermal properties

Differential scanning calorimetry (DSC, **Figure P3_1c**) revealed the absence of endothermic or exothermic peaks associated with ice melting, indicating that all water in the network is non-freezable.^[72] This effect, arising from strong interactions between gelatin, glycerol, and water, prevents ice crystallization even at subzero temperatures. The presence of non-freezable water is a

hallmark of organohydrogels and ensures both flexibility and ionic mobility under cold conditions. Thermogravimetric analysis (TGA, **Figure P3_S2a** and **Table P3_S1, SI**) confirmed that the water content remained constant at ~14 wt% across all samples, demonstrating that observed differences in material behavior arise primarily from network architecture rather than hydration level. Notably, TG concentration did not alter the onset of thermal degradation (~180 °C), which is dictated by glycerol decomposition (**Figure P3_S2b, SI**).

· Electrical properties

Electrical conductivity, originating from the protic nature of type A gelatin (acid-hydrolyzed collagen), was not significantly influenced by TG concentration (**Table P3_S1, SI**). The protons are confined within the extensive hydrogen-bonding network of gelatin and glycerol, enabling stable conductivity without the need for added salts or dopants. Importantly, this conductivity remains highly robust under humidity variations: resistance measurements from 20% to 60% RH showed minimal change, with only a slight decrease above 70% RH (**Figure P3_S3, SI**). This stability stands in sharp contrast to ionic hydrogels incorporating mobile metal salts (e.g., NaCl, LiCl, FeCl₃), where hydration promotes ion dissociation and Grotthuss-type proton hopping, causing pronounced conductivity shifts.^[97–99] In GELTG systems, the absence of mobile ions eliminates osmotic water uptake and suppresses extrinsic conduction pathways, ensuring reliable electrical performance across varying humidity levels.

These findings show that TG concentration governs functional properties mainly through crosslinking density, rather than environmental fluctuations such as humidity or water content.

2.3.4 Thermal Stability and Responsivity

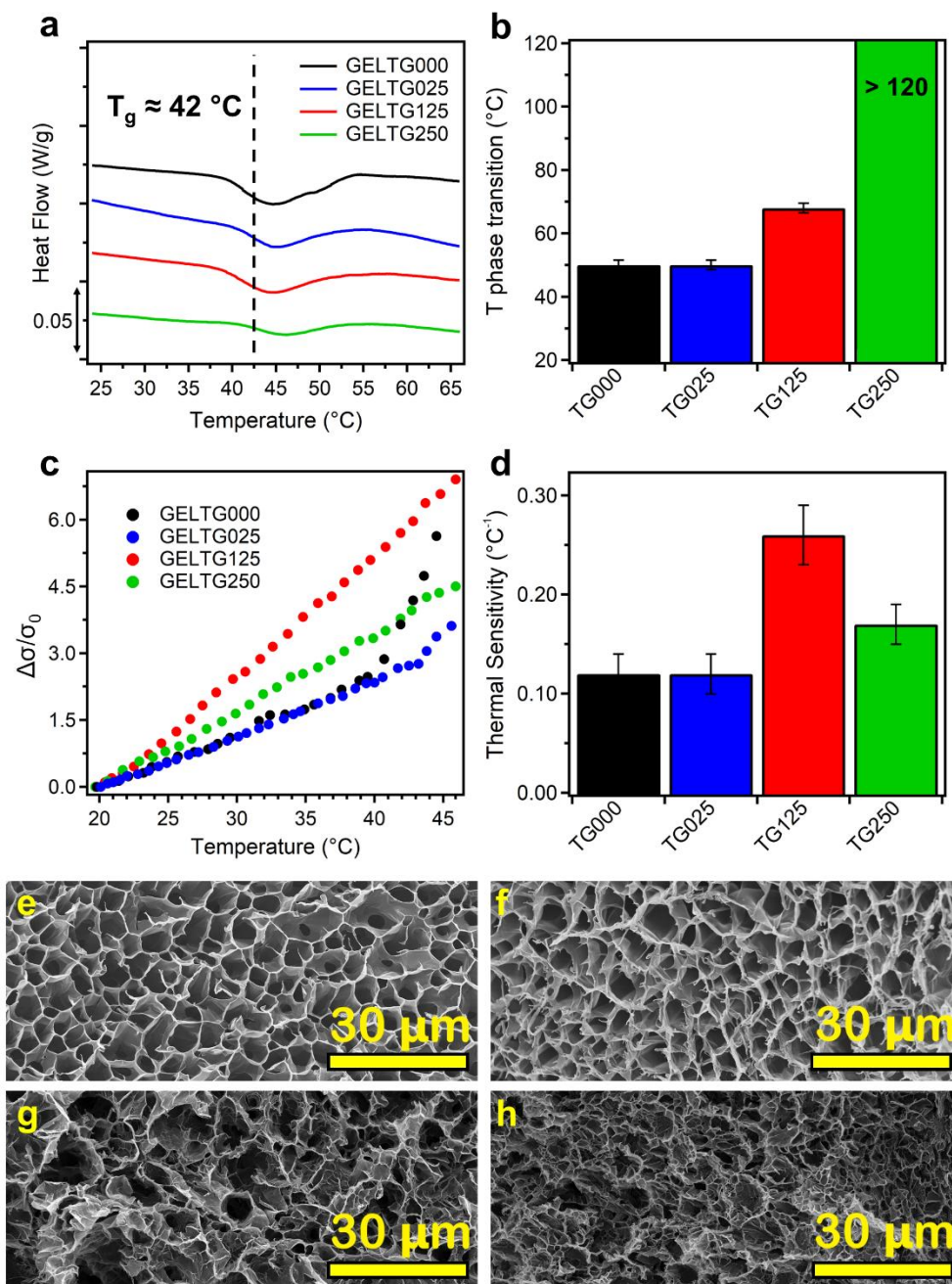


Figure P3_2. a) DSC thermograms showing a consistent glass transition temperature ($T_g \approx 42^\circ\text{C}$) across all samples. b) GELTGXXX phase transition temperature assessed via probe penetration tests, indicating improved thermal stability with increasing TG content. Inset:

representative image of GELTG025 morphology above the phase transition. c) GELTGXXX's relative conductivity change ($\Delta\sigma/\sigma_0$) as a function of temperature (20–45 °C). d) Thermal sensitivity values extracted from the $\Delta\sigma/\sigma_0$ curves; GELTG125 shows the highest sensitivity (0.26 °C⁻¹). SEM micrographs of freeze-dried (e) GELTG000, (f) GELTG025, (g) GELTG125, and (h) GELTG250 samples, showing gradual transition from highly porous to more compact structures with increasing TG content. Scale bars: 30 µm.

The thermal behavior of GELTG organohydrogels was investigated to evaluate both their microscopic transitions and their macroscopic stability under increasing temperature. Differential scanning calorimetry (DSC, **Figure P3_2a**) revealed a subtle endothermic inflection near 42 °C across all formulations, corresponding to the glass transition temperature (T_g) of the gelatin-based polymer network (**Table P3_S1, SI**). The nearly constant T_g values indicate that enzymatic crosslinking does not significantly alter the intrinsic segmental mobility of gelatin chains. This observation is consistent with small-angle X-ray scattering (SAXS, **Figure P3_S4, SI**), which showed overlapping scattering profiles for all formulations across the 1.3–63 nm range, confirming that the nanoscale architecture of the gelatin–glycerol–water matrix is preserved regardless of crosslinking density.

In contrast to the invariant microscopic properties, macroscopic thermal stability exhibited a marked dependence on TG concentration. Penetration tests (**Figure P3_2b**) showed that non-crosslinked GELTG000 and lightly crosslinked GELTG025 lose cohesion at ~50 °C, while GELTG125 remains stable up to ~68 °C. Remarkably, GELTG250 preserved structural integrity even above 120 °C, demonstrating the dramatic enhancement of thermal robustness imparted by dense enzymatic crosslinking. These results suggest that the collapse of GELTG000 and GELTG025 originates from the characteristic structural rearrangements of gelatin chains, which lead to sudden loss of cohesion when insufficiently stabilized by covalent crosslinks.

Temperature also modulates proton conductivity in these gels, underscoring their potential for environmental monitoring and electronic skin applications. As shown in **Figure P3_2c**, the relative conductivity change ($\Delta\sigma/\sigma_0$) was measured across 293–318 K (20–45 °C), a range directly relevant for wearable

bioelectronics.^[54–56] All formulations displayed increasing conductivity with rising temperature, consistent with thermally activated proton transport. At low temperatures, protons are localized through hydrogen bonding with carboxylate and hydroxyl groups, whereas increasing temperature weakens these interactions, enhancing proton delocalization and mobility within the gelatin–glycerol network. Lightly crosslinked samples (GELTG000 and GELTG025) exhibited abrupt conductivity spikes near 40 °C, coinciding with their structural collapse. In contrast, GELTG125 and GELTG250 showed smooth, linear conductivity increases, reflecting stable and intact networks. The extracted thermal sensitivities (**Figure P3_2d**) highlight GELTG125 as the optimal formulation ($0.26\text{ }^{\circ}\text{C}^{-1}$), surpassing both the uncrosslinked and densely crosslinked samples.

To elucidate the link between morphology and thermal response, scanning electron microscopy (SEM) was performed on lyophilized samples (**Figure P3_2e–h**). Although glycerol removal induced partial swelling, the images revealed clear trends: GELTG000 and GELTG025 displayed open, loosely connected networks, whereas GELTG250 formed a dense and compact architecture. GELTG125 showed an intermediate structure, combining sufficient porosity to facilitate molecular mobility with adequate crosslinking to preserve mechanical stability. Swelling experiments further supported these findings (**Figure P3_S5, SI**): while GELTG000 and GELTG025 quickly reached an equilibrium swelling ratio (SR) of ~ 1.2 and lost structural integrity, GELTG125 and GELTG250 exhibited more controlled swelling, stabilizing at SR values of ~ 1.76 and ~ 1.39 , respectively. The higher SR of GELTG125 reflects a more flexible network compared to the rigid GELTG250 matrix.^[77]

These results collectively show that thermal responsiveness in GELTG organohydrogels depends primarily on network architecture and porosity, rather than local chain dynamics, which remain largely unchanged across formulations. Non-crosslinked or lightly crosslinked gels collapse and display abrupt conductivity shifts, while heavily crosslinked networks maintain cohesion but limit ion mobility. Intermediate formulations exhibited more

controlled swelling and smoother conductivity increases, reflecting a balance between robustness and molecular mobility.

2.3.5 Mechanical and Electromechanical Properties

The mechanical performance of GELTG organohydrogels was systematically evaluated under uniaxial tension. As shown in **Figure P3_3a**, all samples exhibit a typical elastomer-like response consisting of an initial linear elastic region, followed by strain hardening and eventual rupture. The introduction of enzymatic crosslinking markedly enhances both extensibility and fracture resistance compared to the uncrosslinked control (GELTG000). In particular, GELTG025 and GELTG125 achieve the highest elongation at break and tensile strength, demonstrating that moderate crosslinking provides cohesive networks capable of dissipating mechanical stress. In contrast, GELTG250 fractures at significantly lower strain, indicating that excessive crosslinking induces brittleness and reduces deformability.

The extracted mechanical parameters (**Figure P3_3c**) show that the Young's modulus (YM) remains nearly constant across all formulations (~ 0.16 MPa), suggesting that TG-mediated crosslinking does not alter the initial stiffness of the network. However, the ultimate tensile strength (UTS) varies strongly with enzyme concentration: GELTG025 and GELTG125 exhibit pronounced increases in UTS relative to the control, while GELTG250 shows reduced UTS, consistent with brittle fracture in over-crosslinked matrices.

The electromechanical properties were investigated by monitoring the relative resistance variation ($\Delta R/R_0$) during uniaxial stretching (**Figure P3_3b**). All samples exhibit a reproducible and approximately linear signal up to 300% strain, validating their applicability as stretchable strain sensors. The corresponding gauge factors (GF), summarized in **Figure P3_3d**, fall within 2.38–2.86, values competitive with or superior to most biopolymer-based ionic sensors. Among the tested formulations, GELTG125 shows the highest average GF, although the difference relative to GELTG250 lies within experimental

uncertainty. More importantly, the response divergence becomes evident at higher strain: while strongly crosslinked networks (GELTG125 and GELTG250) preserve linearity and stability of the electrical signal, weakly or non-crosslinked samples (GELTG000 and GELTG025) exhibit deviations from linearity and reduced sensitivity under large deformation, reflecting poor structural integrity and unstable conductive pathways.

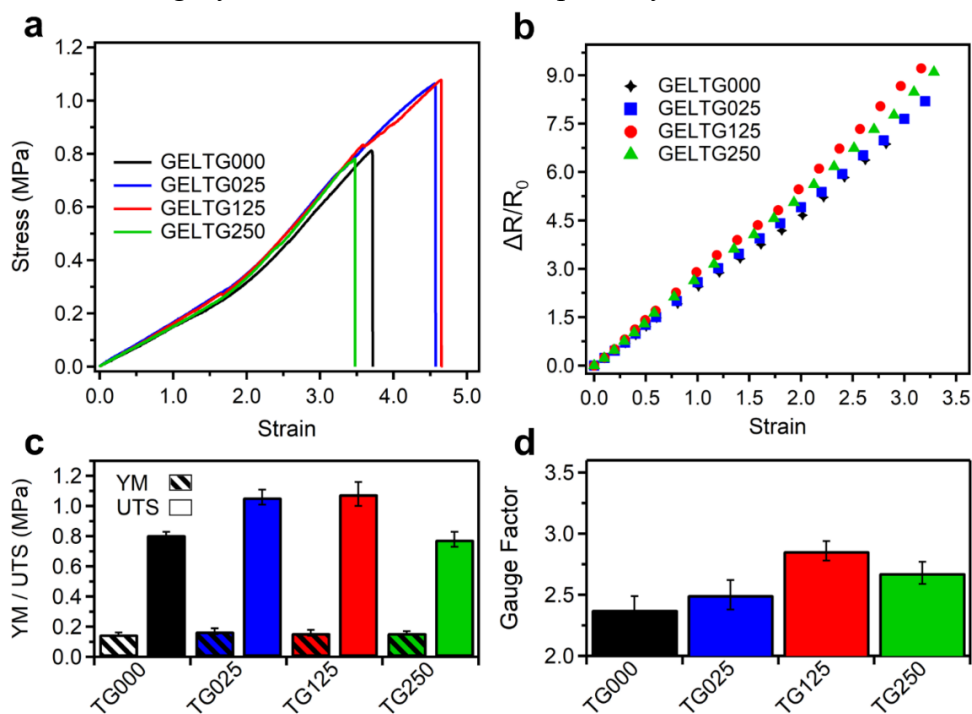


Figure P3_3. a) Stress–strain tensile curves showing enhanced stretchability and strength upon TG-mediated crosslinking. b) Relative resistance variation ($\Delta R/R_0$) as a function of strain, showing linear electromechanical response across all formulations. c) Young’s modulus (YM) and ultimate tensile strength (UTS) values extracted from tensile tests. d) Gauge factor values derived from the linear strain range (0–300%), with GELTG125 achieving the highest value (2.86).

The origin of these behaviors can be rationalized by correlating with the morphological evidence obtained by SEM (**Figure P3_2e–h**). GELTG125 features a moderately crosslinked porous network that can reversibly accommodate large deformations while preserving connectivity, enabling robust modulation of conductive pathways. In contrast, GELTG250 forms an

overly dense, brittle architecture, which restricts network rearrangement and limits electromechanical sensitivity despite high cohesion. The control samples, with insufficient crosslinking, fail to maintain network continuity at large strains, resulting in poor reproducibility of the electrical response.

These findings highlight the critical role of crosslinking density in controlling the balance between mechanical robustness and sensing performance. Moderate crosslinking (GELTG025 and GELTG125) enhanced extensibility and tensile strength compared to the control, while excessive crosslinking (GELTG250) induced brittleness and limited deformability. Electromechanical measurements showed reproducible, linear resistance changes up to 300 % strain, with gauge factors in the range 2.38–2.86. Strongly crosslinked networks maintained stable responses at high strain, whereas weakly crosslinked or uncrosslinked samples deviated from linearity, reflecting insufficient network integrity.

2.3.6 Benchmarking and Device-Level Validation

To contextualize the performance of GELTG organohydrogels within the broader field of hydrogel-based strain sensors, we benchmarked their electromechanical characteristics against state-of-the-art systems reported in the literature (**Figure P3_4a** and **Table P3_S2, SI**).^[83,97,100–122] The results reveal that GELTG125 occupies a rare position among fully biopolymeric systems, combining a relatively high gauge factor ($GF = 2.86$) with an extended linear working range up to 300% strain. This convergence is uncommon: most hydrogel sensors achieve either high sensitivity at low deformation or mechanical compliance at the cost of reduced sensitivity under large strains. For example, gelatin- and cellulose-based matrices typically exhibit GF values below 2 once stretched beyond 150%, underscoring the uniqueness of our enzymatically crosslinked formulation. The synergy between TG-mediated covalent crosslinks and glycerol-driven plasticization enables GELTG125 to simultaneously sustain large deformations and maintain a reproducible, linear electrical response.

A closer inspection of the benchmark further highlights the distinctiveness of our design. Only a limited subset of reported systems (marked by triangle symbols in **Figure P3_4a**) rely exclusively on biopolymeric scaffolds. The majority instead exploit hybrid or synthetic polymers such as PVA to reinforce their networks, which, while effective, detract from sustainability and biocompatibility. By achieving competitive or superior performance within a purely bio-based framework, GELTG125 demonstrates that high electromechanical functionality can be reached without reliance on synthetic additives.

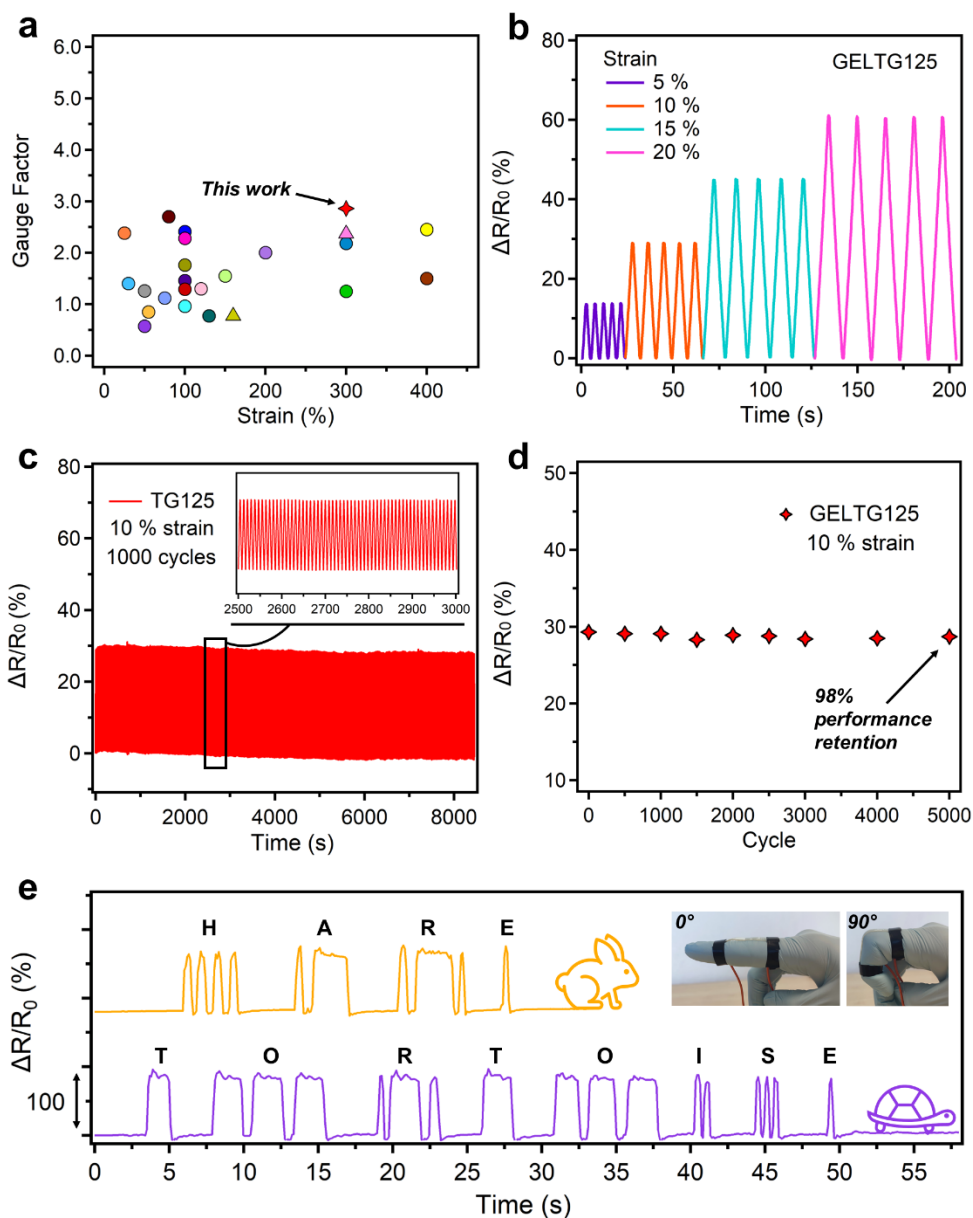


Figure P3_4. a) Comparison of gauge factor versus linear-response working strain range across reported hydrogel-based strain sensors, highlighting the superior combination achieved in this work (GF = 2.86, linear response up to 300% strain). b) Relative resistance variation ($\Delta R/R_0$) of GELTG125 under increasing tensile strains (5%, 10%, 15%, 20%), showing excellent signal responsiveness and reproducibility. c) Long-term cyclic durability test of GELTG125 under 10% strain for 1000 cycles. Inset: zoomed-in region displaying stable and repeatable response. d) Signal retention during 5000 stretch/release cycles, confirming minimal fatigue and consistent performance. e) Proof-of-concept

demonstration of Morse code detection using GELTG125, showing clear signal distinction for the sequences "HARE" (yellow) and "TORTOISE" (purple). The finger was bent of 90° to produce the spike signals reported.

The reproducibility of the sensing response under incremental strains was investigated by applying small step deformations of 5%, 10%, 15%, and 20% (**Figure P3_4b**). GELTG125 exhibited sharp, proportional, and fully reversible resistance changes ($\Delta R/R_0$) at each strain level. The negligible hysteresis and absence of signal drift across repeated cycles indicate the presence of stable and reversible conductive pathways within the enzyme-crosslinked matrix. This behavior highlights the effectiveness of moderate crosslinking density in ensuring both signal fidelity and structural reversibility.

Durability under long-term use was evaluated through cyclic loading experiments. At 10% strain, GELTG125 maintained a stable $\Delta R/R_0$ signal across 1000 cycles (**Figure P3_4c**), with negligible amplitude variation. A magnified region confirms the reproducibility of each individual resistance modulation event, pointing to minimal mechanical fatigue and stable network architecture. Extending the cycling test to 5000 repetitions (**Figure P3_4d**) further validated the durability of the material, with the electrical response retaining 98% of its original amplitude. These results confirm that the covalently crosslinked gelatin network resists progressive damage or rearrangement, enabling consistent sensor function over prolonged use.

Finally, a proof-of-concept device demonstration was implemented to showcase the ability of GELTG125 to function as an interactive soft electronic platform. A Morse code transmission system was designed, where programmable strain pulses encoded digital sequences. As illustrated in Figure 4e, the encoded words *HARE* (yellow trace) and *TORTOISE* (purple trace) were accurately resolved based on pulse width and spacing. Each character was distinctly recognizable, demonstrating the material's capability to convert mechanical input into clear and high-contrast digital signals. The

responsiveness and stability of these signals confirm the suitability of GELTG125 for real-time motion tracking and communication applications.

These tests demonstrate that GELTG125 can sustain repeated strain sensing with high signal fidelity, stable resistance modulation across thousands of cycles, and reproducible performance in a device demonstration. The combination of durability, responsiveness, and clear signal encoding confirms the suitability of enzymatically crosslinked gelatin organohydrogels for reliable strain-sensing applications.

2.3.7 Conclusion

In this work, we introduced a fully bio-based organohydrogel platform composed of gelatin, glycerol, and microbial transglutaminase (TG), advancing the design of multifunctional soft materials for wearable and implantable electronics. The fabrication relies on a one-pot, low-temperature route using only food-grade components, ensuring reproducibility, scalability, and sustainability, qualities rarely achieved in soft electronic materials.

Among the tested formulations, GELTG125 provided the optimal balance of properties. It combined high stretchability and toughness with robust thermoresponsive conductivity and reproducible strain sensitivity over a wide deformation window. Its gauge factor (2.86) remained stable up to 300 % strain, and its thermal sensitivity ($0.26\text{ }^{\circ}\text{C}^{-1}$) was preserved across the physiologically relevant range (20–45 $^{\circ}\text{C}$). These responses were maintained with excellent cycling durability and minimal dependence on ambient humidity, a direct consequence of the absence of mobile salts or synthetic fillers. Multiscale analysis confirmed that these macroscopic functions arise from enzyme-mediated covalent crosslinking, which stabilizes the gelatin network while retaining sufficient porosity for ion and proton mobility.

More broadly, this study highlights enzymatic crosslinking as a powerful yet underutilized route to engineer protein-based organohydrogels for soft electronics. In contrast to ionic or synthetic polymer strategies, TG-mediated

networks demonstrate how enzymatic chemistry can deliver stability, resilience, and eco-compatibility in a single edible matrix. Within the broader framework of this thesis, enzymatic crosslinking complements ionic coordination: while ionic crosslinks provide tunability and dynamic response, enzymatic bonds supply permanence and robustness. Together, they define a versatile toolkit for the next generation of sustainable soft bioelectronics—devices that must operate reliably in wearable, implantable, or even ingestible contexts where safety, functionality, and environmental responsibility converge.

2.4 Project 4. Ion-Directed Assembly of Protein Hydrogels: Sodium Caseinate as a Versatile Platform for Tunable Soft Materials

2.4.1 Introduction

The progression of this thesis has gradually expanded the design rules for sustainable hydrogel systems. Alginate, as a prototypical polyanionic polysaccharide, revealed how ionic coordination can be exploited to tune network density and multifunctionality across diverse applications. By combining alginate with gelatin, we introduced hybrid organohydrogels with enhanced stretchability, multiresponsivity, and suitability for soft electronics. Subsequently, enzymatic crosslinking of gelatin with transglutaminase highlighted how protein-specific chemistry can create permanent, covalent networks with finely balanced thermomechanical and electromechanical properties.

Building upon these foundations, a natural next step is to investigate proteins as stand-alone ionic matrices. Compared to polysaccharides, proteins offer a richer chemical landscape, presenting multiple coordination sites (carboxylates, amines, amides, phosphoserines) and the ability to adopt disordered or partially ordered conformations that respond to their environment. This molecular diversity opens opportunities for programming networks through ion identity, valency, and coordination geometry.

Among available proteins, sodium caseinate (NaCas) represents an especially attractive but underutilized resource (see Section 1.4.3 for further details). Widely available as a by-product of the dairy industry, NaCas is amphiphilic, polyelectrolytic, and already known in food science for its micellar organization in aqueous media. However, in materials science it has been mostly relegated to the role of inert binders or studied under dilute ionic conditions. Strategies to transform concentrated NaCas into robust,

freestanding materials through ionic crosslinking have remained essentially unexplored.

Here we demonstrate, for the first time, that concentrated sodium caseinate solutions can undergo rapid gelation via direct coordination with multivalent cations, yielding mechanically robust, water-rich protein hydrogels (MCas). By systematically varying ion identity across divalent, trivalent, and tetravalent species, we uncover strong ion-specific effects that propagate from molecular coordination to nanoscale packing, microscale porosity, and bulk mechanics. This approach reveals a generalizable packing hierarchy for protein-based ionic networks, providing new design rules analogous to those established earlier for alginate systems.

Crucially, this work elevates caseinate from an inert biopolymer to an active functional platform. Beyond structural and mechanical tunability, selected MCas hydrogels (CuCas, ZnCas) are introduced for the first time as gel polymer electrolytes in supercapacitors. The gels achieve high capacitance and excellent cycling stability, solely through protein–ion interactions, without the need for conductive fillers or added salts.

In this sense, the ionic caseinate study consolidates the dual narrative of the thesis: (i) expanding the material palette of sustainable hydrogels through both polysaccharides and proteins, and (ii) establishing design rules that connect ionic coordination, structural hierarchy, and macroscopic performance. It also sets the stage for future directions where enzymatic and ionic crosslinking strategies may be combined to further exploit the chemical complexity of proteins for multifunctional, application-ready hydrogels.

2.4.2 Preparation and General Properties of Ionically Crosslinked Caseinate Hydrogels

Sodium caseinate (NaCas) hydrogels crosslinked with multivalent cations (MCas) were fabricated through a diffusion-assisted gelation protocol. A concentrated 20 % (w/v) NaCas aqueous solution was cast into silicone molds,

onto which a cellulose paper sheet pre-soaked in 0.5 M MCl_x solution ($M = Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, Zr^{4+}$) was applied as a diffusion barrier. Crosslinking proceeded for 4 h, followed by a 4 h washing step in deionized water, yielding cohesive, free-standing hydrogels. Samples were denoted MCas according to the coordinating cation employed.

The high NaCas concentration ensured close chain packing and suppressed the micelle-like dispersions typically observed in dilute solutions. Under these conditions, exposure to multivalent cations rapidly induced gelation through ionic bridges between carboxylate and amine groups, stabilizing the protein matrix into a continuous network.

Distinct coordination chemistries produced characteristic macroscopic appearances (**Figure P4_1a**). Alkaline-earth cations ($Ca^{2+}, Sr^{2+}, Ba^{2+}$) yielded soft, elastic gels, consistent with weaker coordination and lower crosslinking densities. Transition metals (Mn^{2+}, Cu^{2+}) generated denser and more rigid matrices, with ZnCas undergoing pronounced volumetric contraction during gelation. Strongly acidic salts ($Fe^{3+}, Al^{3+}, Zr^{4+}$, $pH < 3$) further compacted the network via both coordination and partial protonation of the protein backbone, producing highly rigid gels. Volumetric shrinkage measurements confirmed these trends, with ZnCas and AlCas showing the greatest contraction.

Ion uptake quantified by ICP-AES ranged from ≈ 0.4 to 1.5 mmol of metal per gram of caseinate (**Table P4_S1, SI**). This variation reflects the interplay of ionic radius, charge density, hydration energy, and affinity toward caseinate functional groups, providing a means to modulate network topology, hydration, and mechanical behavior across the cation library.

2.4.3 Multiscale Coordination: From Ion–Protein Interactions to Nanoscale Packing

The interplay between multivalent cations and sodium caseinate dictates the hierarchical organization of MCas hydrogels, from local coordination motifs to nanoscale packing. Fourier-transform infrared spectroscopy (FTIR) provides the first evidence of ion–protein interactions, revealing systematic perturbations of both carboxylate and amide groups. Across all MCas samples, the symmetric carboxylate stretching band [$\nu_{\text{sym}}(\text{COO}^-)$, $\sim 1398\text{ cm}^{-1}$] undergoes an upshift upon crosslinking, consistent with direct coordination of carboxylates to metal centers (**Figure P4_1b,c**; **Table P4_S2**, **SI**). In CuCas, ZnCas, FeCas, and AlCas, the shift is so pronounced that the COO^- band overlaps with the $\delta(\text{N-H})$ vibration ($\sim 1446\text{ cm}^{-1}$), preventing separate resolution. Additional perturbations emerge in the N–H stretching region ($\sim 3280\text{ cm}^{-1}$; **Figure P4_1d**), where ZnCas in particular displays a marked downshift ($3291 \rightarrow 3252\text{ cm}^{-1}$), indicating involvement of nitrogen functionalities and reinforced hydrogen bonding. This spectroscopic fingerprint aligns with the pronounced volumetric contraction observed macroscopically, suggesting a highly compact and dehydrated network architecture for ZnCas. X-ray photoelectron spectroscopy (XPS) further resolves the chemical environment of coordinating groups, confirming that multivalent ions interact with both oxygen- and nitrogen-containing functionalities. Representative spectra for NaCas and ZnCas (**Figure P4_1f–h**) highlight the broadening of the C 1s carbonyl and C–O/C–N contributions upon crosslinking, together with analogous broadening in the O 1s region. In the N 1s region, the emergence of a higher binding-energy component ($\approx 402\text{ eV}$) is assigned to protonated or positively polarized nitrogen species, providing direct evidence for nitrogen participation in the coordination environment. Similar trends are observed across all MCas samples, with variations in the intensity of the N^+ component reflecting ion-specific preferences. Notably, CaCas deviates from this general behavior, showing preferential interaction with carboxylate oxygen atoms

rather than nitrogen-containing groups, consistent with the classical affinity of alkaline-earth ions for carboxylates.

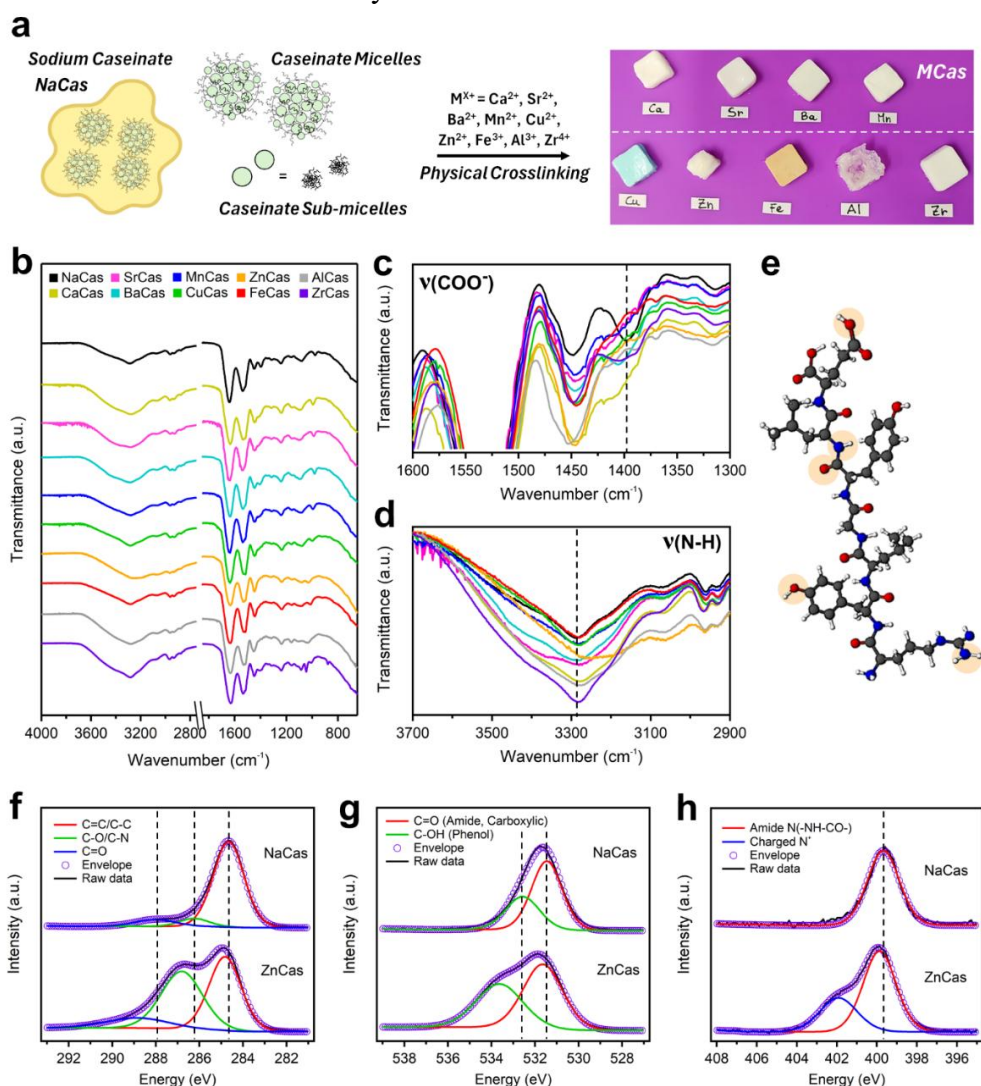


Figure P4_1. a) Schematic of NaCas micelle formation and ionic crosslinking with multivalent metal ions ($M^{X+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, Zr^{4+}$), forming metal-caseinate (MCas) hydrogels with distinct appearances. b) FTIR spectra of NaCas and MCas samples showing metal-dependent shifts. Enlarged regions highlighting changes in c) carboxylate asymmetric stretching and d) N-H stretching, indicating coordination with carboxyl and amino groups. e) Casein peptide model in which residues involved in metal binding are highlighted. High-resolution C 1s (f), O 1s (g) and N 1s (h) XPS spectra of NaCas and ZnCas. FTIR spectra are offset for clarity; the assignments of the most significant bands are reported in **Table P4_S2 (SI)**.

While FTIR and XPS elucidate the local binding motifs, differential scanning calorimetry (DSC) probes how these interactions affect segmental dynamics of the protein matrix. Native NaCas displays a T_g of ~ 72.2 °C, reflecting the intrinsic mobility of caseinate chains. Crosslinking with alkaline-earth ions (Ca^{2+} , Sr^{2+} , Ba^{2+}) results in negligible T_g shifts, consistent with weak coordination and minimal restriction of chain mobility. By contrast, transition metal and high-valent ions (Mn^{2+} , Cu^{2+} , Zn^{2+} , Fe^{3+} , Al^{3+} , Zr^{4+}) raise T_g values up to ~ 76.6 °C (AlCas), indicating tighter interchain associations and suppressed segmental motions.^[77,123] These results corroborate the spectroscopic evidence of stronger coordination in these systems, establishing a clear connection between ion identity, binding strength, and macroscopic rigidity.

To move beyond average thermal signatures, small-angle X-ray scattering (SAXS) was employed to directly resolve nanoscale packing. Dispersions of NaCas exhibit a broad correlation peak at $q \approx 0.031$ Å⁻¹ ($d = 20.3$ nm), indicative of short-range correlations among micelle-like aggregates. Upon crosslinking, this peak disappears, replaced by scattering profiles well-described by a Porod–Lorentzian model (Eq. P4_S2), consistent with the formation of disordered but percolated polymer networks lacking inter-aggregate order (**Figure P4_2b,e**). The extracted correlation length (ξ_1), corresponding to the dominant low- q Lorentzian term, provides a quantitative measure of the average spacing between crosslinked domains (**Figure P4_2d; Table P4_S4, SI**).^[73–77,123]

A clear structural hierarchy emerges: BaCas, SrCas, MnCas, and CaCas display long correlation lengths ($\xi_1 = 4.7$ – 6.4 nm), indicative of relatively open networks with lower packing density. CuCas, FeCas, AlCas, and ZrCas form intermediate structures ($\xi_1 = 2.3$ – 2.9 nm), while ZnCas again stands apart with an ultracompact network ($\xi_1 = 1.0$ nm). In some cases, an additional high- q feature (ξ_2) reflects substructures at shorter length scales, though this does not affect the ξ_1 -based ranking. Importantly, this nanoscale hierarchy mirrors the

macroscopic mechanical stiffness discussed later, highlighting the direct propagation of ion-specific coordination down to bulk performance.

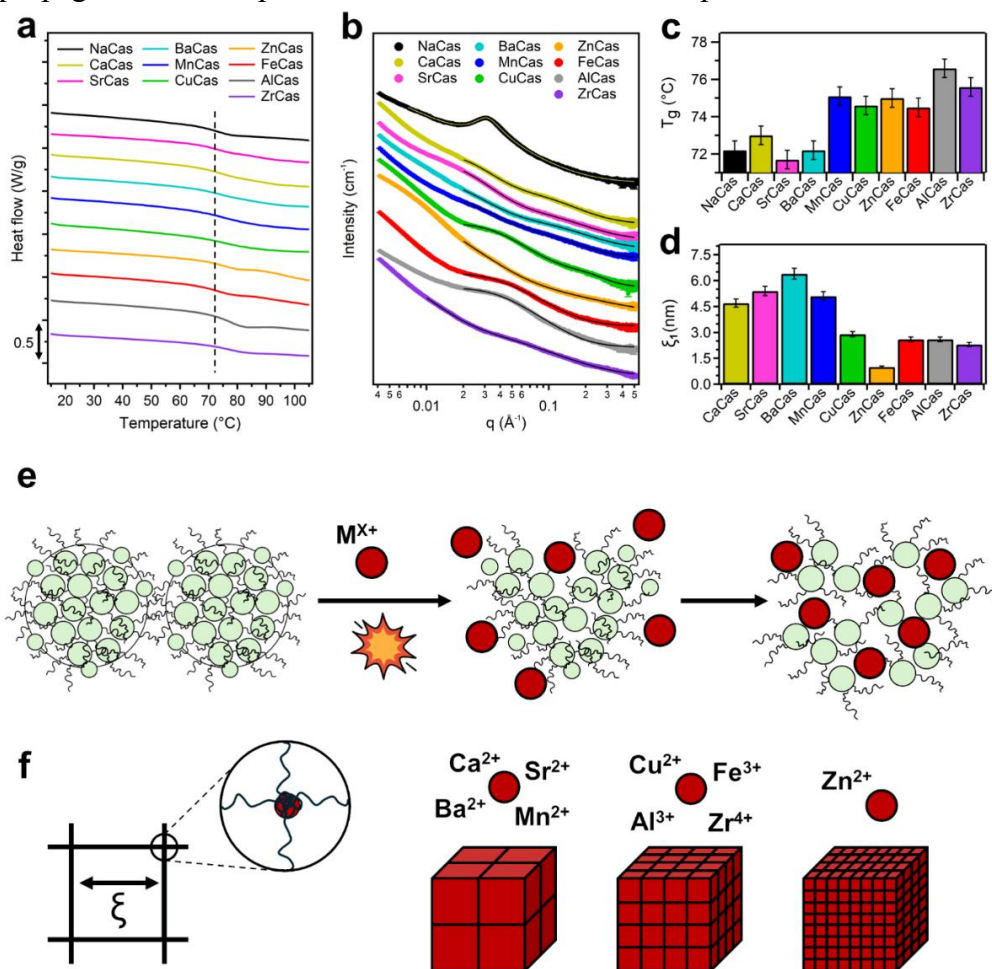


Figure P4_2. a) DSC thermograms and (b) SAXS curves of NaCas and MCas gels. c) Extracted T_g values and d) correlation lengths (ξ) for NaCas and MCas, highlighting how ionic crosslinking governs polymer chain assembly. e) Schematic illustration of the transition from micellar dispersions to ionically crosslinked networks via M^{X+} coordination. f) Conceptual visualization of the influence of cation identity on nanostructural packing and correlation length.

FTIR and XPS identify the specific functional groups engaged in cation coordination, DSC reveals the impact of these interactions on chain mobility, and SAXS resolves the resulting nanoscale packing. Together, these complementary techniques map a hierarchy that spans from local binding

motifs to network-scale organization, showing how ion identity systematically reshapes caseinate architecture. This direct correspondence between coordination chemistry and structural hierarchy provides the foundation for understanding and tuning the macroscopic and electrochemical behavior of MCas hydrogels.

2.4.4 Microscale Packing and Mechanical Properties: From Porosity to Stiffness

Having established the nanoscale packing hierarchy of MCas hydrogels, the investigation was extended to the microscale to uncover how ion–protein coordination translates into emergent architecture and macroscopic mechanics. Scanning electron microscopy (SEM) of freeze-dried samples reveals striking ion-dependent differences in porosity and network texture (**Figure P4_3**).

Hydrogels crosslinked with alkaline-earth ions (Ca^{2+} , Sr^{2+} , Ba^{2+}) form highly porous, open networks with large, interconnected macropores (**Figure P4_3b,c** and **Figures P4_S11–S13, SI**). MnCas exhibits a similar morphology, despite its transition-metal nature, suggesting that its relatively low charge density and weak coordination affinity allow the protein chains to assemble into expanded, loosely packed structures (**Figure P4_S14, SI**).

In sharp contrast, ZnCas, FeCas, and ZrCas produce compact, finely textured architectures with minimal pore size and uniform morphology (**Figure P4_3d,e** and **Figures P4_S16–S17, P4_S19, SI**). These tightly packed structures reflect the strong, localized coordination imposed by high charge density and multidentate binding. AlCas also yields a compact morphology, but with notable heterogeneity: alternating domains of dense, nearly pore-free material and regions of pronounced porosity (**Figure P4_S18, SI**). This irregularity likely originates from uneven local crosslinking and partial phase separation during gelation. CuCas occupies an intermediate regime (**Figure P4_S15, SI**), combining features of both porous and compact architectures, consistent with its moderate coordination strength.

These SEM observations underscore the hierarchical propagation of ion identity across length scales: cations not only tune nanoscale packing (ξ_1 from SAXS) but also dictate microscale porosity, producing networks that range from expanded, sponge-like scaffolds to ultracompact, uniform matrices. Such morphological diversity provides a direct handle to program material density, solvent permeability, and ultimately bulk mechanical response.

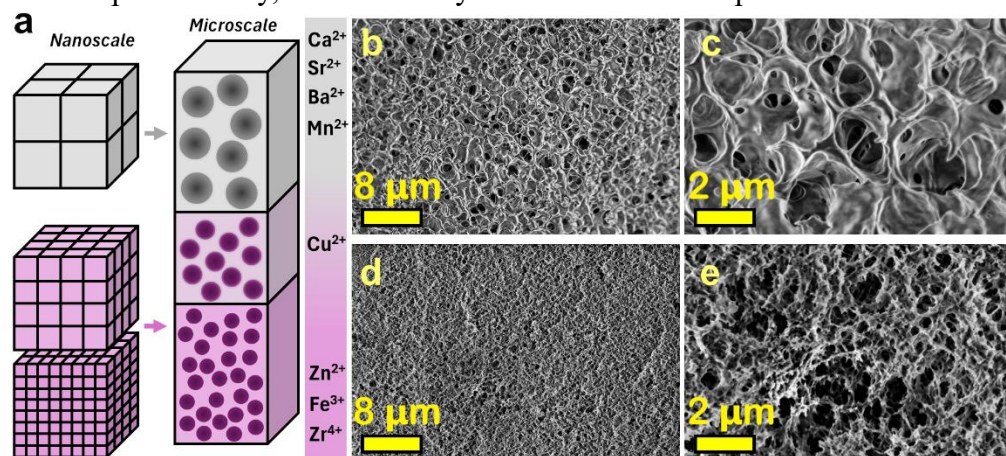


Figure P4_3. a) Schematic representation of the relationship between nanoscale packing density (left) and resulting microscale porosity (right), as modulated by cation identity. Loosely packed nanonetworks (e.g. Ca²⁺, Sr²⁺, Ba²⁺, Mn²⁺) give rise to large, well-defined pores, whereas densely crosslinked systems (e.g. Zn²⁺, Fe³⁺, Zr⁴⁺) form compact architectures with minimal porosity. b,c) SEM images of freeze-dried CaCas hydrogels, representative of SrCas, BaCas, and MnCas. d,e) SEM images of freeze-dried ZnCas hydrogels, representative of FeCas, and ZrCas. Scale bars: 8 μm (b,d); 2 μm (c,e).

Compressive testing (**Figure P4_4; Table P4_S5, SI**) quantitatively confirms the direct link between coordination chemistry, morphology, and mechanical stiffness. ZnCas emerges as the stiffest material, reaching a compressive modulus (CM) of 1.8 MPa, followed by FeCas (844 kPa), AlCas (557 kPa), and ZrCas (359 kPa). These high stiffness values align with the densest nanoscale structures and compact morphologies observed by SAXS and SEM. Conversely, CaCas, SrCas, BaCas, and MnCas exhibit exceptionally soft gels (CM ≤ 11.4 kPa), consistent with their loosely packed networks and large-pore

architectures. CuCas again occupies an intermediate regime (76 kPa), reinforcing its transitional position between the weakly coordinating alkaline-earths and the strongly coordinating transition/high-valent ions.

Taken together, these results show that cation identity dictates nanoscale packing, which propagates to microscale porosity and ultimately defines the mechanical stiffness of MCas hydrogels. Strongly interacting ions yield compact, stiff networks, while weakly coordinating ones produce open, compliant structures, with Cu^{2+} again occupying an intermediate regime.

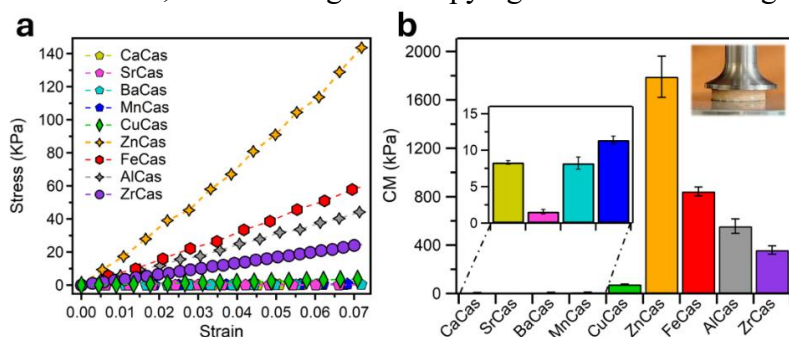


Figure P4_4. a) Compressive stress-strain curves showing cation-dependent stiffness; Full range curves in **Figure P4_S20 (SI)**. b) Compressive modulus (CM) values, with ZnCas as the stiffest and CaCas, SrCas, BaCas and MnCas as the softest. CuCas shows intermediate stiffness. Inset: expanded view of the soft MCas hydrogels' CM values.

2.4.5 Energy Storage Applications: Caseinate Hydrogels as Gel Polymer Electrolytes

Consistently, MCas hydrogels retain mobile counterions that form percolated aqueous pathways, yielding measurable ionic conductivity even after extensive washing (**Table P4_S6, SI**). Representative values, such as 13.5 mS/m for CuCas, underscore the sustained ion retention within the protein network. Importantly, this ion-mediated conductivity transforms caseinate (traditionally employed as an electrically inert binder^[124,125]) into an active gel polymer electrolyte (GPE) for energy storage. Here, the metal–protein interactions provide not only mechanical cohesion but also efficient ion transport, bridging structural stability with electrochemical function.

To validate this concept, symmetric supercapacitors were assembled using activated carbon (AC) electrodes and MCas hydrogels as the electrolyte medium. The homogeneous porosity and thermally robust nature of the gels (**Figure P4_S21, Table P4_S7, SI**) enabled seamless device integration without the need for additional dopants or processing steps. Among the ion library, CuCas and ZnCas were selected for detailed investigation as model systems, chosen for their contrasting network density, stiffness, and redox activity.

Electrochemical impedance spectroscopy (EIS) revealed clear differences in ion transport properties. Nyquist plots (**Figure P4_5b**) show that both gels exhibit low bulk resistance (R_b , **Table P4_S8, SI**), confirming good ionic mobility within the polymer matrix. However, ZnCas displayed a larger high-frequency semicircle corresponding to the charge-transfer resistance (R_{ct}), indicating slower interfacial ion dynamics. This observation aligns with SAXS and SEM findings, which highlighted ZnCas as the most compact and densely coordinated system, thereby restricting ion mobility. In contrast, CuCas exhibited lower R_{ct} values, suggesting more favorable charge transport at the electrode–electrolyte interface.

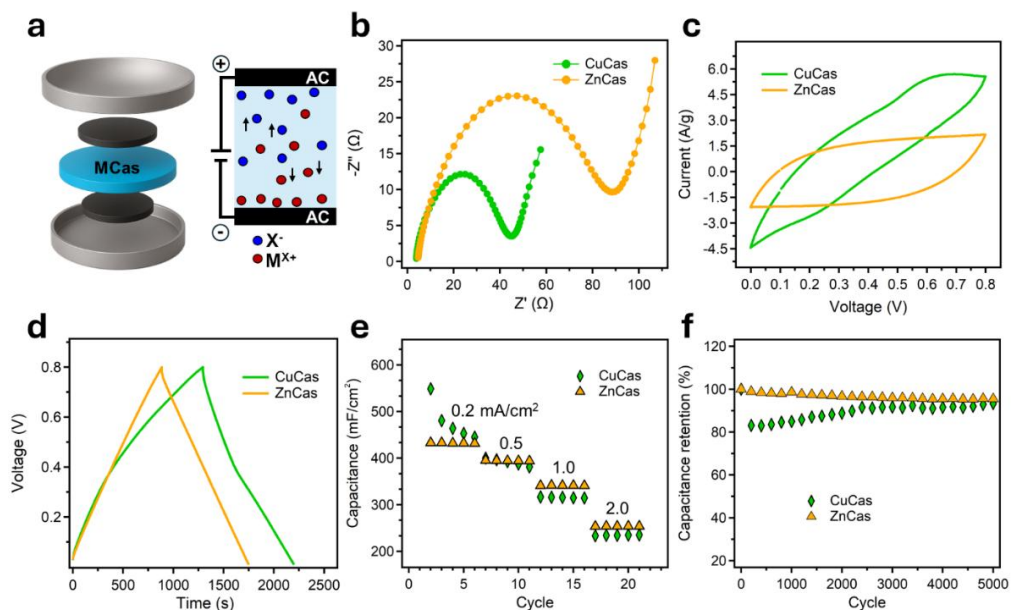


Figure P4_5. a) Schematic of the coin cell configuration with MCas-based GPE (i.e. CuCas and ZnCas). b) Nyquist plots (EIS) showing ion-dependent impedance behavior. c) Cyclic voltammetry (CV) profiles at 10 mV/s. CV at different scan rates (*i.e.*, 2 mV/s, 4 mV/s, 10 mV/s) in **Figure P4_S22 (SI)**. d) Galvanostatic charge–discharge (GCD) curves at 0.2 mA/cm². GCD at different current densities (0.2 mA/cm², 0.5 mA/cm², 1.0 mA/cm², 2.0 mA/cm²) in **Figure P4_S23 (SI)**. e) Capacitance values at increasing current densities (0.2-2.0 mA/cm²). f) Capacitance retention over 5000 cycles for MCas-based systems.

Cyclic voltammetry (CV, **Figure P4_5c**) further emphasized the ion-specific behavior. ZnCas showed quasi-rectangular profiles characteristic of double-layer capacitive storage, albeit slightly distorted by ion transport limitations. CuCas, on the other hand, displayed broader CV loops with superimposed redox features attributable to Cu²⁺-centered pseudocapacitive processes, offering enhanced charge storage beyond electrostatic accumulation.

Galvanostatic charge–discharge (GCD) measurements (**Figure P4_5d**) confirmed these distinctions. ZnCas produced nearly ideal triangular curves with minimal IR drop, consistent with its robust double-layer behavior. CuCas, in contrast, exhibited slight deviations from linearity, coherent with pseudocapacitive contributions. At 0.2 mA cm⁻², the areal capacitance reached 432.4 mF cm⁻² for ZnCas and 454.1 mF cm⁻² for CuCas (**Figure P4_5e**),

placing both systems among the highest-performing sustainable GPEs reported to date.

Long-term cycling stability (**Figure P4_5f**) further underscored the durability of these protein-based electrolytes. ZnCas maintained ~96 % of its initial capacitance after 5000 cycles, while CuCas stabilized at comparable retention values after an initial equilibration phase attributed to matrix reorganization and ion redistribution.

When benchmarked against state-of-the-art hydrogel electrolytes, many of which rely on synthetic dopants such as PEDOT:PSS, H₂SO₄, or LiCl to boost conductivity and capacitance,^[79,83,126–134] MCas hydrogels stand out for their dopant-free, fully sustainable performance. Their competitive capacitance and exceptional cycling stability arise solely from metal–protein coordination, without auxiliary fillers or salts. This intrinsic functionality highlights the power of ionically crosslinked proteins as a new materials platform for energy storage. Furthermore, the modularity of the caseinate scaffold offers straightforward opportunities for future optimization, including post-synthetic salt loading or hybridization with mixed conductors, without altering the fundamental protein–ion network.

These results confirm that CuCas and ZnCas hydrogels function as effective gel polymer electrolytes, combining competitive capacitance with long-term cycling stability. The contrasting behaviors (double-layer dominated ZnCas versus pseudocapacitive CuCas) highlight how ion identity governs both transport and charge storage mechanisms within protein-based networks.

2.4.6 Conclusion

This work introduces a previously unexplored class of ionically crosslinked hydrogels based on sodium caseinate—a renewable, amphiphilic protein traditionally regarded as an inert binder in materials science and widely available as a by-product of the food industry. By harnessing its latent coordination properties toward multivalent cations, we demonstrate that

concentrated NaCas solutions can undergo rapid gelation to form robust, freestanding hydrogels stabilized entirely through non-covalent ionic crosslinking.

A broad library of ions (Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} , Fe^{3+} , Al^{3+} , Zr^{4+}) was systematically explored, revealing a pronounced ion-specific modulation of network architecture and macroscopic properties. Multiscale characterization (FTIR, XPS, SAXS, DSC, SEM, and compressive mechanics) established a direct correlation between ion identity, nanoscale packing, and bulk stiffness, culminating in an empirical packing hierarchy that provides a practical design rule for protein-based ionic materials. Among tested systems, Zn^{2+} produced the most compact and rigid networks, while alkaline-earth ions yielded open, compliant gels—underscoring the versatility of caseinate as a tunable matrix. Crucially, we demonstrate for the first time that these MCas hydrogels can operate as gel polymer electrolytes (GPEs) in energy storage devices. Implemented in symmetric supercapacitors, CuCas and ZnCas exemplified the functional breadth of the platform: CuCas exhibited redox-assisted pseudocapacitance, while ZnCas delivered nearly ideal double-layer behavior. Both systems achieved high capacitance values (up to 454.1 mF cm^{-2}), outstanding cycling stability (96% retention after 5000 cycles), and robust performance without the need for added salts or conductive fillers.

Altogether, this study positions ionically crosslinked caseinate hydrogels as a versatile, sustainable, and multifunctional platform that unites structural tunability, mechanical robustness, and electrochemical activity within a single bio-derived matrix. By bridging protein chemistry with ionic coordination, we establish caseinate as a viable building block for next-generation green materials in energy storage, bioelectronics, and soft sustainable devices.

2.5 Project 5. Mimicking Synaptic Plasticity: Optoionic MoS₂ Memory Powered by Biopolymer Hydrogels as a Dynamic Cations Reservoir

This section originates from the publication:

Y. Jeong; P. Tordi; A. Tamayo; B. Han; M. Bonini; P. Samorì, “Mimicking Synaptic Plasticity: Optoionic MoS₂ Memory Powered by Biopolymer Hydrogels as a Dynamic Cations Reservoir,” *Advanced Functional Materials*, 2025, 35 (50), e09607.

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2.5.1 Introduction

The research presented so far has established a systematic framework for engineering protein- and polysaccharide-based hydrogels through both enzymatic and ionic crosslinking strategies. These studies demonstrated how careful control of nanoscale packing and coordination chemistry translates into macroscopic functions spanning mechanical robustness, ionic conductivity, and electrochemical stability, ultimately enabling practical applications in energy storage and bioelectronics.

The next frontier of soft matter lies in expanding functionality into domains traditionally reserved for solid-state physics and nanodevices. Among these, neuromorphic electronics represents one of the most transformative areas. Conventional computing remains constrained by the von Neumann bottleneck, where energy-inefficient data transfer between memory and logic limits scalability. Neuromorphic systems, inspired by biological synapses, overcome this limitation by integrating memory and processing within the same unit, enabling adaptive, energy-efficient information handling.^[135,136]

In this landscape, two-dimensional transition metal dichalcogenides (2D TMDs) such as MoS₂ stand out for their strong electrostatic sensitivity and exceptional light–matter interactions, making them ideal candidates for optoelectronic synaptic devices.^[137–142] Current approaches, however, often rely on toxic or unsustainable components (*e.g.*, Cd- or Pb-based quantum dots) or suffer from poor retention when gated with conventional electrolytes.^[143–148]

This establishes a clear need for neuromorphic functionality that is achieved through sustainable, bio-derived materials without sacrificing performance.

Building on our expertise in ionically conductive hydrogels, we introduced a new paradigm: biopolymer hydrogels as dynamic ionic reservoirs interfaced with 2D materials. Specifically, sodium alginate (SA), a biocompatible polysaccharide rich in carboxylate groups, was exploited as a supramolecular coating on MoS₂ channels. Under illumination, the alginate layer actively mediates ion migration, giving rise to a photo-induced ionic gating effect. This unprecedented mechanism enables persistent photoconductivity (PPC) and multilevel memory states that emulate synaptic plasticity (including sensory memory (SM), short-term memory (STM), and long-term memory (LTM)) all triggered by light.

Going a step further, the integration of ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] on the bottom face of MoS₂ produced a Janus device architecture with dual control: ferroelectric gating from below and ionic gating from above. This hybrid system expanded the number of accessible memory states to sixty and extended photodetection capabilities into the near-infrared region, highlighting the power of asymmetric, supramolecular functionalization.

This chapter presents the development of an optoionic MoS₂ synaptic memory FET as a proof-of-concept demonstration of how sustainable biopolymer hydrogels can transcend classical applications and enter the arena of neuromorphic computing (see **Table P5_S1, SI**) The work illustrates how the concepts developed throughout this thesis (ionic coordination, network dynamics, and sustainable materials design) can be translated into an entirely new class of multifunctional, biopolymer–2D hybrid devices.

2.5.2 Preparation of Optoionic Janus MoS₂ Devices

The optoionic synaptic memory devices were fabricated through a multistep process integrating exfoliated 2D semiconductors with biopolymer and

ferroelectric layers to yield asymmetric Janus architectures. The methodology was designed to ensure high-quality interfaces, reproducibility, and compatibility with the supramolecular functionalization required for optoionic operation.

· *MoS₂/h-BN FET fabrication*

As a first step, SiO₂ (270 nm)/n⁺-Si substrates were cleaned in acetone and ethanol by ultrasonication for 30 min each, ensuring removal of surface contaminants. Few-layer hexagonal boron nitride (h-BN) flakes were then exfoliated onto polydimethylsiloxane (PDMS) stamps (SYLGARD 184) and inspected under an optical microscope to select crystals with lateral dimensions and uniformity suitable for device channels. The h-BN flakes were transferred onto the cleaned substrates by deterministic stamping. Subsequently, semiconducting MoS₂ flakes (thickness 5–10 nm) were exfoliated on PDMS and aligned with the h-BN/SiO₂/n⁺-Si substrate using a CCD-assisted microaligner. Vertical pressure ensured conformal contact and transfer onto the h-BN surface, producing well-defined heterostructures. Source/drain electrodes (Au, 50 nm) were patterned via photolithography (AZ1505 resist), thermal evaporation, and lift-off. To improve contact resistance and minimize sulfur vacancies, the completed devices were annealed at 150 °C for 2 h in a nitrogen glovebox.

· *MoS₂/P(VDF-TrFE) FeFET fabrication*

For the Janus ferroelectric devices, Au/Cr (12/3 nm) bottom-gate electrodes were deposited on SiO₂/n⁺-Si substrates. A 3 wt.% solution of poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] in 2-butanone was spin-coated onto the patterned electrodes and annealed at 100 °C for 1 min to remove residual solvent. Subsequently, MoS₂ flakes were transferred onto the P(VDF-TrFE)/Au layers via PDMS stamping. A second annealing step at 142 °C for 2 h under nitrogen crystallized the ferroelectric polymer, stabilizing its dipolar alignment. Top source/drain electrodes (Au, 50 nm) were then defined by the same lithographic and lift-off process, followed by a final annealing step at 100 °C for 2 h to optimize contact quality.

· *Sodium alginate deposition*

To introduce the ionic reservoir, sodium alginate (SA, 250 mg) was dissolved in 100 mL of Milli-Q water under gentle stirring for 1 h at room temperature. A 2 μ L aliquot of the resulting 0.25 wt.% SA solution was drop-cast onto the MoS₂ channels of both MoS₂/h-BN FET and MoS₂/P(VDF-TrFE) FeFET devices. Following deposition, excess solvent was removed by N₂ blow-drying, leaving a thin alginate hydrogel layer conformally covering the MoS₂ surface. This supramolecular coating established a dynamic ionic reservoir that mediates photogating behavior and enables optoionic synaptic functionality. Altogether, this process yields two complementary device configurations: (i) SA/MoS₂/h-BN FETs, where synaptic plasticity arises predominantly from photoinduced ionic gating, and (ii) SA/MoS₂/P(VDF-TrFE) FeFETs, where the asymmetric Janus design combines ionic and ferroelectric gating to expand memory capacity and broaden photoresponse into the near-infrared.

2.5.3 Photo-Induced Ionic Gating in SA/MoS₂ Synaptic FETs

The SA/MoS₂ synaptic transistor relies on a photo-induced ionic gating effect that emerges when a thin alginate layer acts as a dynamic cation reservoir. As illustrated in **Figure P5_1a,b**, the device consists of an atomically thin MoS₂ channel coated with a 500 nm sodium alginate (SA) top layer. Upon photon irradiation at $\lambda = 680$ nm, photoexcited electrons are generated in the MoS₂ channel due to the intrinsic photogating effect.^[149,150] This increase in the Fermi energy of MoS₂ drives migration of cations within the SA hydrogel toward the semiconductor interface, locally modulating the channel conductance. In this way, the supramolecular SA coating introduces an additional ionic degree of freedom into the photoresponse, enabling a unique optoionic gating mechanism that underpins the observed synaptic plasticity.

To minimize parasitic effects from interfacial traps, a 2D h-BN flake was used as a dielectric support for the MoS₂ channel. The atomically flat, hydrophobic surface of h-BN avoids the high density of surface states characteristic of

hydrophilic SiO₂, which otherwise complicates the photoresponse of MoS₂-based devices. Comparative measurements confirm this benefit: under 680 nm illumination (0.03 mW cm⁻²), the MoS₂/h-BN FET exhibits a photocurrent (I_{PHOTO}) twenty times higher and a photoswitching speed three times faster than a control MoS₂ FET fabricated directly on SiO₂ (**Figure P5_S1, SI**). Atomic force microscopy (AFM) confirms the thickness of the transferred flakes (MoS₂ $\approx$ 6 nm, h-BN $\approx$ 25.5 nm; **Figure P5_S2, SI**), validating the reproducibility of the heterostructure. For all subsequent SiO₂ bottom-gate devices, h-BN was therefore employed as the dielectric layer.

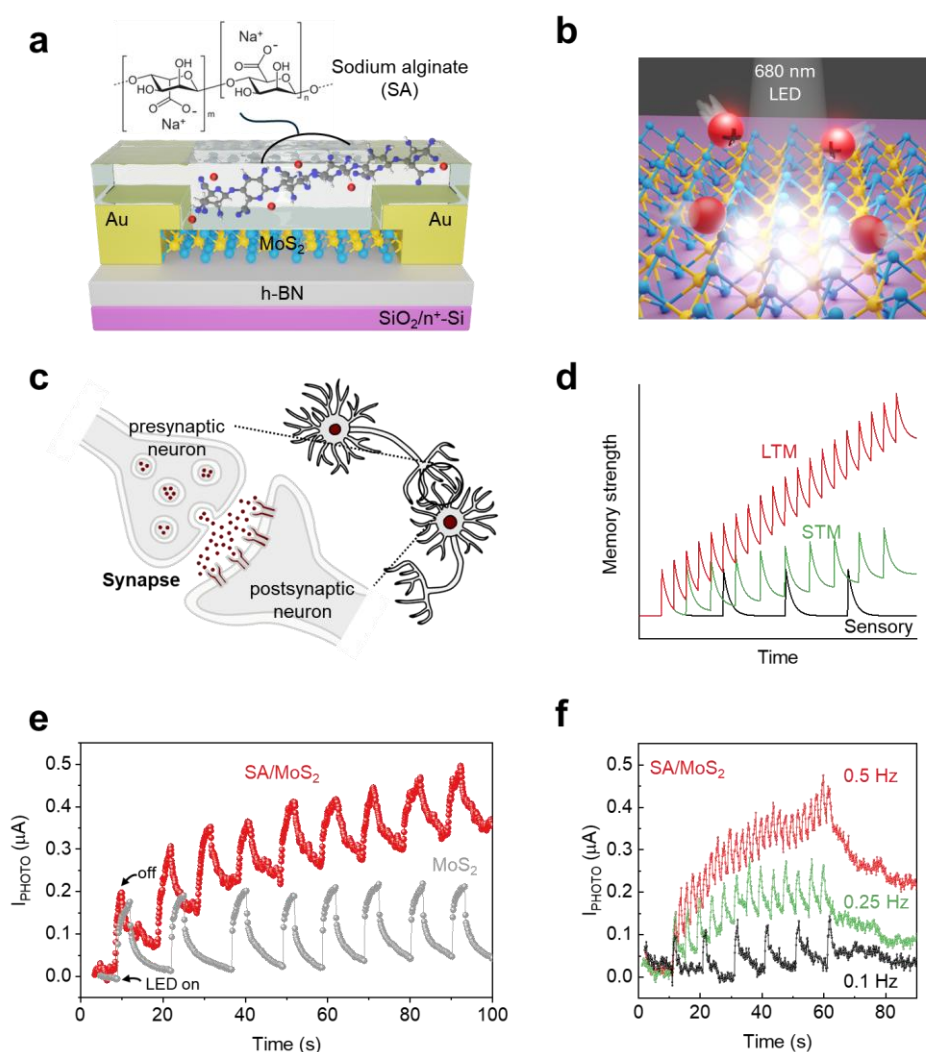


Figure P5_1. Optoionic synaptic plasticity of SA/MoS₂ FET. a) 3D schematic view of a MoS₂ synaptic memory FET with a 500 nm thick-SA layer. b) Cartoon of the photo-induced ionic gating effect at magnified van der Waals heterojunction between SA and MoS₂ under 680 nm LED illumination. c) Schematic illustration of a biological synapse in the human neural system. d) Memory model of the artificial synaptic device as a function of stimulus frequency, illustrating sensory memory (SM) in black, short-term memory (STM) in green, and long-term memory (LTM) in red. These correspond to the transient response, short-term plasticity (STP), and long-term plasticity (LTP) of biological synapses, respectively. e) Time-resolved photoresponse of the SA/MoS₂ synaptic memory and control sample under 680 nm LED illumination at $V_{GS} = 0$ V and $V_{DS} = 1$ V. f) Time-resolved photoresponse of SA/MoS₂ synaptic memory under 680 nm LED illumination at frequencies of 0.1, 0.25, and 0.5 Hz with $V_{GS} = 0$ V and $V_{DS} = 1$ V, demonstrating SM (black), STM (green), and LTM (red) operations, respectively.

Decoration of the MoS₂ channel with the SA layer provides not only the ionic gating functionality but also a protective barrier for the underlying device components. Thermogravimetric analysis demonstrates the high thermal stability of SA, with degradation onset above 220 °C (**Figure P5_S3, SI**), ensuring device durability under processing and operation. Ultraviolet–visible spectroscopy confirms that SA remains transparent across the visible spectrum (**Figure P5_S4, SI**), allowing efficient propagation of 680 nm photons to the MoS₂ active layer. Indeed, the initial photocurrent of both SA-coated and pristine MoS₂ FETs approaches ≈ 200 nA, confirming that the 500 nm SA overlayer does not attenuate incident light.

Harnessing this architecture, the SA/MoS₂ FET emulates the behavior of a biological synapse, where incoming stimuli dynamically tune synaptic efficacy. In neuronal systems, action potentials trigger neurotransmitter release into the synaptic cleft, strengthening or weakening the postsynaptic response (potentiation and depression, respectively). Analogously, optical stimuli act as presynaptic triggers in our artificial synapse, modulating the channel conductance of MoS₂ through ion redistribution in the SA layer. This mechanism yields parallel processing and analog-like modulation of signal strength, hallmarks of synaptic plasticity.

Figure P5_1d depicts a conceptual memory model spanning sensory memory (SM), short-term memory (STM), and long-term memory (LTM), which are emulated by tuning the frequency of optical stimulation. Experimentally, the

SA/MoS₂ FET exhibits more than eight distinct memory states under continuous 680 nm LED illumination (0.03 mW cm⁻²; **Figure P5_1e**). Notably, these states are achieved solely through optical inputs, without electrical biasing, highlighting the intrinsic photonic control afforded by the SA layer. Moreover, by modulating the frequency of light pulses at 0.1, 0.25, and 0.5 Hz (intensity 0.01 mW cm⁻²), the system reproducibly accesses SM, STM, and LTM regimes. These operating modes represent a unique form of photonic synaptic plasticity, where transient response, short-term potentiation (STP), and long-term potentiation (LTP) are faithfully mimicked by a soft-matter device. Altogether, this section establishes the SA/MoS₂ synaptic FET as an unprecedented optoionic device. By coupling the photogating of MoS₂ with ionic gating from a biopolymer reservoir, it delivers multilevel optical memory and frequency-dependent learning behaviors that parallel the adaptive functions of biological synapses.

The synaptic plasticity of the SA/MoS₂ hybrid FET originates from the controlled migration of cations within the alginate layer under and after light illumination. **Figure P5_2a–c** depicts the van der Waals interface between MoS₂ and SA, along with corresponding band diagrams that clarify the underlying mechanism. MoS₂, characterized by intrinsic sulfur vacancies and Fermi-level pinning at the Au contacts, establishes electron-dominant band diagrams under dark conditions (**Figure P5_2a**).^[151,152] Upon exposure to 680 nm photons, a photogating effect generates electron doping in the MoS₂ channel (**Figure P5_2b**).^[149,153–155] The resulting accumulation of photoexcited electrons induces an electrostatic force that drives Na⁺ migration from the SA reservoir toward the MoS₂/SA interface.

To confirm that no Na⁺ intercalation into the MoS₂ lattice occurs under operational conditions, Raman spectroscopy and XPS analyses were performed on devices coated with 0.25 wt.% SA (**Figures P5_S5 and P5_S6, SI**). These results validate that ion redistribution is confined to the hydrogel interface. Even after illumination is switched off, MoS₂ retains accumulated electrons due to persistent ion–electron electrostatic attraction, resulting in a pronounced

persistent photoconductivity (PPC). The anionic backbone of alginate plays a crucial role by progressively retrieving sodium ions once light is removed, ensuring reversible PPC and stable, reproducible synaptic behavior.

This mechanism contrasts with conventional PPC in MoS₂, which is typically attributed to charge trapping at defects under UV excitation.^[156,157] In the SA/MoS₂ device, the presence of mobile ions introduces an electrostatically mediated, reversible mechanism distinct from defect-dominated pathways. The transfer characteristics (**Figure P5_2d** and **P5_S7, SI**) confirm this effect: under 680 nm illumination, the threshold voltage shifts by ~ 4 V toward more negative values, reflecting electron doping in MoS₂. After illumination, the transfer curve remains displaced, confirming retention of electron accumulation by ion–electron interactions. Control devices fabricated without SA lack this PPC effect, underscoring the necessity of the ionic reservoir.

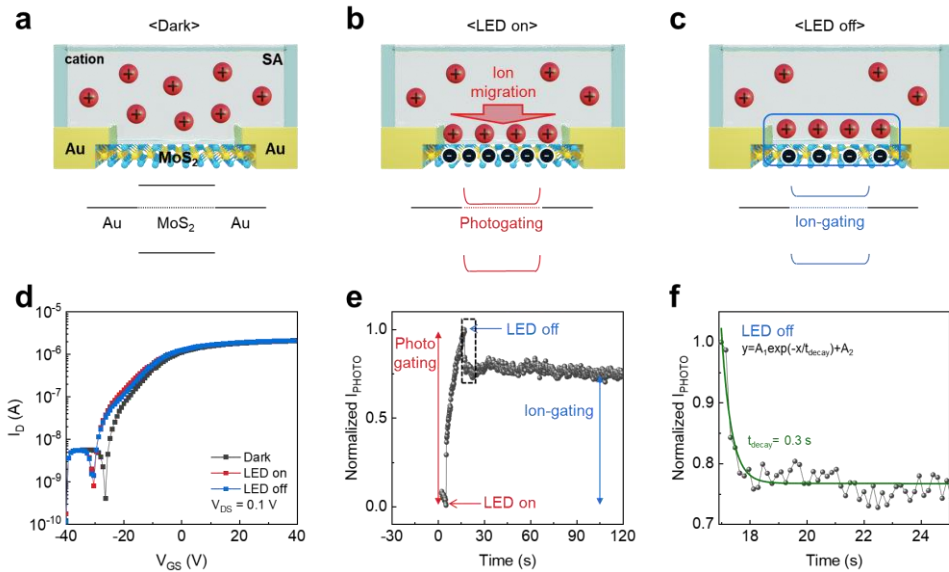


Figure P5_2. Working mechanism of PPC in SA/MoS₂ FET. 2D schematics of the SA/MoS₂ FET and corresponding energy band diagrams of Au-MoS₂-Au under different conditions: a) equilibrium in dark, b) photogating effect under 680 nm LED illumination, and c) photo-induced ionic gating effect after LED off, leading to PPC in the SA/MoS₂ FET via electron-cation attraction. d) Transfer curves of the SA/MoS₂ FET, showing PPC after 680 nm LED illumination at $V_{DS} = 0.1$ V. e) Time-resolved photoresponse of the SA/MoS₂ FET under 680 nm LED illumination, and f) its I_{PHOTO} decay over time, with a decay time constant of 0.3 s.

Experimental data (black dots) were fitted using an exponential decay function to determine the decay time constants.

Time-resolved measurements further corroborate this behavior. As shown in **Figure P5_2e**, under 680 nm illumination (0.5 mW cm^{-2}), I_{PHOTO} decays rapidly ($\tau \approx 0.3 \text{ s}$) due to intrinsic electron–hole recombination in MoS_2 . Beyond this fast decay, PPC induced by ionic gating persists for more than 100 s. This long-lived response corresponds to LTM in artificial synaptic devices and is fully consistent with the STM-to-LTM transition (**Figure P5_2f**).^[158] Notably, pristine MoS_2 FETs exhibit slower but purely electronic PPC ($\tau \approx 4 \text{ s}$), an order of magnitude shorter than the sustained ionic effect in SA/ MoS_2 devices.

Environmental control further highlights the ionic origin of the effect. In vacuum (1.3 mbar), where cation mobility is suppressed due to the absence of free water within the alginate matrix, PPC disappears entirely (**Figure P5_S8, SI**). This observation is consistent with the hygroscopic nature of SA: thermogravimetric and DSC analyses show that the hydrated SA network contains $\sim 17.7 \text{ wt.}\%$ water at 40% RH, which is tightly bound to carboxylate and hydroxyl groups, ensuring ionic mobility under ambient conditions.

The concentration of the SA layer is also critical for achieving stable ionic gating. As shown in **Figure P5_S9 (SI)**, excessive SA content (2.5 wt.%) leads to uncontrolled electrostatic doping, masking the photo-induced effect, while insufficient loading (0.025 wt.%) provides too few mobile ions to sustain PPC, yielding baseline behavior similar to pristine MoS_2 FETs. The optimized concentration (0.25 wt.%) enables balanced ion migration and retrieval, producing reproducible STM and LTM characteristics.

These measurements confirm that photo-induced ionic gating in SA/ MoS_2 devices originates from ion redistribution within the hydrated alginate layer. Optimized SA concentration (0.25 wt.%) enables balanced ion migration, producing reproducible STM and LTM characteristics with retention times exceeding 100 s.

The ability of the SA/ MoS_2 FET to mimic biological learning processes extends beyond transient and persistent photoconductivity, manifesting as multilevel

memory states that can be tuned by external parameters. **Figure P5_3a** demonstrates that increasing the light intensity progressively enhances both the maximum photocurrent ($I_{\text{MAX,PHOTO}}$) and the persistent photocurrent (I_{PPC}). Under 680 nm illumination, $I_{\text{MAX,PHOTO}}$ reaches ~ 820 nA at 0.50 mW cm^{-2} , with I_{PPC} stabilizing near 350 nA. This clear dependence indicates that stronger photogating amplifies ion migration within the SA matrix, producing higher PPC and enabling light-intensity-dependent transitions from sensory memory (SM) to long-term memory (LTM). Specifically, weak illumination (0.01 mW cm^{-2}) induces only transient responses consistent with SM, while intensities above 0.03 mW cm^{-2} reliably yield STM and LTM behavior.

The persistence of LTM states under strong illumination further enables stepwise modulation of I_{PPC} by varying exposure time (**Figure P5_3b**). Sequential 5 s light pulses (4 cycles, total 20 s) yield cumulative I_{PPC} of ~ 620 nA, while shorter 1.5 s pulses (6 cycles, total 9 s) converge near 410 nA. This demonstrates that both intensity and duration of optical stimuli contribute to memory state formation. However, the intrinsic nonlinearity of MoS_2 photogating leads to abrupt PPC increases and limits the number of stable, nonvolatile LTM states (black squares in **Figure P5_3c**).

Gate bias (V_{GS}) provides an additional lever to modulate this behavior. When a negative bias ($V_{\text{GS}} = -20 \text{ V}$) is applied, the absolute I_{PPC} decreases, but the relationship between I_{PPC} and exposure time becomes nearly linear (triangles in **Figure P5_3c** and **Figure P5_S10, SI**). This improvement in linearity (a critical parameter for practical synaptic devices) originates from suppressed photogating, which restricts the number of ions migrating toward MoS_2 and allows more gradual accumulation. Conversely, at positive bias ($V_{\text{GS}} = 20 \text{ V}$), the photo-induced ionic gating effect is suppressed, and the device operates as a conventional photodetector, exhibiting fast photoswitching (rise/fall times of 120 ms) and high responsivity. The photodetection capabilities extend across the visible spectrum, with responsivities of 20, 37, and 100 kA W^{-1} under 680, 530, and 455 nm illumination, respectively (**Figure P5_3d** and **Figure P5_S11, SI**).

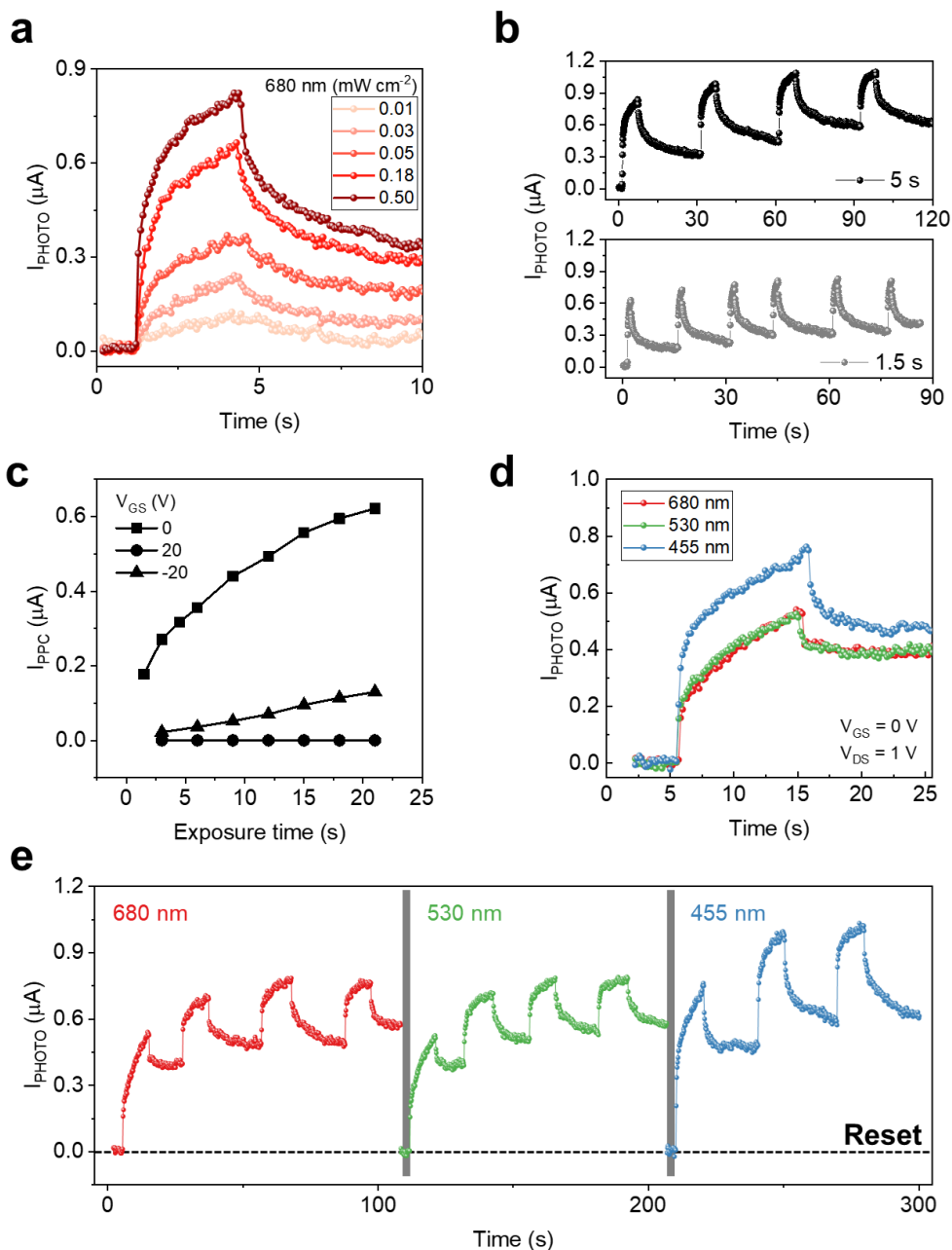


Figure P5_3. Optoelectrical characteristics of SA/MoS₂ photonic-multilevel memory. a) Time-resolved photoresponse of the SA/MoS₂ FET under 680 nm LED illumination with varying light intensities from 0.01 to 0.50 mW cm⁻² at $V_{GS} = 0$ V and $V_{DS} = 1$ V. b) Time-resolved photoresponse of the SA/MoS₂ FET under 680 nm LED, comparing maximum I_{PPC} values for exposure times of 20 s (top) and 9 s (bottom) at $V_{GS} = 0$ V and $V_{DS} = 1$ V. c) I_{PPC} of

SA/MoS₂ FET as a function of exposure time at different V_{GS} . d) Time-resolved photoresponse upon exposure to visible LED illumination at three different wavelengths. e) Photoresponse upon device exposure at successive light pulses at $V_{GS} = 0$ V and $V_{DS} = 1$ V, demonstrating that the device returns to its idle (reset) state once the voltage sources are disconnected. Voltage disconnection, represented by gray segments between measurements, resets the device. Different devices (with similar order of estimated responsivity) were used for the measurements: Device 1 for (a-c) and Device 2 For (d,e); (see **Figure P5_S12, SI**).

This dual-mode behavior highlights the multifunctionality of the SA/MoS₂ FET: under $V_{GS} < 0$, the device operates as a synaptic memory with improved linearity, while under $V_{GS} > 0$ it functions as a high-performance photodetector. Importantly, the spectral responsivity (**Figure P5_3d,e**) confirms that the device fully exploits the intrinsic broadband absorption of MoS₂, unlike previous photonic memory systems limited to narrow wavelength windows.

A distinctive advantage of the SA/MoS₂ architecture lies in its efficient reset capability. By simply turning off the drain bias (V_{DS}), electron injection from the source is interrupted, and accumulated Na⁺ ions diffuse back into the alginate matrix. This spontaneous ion redistribution restores the device to its baseline state without requiring external voltage pulses or high reset fields, in sharp contrast to prior systems where large voltages were needed to erase trapped charges.^[143,144,146–148,156,157] Measurements in **Figure P5_3e** confirm the repeatability of this reset mechanism, while endurance tests (**Figure P5_S13, SI**) demonstrate stable switching behavior over multiple cycles.

Altogether, these results highlight how the SA/MoS₂ hybrid simultaneously achieves multilevel memory formation, linear weight modulation, and broadband photodetection. The ability to toggle between synaptic and photodetector modes via gate control represents a rare convergence of neuromorphic and optoelectronic functionality in a single bio-integrated hybrid platform.

2.5.3 Energy-Efficient Neuromorphic Operation via Ferroelectric–Ionic Coupling

While applying a constant negative gate voltage improves the linearity of LTM characteristics in SA/MoS₂ synaptic devices, such operation would inherently result in high energy consumption and limit scalability in neuromorphic systems. To circumvent this drawback, a permanent gating mechanism was introduced by integrating a ferroelectric polymer layer beneath the MoS₂ channel. Specifically, the bottom surface of MoS₂ was interfaced with a 200 nm-thick film of poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)], exploiting its spontaneous polarization to impart non-volatile electrostatic modulation. This architecture effectively couples the ionic reservoir of the SA top layer with a programmable ferroelectric bottom gate, creating a supramolecular Janus functionalization scheme.

Conventional MoS₂ ferroelectric FETs (FeFETs) have almost exclusively relied on P(VDF-TrFE) as a top-gate dielectric, since the crystalline β -phase of the polymer typically develops a high surface roughness that complicates flake transfer.^[159,160] In contrast, here the MoS₂ was transferred onto a spin-coated P(VDF-TrFE) film prior to thermal curing, leveraging its relatively flat pre-crystallization surface.^[161,162] A subsequent crystallization step yielded the ferroelectric β -phase while maintaining intimate contact at the van der Waals interface (**Figure P5_4a**). Optical and AFM inspections confirmed the successful transfer of a ~ 6 nm-thick MoS₂ flake onto the polymer, producing devices with a channel length of 10 μm (**Figure P5_S14, SI**). X-ray diffraction (**Figure P5_S15, SI**) validated the presence of the β -phase, which underpins the ferroelectric functionality of the layer.

Topographical AFM analysis before and after curing (**Figure P5_4b**) revealed a pronounced increase in root-mean-square roughness (R_{RMS}) from 2.1 to 12.5 nm across a $2 \times 2 \mu\text{m}^2$ MoS₂ region, consistent with the crystalline transition of the polymer. Raman spectroscopy of MoS₂ confirmed that this process did not alter its in-plane vibrational modes (**Figure P5_4c**), indicating minimal strain transfer from the underlying ferroelectric. With a thickness of 200 nm

and a coercive electric field of $\sim 80 \text{ MV m}^{-1}$, reliable polarization programming was achieved by applying short gate pulses: -20 V for 1 s to reach the Program state and $+20 \text{ V}$ for 1 s to reach the Erase state (**Figure P5_4d**).

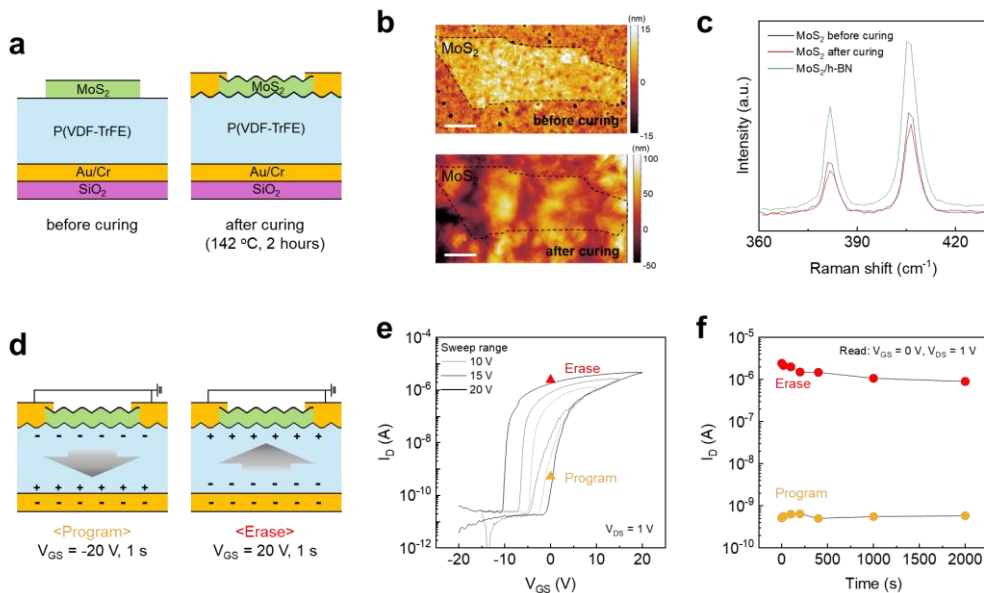


Figure P5_4. Non-volatile MoS₂ memory FET using ferroelectric P(VDF-TrFE). a) Side-view scheme of the MoS₂/P(VDF-TrFE) heterojunction before and after curing. b) Topographical AFM image of MoS₂/P(VDF-TrFE), showing significant changes in the root-mean-square roughness (R_{RMS}) before and after curing. Scale bar represents $2 \mu\text{m}$. c) Raman spectra of MoS₂ crystals supported on different insulators: black (before curing of P(VDF-TrFE)) and red (after curing of P(VDF-TrFE)) and green (h-BN). d) Side-view scheme of a MoS₂ FeFET to describe ferroelectric dipole alignment in P(VDF-TrFE) under Program state after $V_{\text{GS}} = -20 \text{ V}$, 1 s pulse and Erase state after $V_{\text{GS}} = +20 \text{ V}$, 1 s pulse. e) Transfer curves of the MoS₂ FeFET at $V_{\text{DS}} = 1 \text{ V}$, showing a maximum ferroelectric hysteresis of 10 V depending on the gate voltage sweep. Program and Erase states are measured at $V_{\text{GS}} = 0 \text{ V}$ and $V_{\text{DS}} = 1 \text{ V}$ after applying -20 V and 20 V pulses. f) Memory retention properties of the non-volatile MoS₂ FeFET for 2000 s .

The resulting FeFET exhibited robust non-volatile memory characteristics (**Figure P5_4e**). Transfer measurements under variable gate sweep ranges ($\pm 10 \text{ V}$ and $\pm 20 \text{ V}$) revealed a clear hysteresis window, widening from $\sim 5 \text{ V}$ to $\sim 10 \text{ V}$ as the polarization range increased. Distinct Program and Erase states were reproducibly maintained at $V_{\text{GS}} = 0 \text{ V}$ following the respective pulses, enabling binary-like operation without the need for continuous gate bias. Retention tests

(**Figure P5_4f**) demonstrated stable memory states for at least 2000 s, with a Program/Erase current ratio of $\sim 10^3$ maintained throughout, highlighting the durability of the ferroelectric polarization in modulating the MoS₂ channel.

This integration of ferroelectric P(VDF-TrFE) as a bottom gate establishes an energy-efficient, non-volatile platform that complements the dynamic, light-driven ion gating of the SA layer. Together, they provide a dual-mode functionality (ferroelectric programming for persistent memory states and photo-ionic gating for synaptic plasticity) paving the way for hybrid neuromorphic architectures where polymeric functionality synergizes with 2D semiconductors.

As a culminating step, the alginate-based ionic reservoir (SA) was integrated into the MoS₂ FeFET platform, yielding a Janus hybrid device in which top-side ionic gating and bottom-side ferroelectric modulation coexist. This dual-functionalization approach enables independent and complementary modes of control: electrical pulses induce non-volatile polarization switching in the ferroelectric P(VDF-TrFE) layer, while optical excitation drives photo-induced ionic gating within the SA top layer (**Figure P5_5a**). Together, these mechanisms provide a multidimensional control scheme for conductivity modulation, uniting ferroelectric memory retention with light-driven synaptic plasticity.

Electrical characterization confirmed that the integration of SA did not compromise the ferroelectric memory characteristics of the MoS₂/P(VDF-TrFE) device. Transfer curves in **Figure P5_5b** show that the 10 V memory hysteresis window remained intact after SA deposition, with Program/Erase current ratios exceeding 10^3 . Retention measurements further demonstrated stable polarization states over 10,000 s, indicating that the dominant mechanism underlying non-volatile memory operation is preserved, with negligible interference from cation migration in the SA layer. Thus, the ferroelectric component reliably ensures static memory functionality.

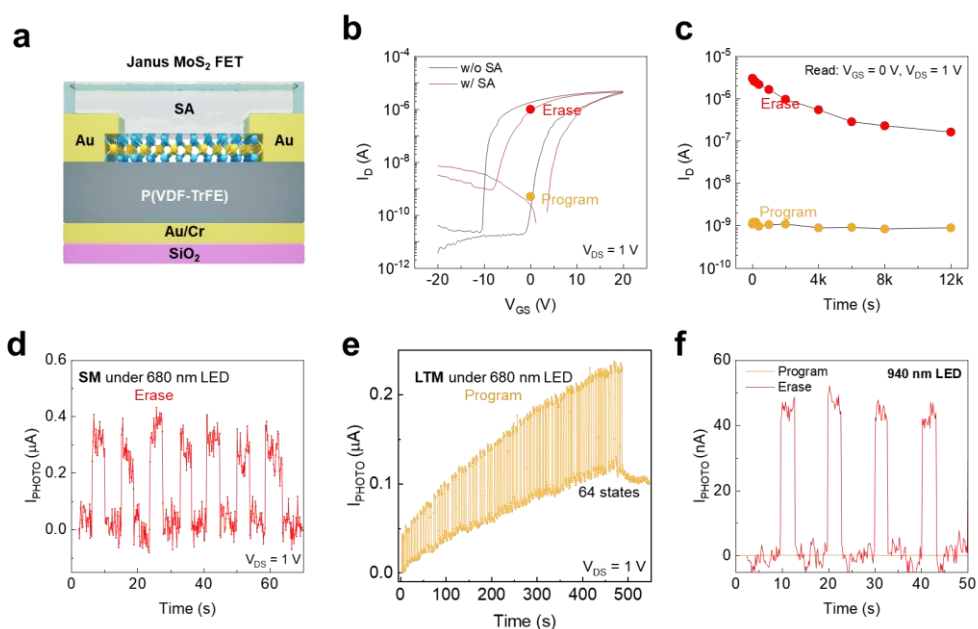


Figure P5_5. Asymmetric supramolecular functionalization of 2D MoS₂ FET with SA and ferroelectric polymer. a) Side-view scheme of the Janus MoS₂ FET achieved by interfacing SA with the MoS₂ FeFET. b) Transfer curves of the MoS₂ FeFET (black) and Janus MoS₂ FET (red) at V_{DS} = 1 V, showing a maximum ferroelectric hysteresis of 10 V, regardless of the presence of SA. c) Memory retention properties of the Janus MoS₂ FET over 12,000 s. Time-resolved photoresponse of the Janus MoS₂ at V_{GS} = 0 V and V_{DS} = 1 V, demonstrating d) sensory memory (SM) under 680 nm LED illumination at the ferroelectric Erase state, e) synaptic LTM under 680 nm LED illumination at the ferroelectric Program state, and f) SM by leveraging the ferroelectric Erase state under NIR LED illumination.

Beyond retention, the Janus hybrid device exhibits remarkable multifunctionality. By coupling ferroelectric programming with light-induced ionic gating, the system mimics synaptic plasticity with both short-term memory (SM) and long-term memory (LTM) modes (**Figure P5_3**). Importantly, this is achieved without requiring continuous or high-voltage gate biasing, thereby ensuring energy-efficient operation. A comparative analysis of power consumption (**Figure P5_S16, SI**) highlights this advantage: the SA/MoS₂/h-BN FET requires a sub-nW average gate power ($P_G \approx 0.2$ nW at V_{GS} = -20 V for 80 s), whereas the Janus SA/MoS₂/P(VDF-TrFE) device achieves zero gate power (**P_G = 0 nW**) at V_{GS} = 0 V. Although the drain power

consumption (P_D) remains in the tens of nW, the complete elimination of gate power dissipation is a critical step toward scalable and thermally stable neuromorphic architectures.

Functional testing revealed that the Janus hybrid can resolve up to 60 linear multilevel conductance states (**Figure P5_5e**), with an average resolution of ~ 2 nA (**Figure P5_S17, SI**) across a total range of 0–120 nA. This fine gradation enables precise analog tuning of synaptic weights, a key requirement for high-density neuromorphic computing. Additionally, the device extends its photodetection range into the near-infrared (NIR) domain. In the ferroelectric Erase state, responsivity under photon stimulation covers wavelengths up to 940 nm (**Figure P5_5f**). While MoS₂ NIR detection has been previously reported,^[163,164] the novelty here lies in combining it with non-volatile memory characteristics via polymeric functionalization. This integration directly reduces energy consumption while broadening spectral response, a synergy rarely achieved in conventional optoelectronic systems.

These results show that the Janus SA/MoS₂/P(VDF-TrFE) device combines stable ferroelectric memory retention with light-driven ionic gating, enabling energy-efficient operation, fine analog tuning across 60 conductance states, and extended photodetection into the NIR range.

2.5.4 Conclusion

In this work, we realized an optoionic artificial synapse that leverages photo-induced ionic gating at the interface between MoS₂ and sodium alginate (SA), a sustainable biopolymer that acts as a dynamic cation reservoir. This mechanism faithfully emulates synaptic plasticity (spanning sensory memory (SM), short-term memory (STM), and long-term memory (LTM)) and enables multilevel memory operation controlled solely by photon stimulation. By tuning light intensity and exposure time, the SA/MoS₂/h-BN device achieved more than eight discrete, optically programmable states, resettable by simple

voltage disconnection rather than high reset biases typical of trap/detrapping optoelectronic memories.

To expand functionality, we developed a Janus MoS₂ heterostructure incorporating a ferroelectric P(VDF-TrFE) bottom gate. This dual-modulation design unites photo-induced ionic gating with nonvolatile polarization control, producing a multifunctional photonic memory device with 60 distinct, linear conductance states. The integration of ferroelectric polarization eliminates the need for continuous back-gating, reducing power consumption and advancing the prospects for energy-efficient neuromorphic systems.

Beyond synaptic emulation, the Janus MoS₂ device demonstrates broad-spectrum photodetection extending into the near-infrared (up to 940 nm), further underscoring the versatility of this hybrid strategy. Overall, this study establishes supramolecular functionalization of 2D semiconductors with biopolymeric ionic reservoirs as a sustainable and tunable route to optoelectronic memory. The unique combination of photonic memory, analog synaptic behavior, and energy-efficient design positions this platform at the forefront of neuromorphic computing and multifunctional 2D electronics.

3. Final Remarks

Beginning with alginate as a model system, this thesis demonstrated how cation valency, size, and coordination geometry dictate network structure, ionic mobility, and mechanical response. These insights provided a transferable set of design principles that guided subsequent studies. Blending alginate with gelatin introduced elasticity and thermoresponsiveness, while organohydrogel chemistry stabilized hydration and enabled robust performance under realistic conditions. Gelatin was further advanced into enzymatically crosslinked networks, highlighting the potential of sustainable covalent stabilization strategies. Finally, caseinate emerged as an unconventional yet highly promising platform, forming robust ionic hydrogels with multivalent cations and expanding the chemical space of protein-derived functional materials.

These systems were not studied in isolation but were implemented directly in stretchable sensors, gel polymer electrolytes for supercapacitors, and neuromorphic optoionic devices. Across these applications, the interplay between ion identity, network architecture, and medium composition consistently determined performance. This confirmed that soft electronics can be programmed not by adding opaque fillers, but by tuning the intrinsic chemistry of biopolymers.

The central outcome of this thesis is that sustainability and performance need not be in conflict. By exploiting the chemical richness of natural polymers, it is possible to design transparent, filler-free, and durable materials that combine mechanical compliance with ionic functionality. In doing so, this work broadens the material palette of soft electronics while establishing generalizable strategies for their future development.

At the same time, several challenges remain. The mechanical robustness of biopolymer gels, though improved through ionic or enzymatic stabilization, still falls short of synthetic elastomers under extreme deformation. Environmental sensitivity, while mitigated by organohydrogel strategies, remains a limitation for long-term outdoor use. Device integration is still at a

proof-of-concept stage, with further optimization needed to achieve scalable manufacturing.

Looking forward, the design rules developed here can be extended in multiple directions. Combining ionic coordination with dynamic covalent chemistries could yield hydrogels that unite robustness with self-healing. Exploring underutilized biopolymers, such as cellulose derivatives or silk fibroin, may expand the range of available functionalities. On the application side, interfacing biopolymer gels with advanced electrodes and semiconductors opens opportunities in bioelectronics, energy storage, and neuromorphic computation. Finally, valorizing industrial byproducts and renewable feedstocks points toward an emerging paradigm in which high-performance electronics are also biodegradable, recyclable, and environmentally benign.

In conclusion, this thesis establishes that biopolymers are not passive matrices but active building blocks for next-generation soft electronics. By uniting molecular design with device translation, it demonstrates how sustainable polymers can serve as programmable, multifunctional components at the interface of biology and electronics—where ecological responsibility and technological innovation converge.

4. Supporting Information

4.1_P1_S_Project 1

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8. References

1. Morphological characterization

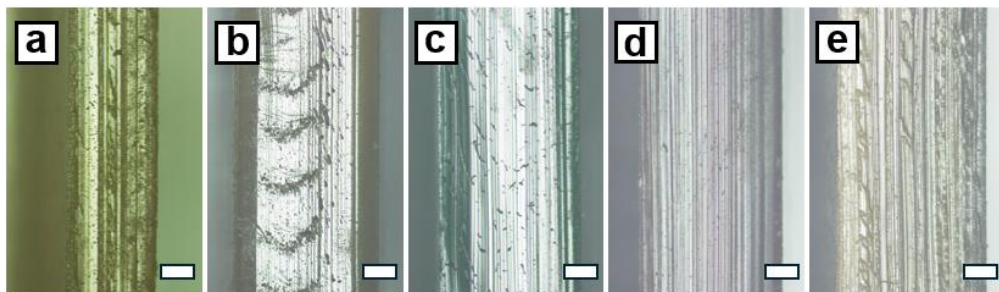


Figure P1_S1. Cross sectional optical images of AlgGel (a), MnAlgGel (b), CuAlgGel (c), FeAlgGel (d) and ZrAlgGel (e). The scale bar is 200 μm .

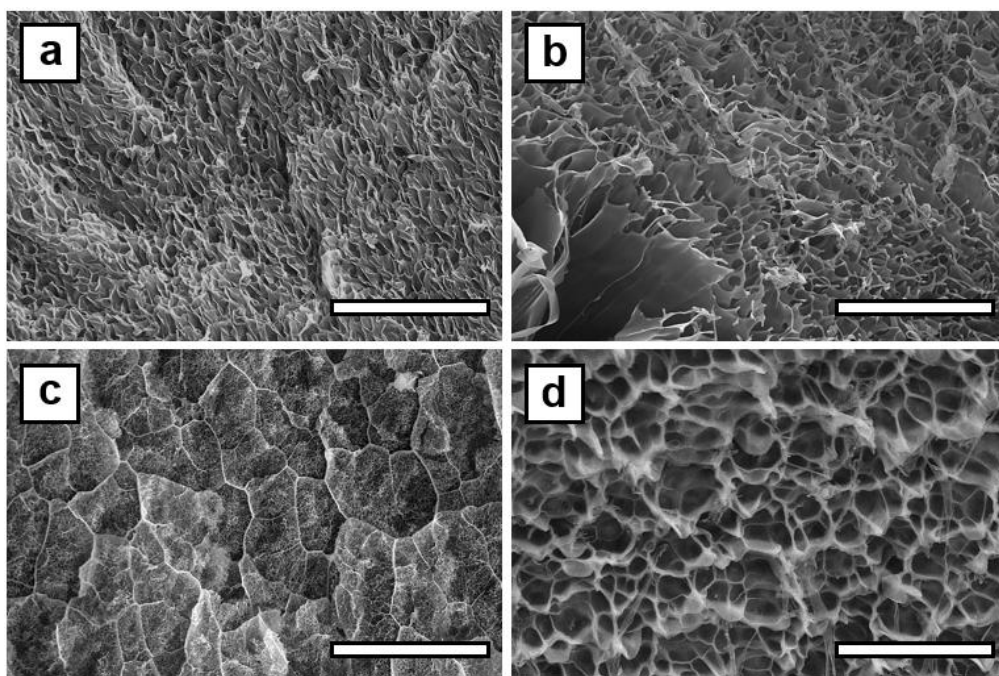


Figure P1_S2. SEM images of lyophilized gelatin (a), alginate (b), MnAlg (c) and MnAlgGel prior glycerol addition (d). The scale bar is 40 μm .

Table P1_S1. Physicochemical properties of the MAlgGel organohydrogels.

	<i>AlgGel</i>	<i>MnAlgGel</i>	<i>CuAlgGel</i>	<i>FeAlgGel</i>	<i>ZrAlgGel</i>
Thickness (μm)	511 ± 15	817 ± 24	805 ± 24	829 ± 25	847 ± 26
Polymer content (w/w%)	18.3 ± 1.0	28.4 ± 1.5	24.7 ± 1.0	21.9 ± 0.6	21.4 ± 1.1
Glycerol content (w/w%)	74.3 ± 0.8	57.9 ± 1.2	60.7 ± 0.7	63.2 ± 0.3	63.7 ± 0.8
Water content (w/w%)	7.4 ± 0.2	13.7 ± 0.3	14.6 ± 0.3	14.9 ± 0.3	14.9 ± 0.3
Degradation onset (°C)	148.9	171.3	168.7	167.8	169.6
M^{X+} content (mmol/g)	-	(7.1 ± 0.4) · 10 ⁻²	(5.9 ± 0.3) · 10 ⁻²	(7.5 ± 0.4) · 10 ⁻²	(6.3 ± 0.3) · 10 ⁻²
T_g (°C)	41.7 (57.1) ^a	42.4	42.5	52.5	62.8
YM (MPa)	1.87 ± 0.14	0.52 ± 0.08	2.44 ± 0.06	2.57 ± 0.16	2.46 ± 0.06
UTS (MPa)	1.45 ± 0.06	0.64 ± 0.02	1.88 ± 0.04	1.17 ± 0.11	1.42 ± 0.05

^aSecond peak resulting from the re-assembling of the chains during the first thermal event. *T_g*, *YM* and *UTS* stand for *Glass transition temperature*, *Young's modulus* and *Ultimate tensile strength*, respectively.

2. Thermal characterization

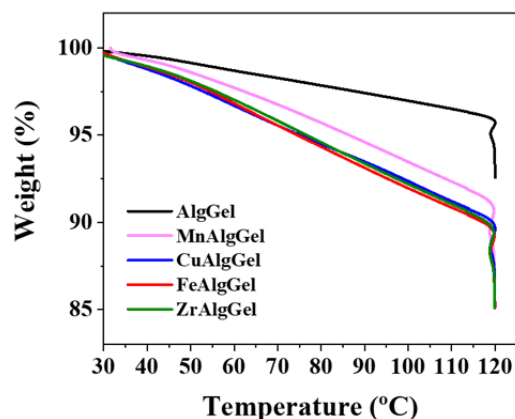


Figure P1_S3. TGA thermograms of AlgGel (black), MnAlgGel (pink), CuAlgGel (blue), FeAlgGel (red) and ZrAlgGel (green).

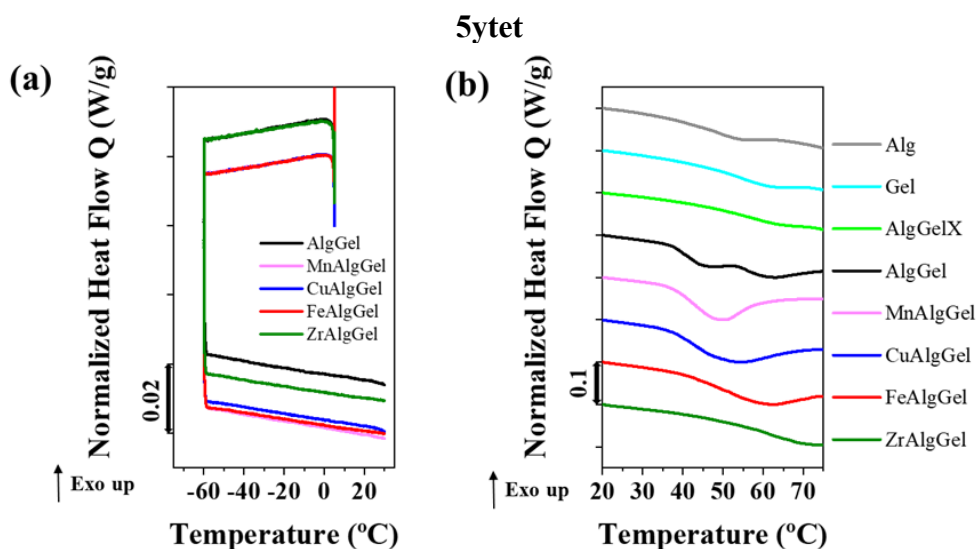


Figure P1_S4. (a) DSC thermograms of AlgGel (black), MnAlgGel (pink), CuAlgGel (blue), FeAlgGel (red) and ZrAlgGel (green) for the determination of the state of the water in the samples. (b) DSC curves of Sodium alginate (Alg, grey), Gelatin (Gel, cyan), AlgGelX (light green, same formulation of AlgGel, but without addition of glycerol), AlgGel (black), MnAlgGel (pink), CuAlgGel (blue), FeAlgGel (red) and ZrAlgGel (green) for the determination of the glass transition temperature (T_g). The DSC curves in Figure S4b were offset for clarity.

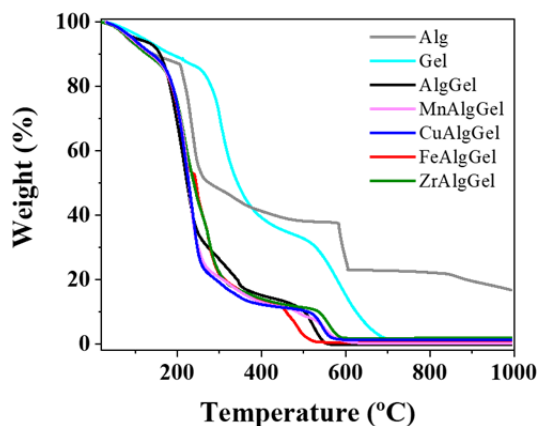


Figure P1_S5. TGA thermograms of Sodium alginate (Alg, grey), Gelatin (Gel, cyan), AlgGel (black), MnAlgGel (pink), CuAlgGel (blue), FeAlgGel (red) and ZrAlgGel (green).

Table P1_S2. TGA weight losses for the samples illustrated in **Figure S5**. **Region I** (RT - 130 °C), **Region II** (130 °C - 250 °C), **Region III** (RT 250 °C - 430 °C), **Region IV** (430 °C - 950 °C).

<i>Sample</i>	<i>Region</i>	<i>Weight loss (%)</i>	<i>Norm. weight loss (%)</i>	<i>Onset I polymeric deg. (°C) degradation (°C)</i>
Sodium Alginate	I	9.2	-	
	II	35.5	39.1	208.5
	III	15.3	16.8	
	IV	21.7	23.9	
Gelatin	I	5.9	-	
	II	8.3	8.8	
	III	49.1	52.2	258.7
	IV	35.3	37.5	
AlgGel	I	6.3	-	
	II	59.4	63.4	148.9
	III	20.2	21.6	
	IV	14.1	15.0	
MnAlgGel	I	9.2	-	
	II	60.9	67.1	171.3
	III	17.9	19.7	
	IV	12.0	13.2	
CuAlgGel	I	8.9	-	
	II	62.9	69.1	168.7
	III	16.5	18.1	
	IV	10.4	11.4	
FeAlgGel	I	9.8	-	
	II	44.5	49.3	167.8
	III	33.0	36.6	
	IV	12.7	14.1	

ZrAlgGel	I	10.1	-	
	II	45.7	50.9	169.6
	III	31.2	34.7	
	IV	11.1	12.3	

3. Small angle X-ray scattering (SAXS) and responsiveness' summary

The SAXS curves of MnAlgGel, CuAlgGel, FeAlgGel and ZrAlgGel are reported in **Figure 1d**, with their respective fitting curves. A double Lorentzian function was used to fit the SAXS curves of MnAlgGel, CuAlgGel, FeAlgGel and ZrAlgGel.^[3,4] The scattering intensity $I(q)$ is defined by the following equation (from NIST, <https://www.sasview.org/>)

$$I(q) = \frac{A}{1 + (Q\xi_1)^n} + \frac{C}{1 + (Q\xi_2)^m} + B \quad (\text{Eq. P1_S1})$$

in which B is the background, A is the Lorentzian scale factor 1 (LSF1 in **Table S2**), C is the Lorentzian scale factor 2 (LSF2 in **Table S2**), ξ_1 and ξ_2 are the respective correlation lengths and n and m are the corresponding power law exponents (PLE1 and PLE2 in **Table S2**, respectively). The results of the fitting are reported in **Table S2**. All the samples show a “long-distance” correlation length (ξ_1), while only CuAlgGel and ZrAlgGel also show “short-distance” correlation lengths (ξ_2). In the first case, the ξ_1 of MnAlgGel (i.e. 25.1 nm) is the highest among the ones of the other MAlgGel samples (i.e. 6.3 - 8.4 nm). Similar characteristic implies a weaker interaction between the Mn^{2+} ions and the alginate chains (coherently with literature reports) that reduces the ability of alginate to impart rigidity to the interpenetrating polymer network (IPN). Fe^{3+} ions in FeAlgGel, showing the lowest ξ_1 among the $\text{M}^{\text{x}+}$ -crosslinked samples, are probably the strongest interacting with the polymeric structure. Interestingly, it is possible to highlight a relevant contribution of ξ_2 to the scattering of CuAlgGel and ZrAlgGel: the correlation lengths in this case are equal to 2.7 nm and 0.4 nm, respectively, and indicate the formation of small domains with high density of $\text{M}^{\text{x}+}$ ions interacting with the polymer chains.

Table P1_S3. Results of the Double Lorentzian fitting of the scattering curves shown in **Figure 1d**.

	MnAlgGel	CuAlgGel	FeAlgGel	ZrAlgGel
scale*	0.90	0.84	0.80	0.80
bkg§	0.059	0.034	0.067	0.068
LSF1	658.3 ± 32.9	6.4 ± 0.3	21.9 ± 1.1	32.1 ± 1.6
ξ1 (nm)	25.1 ± 1.3	8.4 ± 0.4	6.3 ± 0.3	8.0 ± 0.4
PLE1	2.6 ± 0.1	2.3 ± 0.1	2.2 ± 0.1	2.2 ± 0.1
LSF2	-	2.6 ± 0.1	-	0.3 ± 0.1
ξ2 (nm)	-	2.7 ± 0.1	-	0.4 ± 0.1

*scale is equal to the volume fraction of the sample. § bkg stands for background.

Table P1_S4. Conductivity, mechanical response, thermal-response, humidity and photoresponse of AlgGel and MAlgGel samples. The sensitivity parameters are averaged from 3 different measurements.

	AlgGel	MnAlgGel	CuAlgGel	FeAlgGel	ZrAlgGel
Conductivity (mS m⁻¹)^a	0.17 ± 0.06	1.3 ± 0.3	3.7 ± 0.5	6.0 ± 1.4	6.1 ± 0.9
Temperature Response (K⁻¹)	- ^b	0.19 ± 0.02	0.16 ± 0.03	0.06 ± 0.01	0.13 ± 0.02
B (kJ mol⁻¹)^c	6.4 ± 0.7	2.7 ± 0.2	2.2 ± 0.3	2.3 ± 0.6	2.2 ± 0.2
Humidity Response (RH(%)⁻¹)	(2.1±0.2)·10 ⁻²	(2.2±0.3)·10 ⁻²	(2.1±0.3)·10 ⁻²	(1.8±0.1)·10 ⁻²	(1.5±0.1)·10 ⁻²
RH sensitivity range (%)	20-60	20-60	20-60	20-70	20-80
Photo-responsivity (μA W⁻¹)	0.6	9.2	5.1	4.3	5.8
Photo switching speed (s)	3.42/4.35	2.23/3.13	3.31/3.61	4.00/4.28	3.76/3.92
GF1 (Region I)	2.80 ± 1.15	2.25 ± 0.57	1.67 ± 0.19	2.29 ± 0.22	2.38 ± 0.26
GF2 (Region II)	2.18 ± 0.38	2.02 ± 0.40	1.73 ± 0.18	2.15 ± 0.07	2.27 ± 0.18

^a Extracted using Cu electrode. ^b Non-linear temperature responsiveness. ^c Activation energy of the ionic movement.

4. Temperature sensitivity

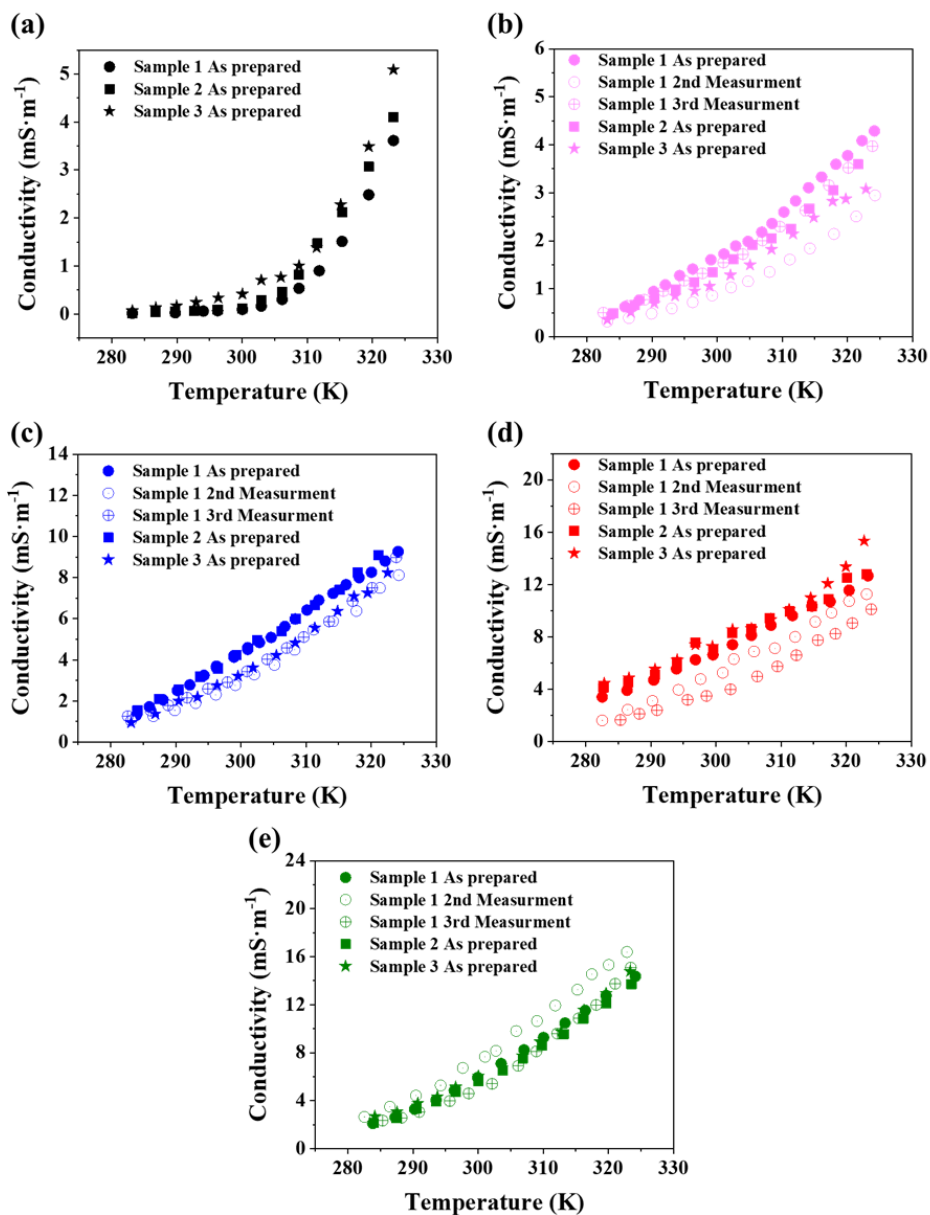


Figure P1_S6. Influence of temperature on the conductivity of the MAAlgGel sensors, where three different devices were tested and the Sample 1 was characterized three times to analyze its self-stability for (a) AlgGel, (b) MnAlgGel, (c) CuAlgGel, (d) FeAlgGel and (e) ZrAlgGel.

5. Humidity sensitivity

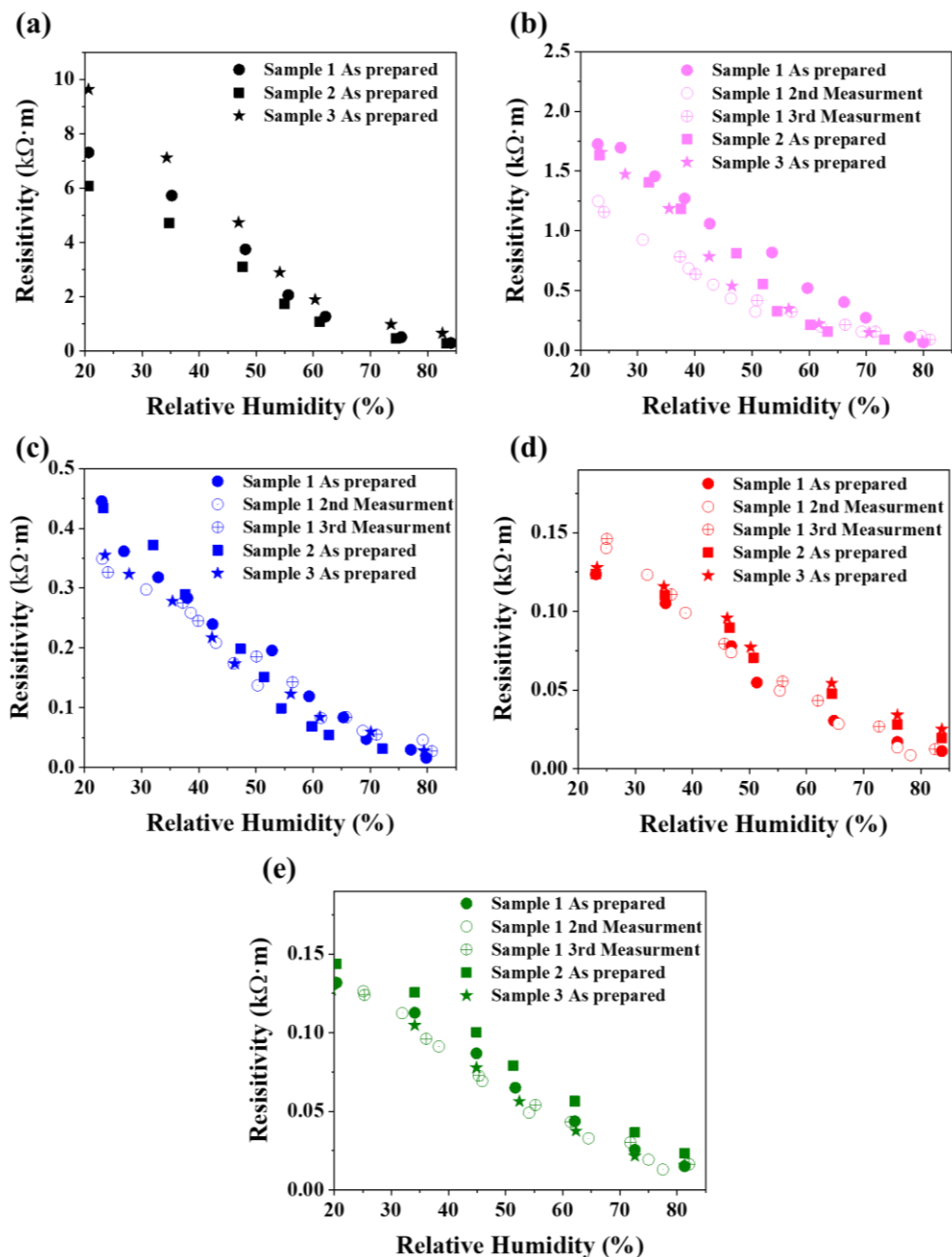


Figure P1_S7. Influence of humidity on the resistivity of the MAlGel sensors, where three different devices were tested and the Sample 1 was characterized three times to analyze its self-stability for (a) AlgGel, (b) MnAlGel, (c) CuAlGel, (d) FeAlGel and (e) ZrAlGel..

6. Photosensitivity

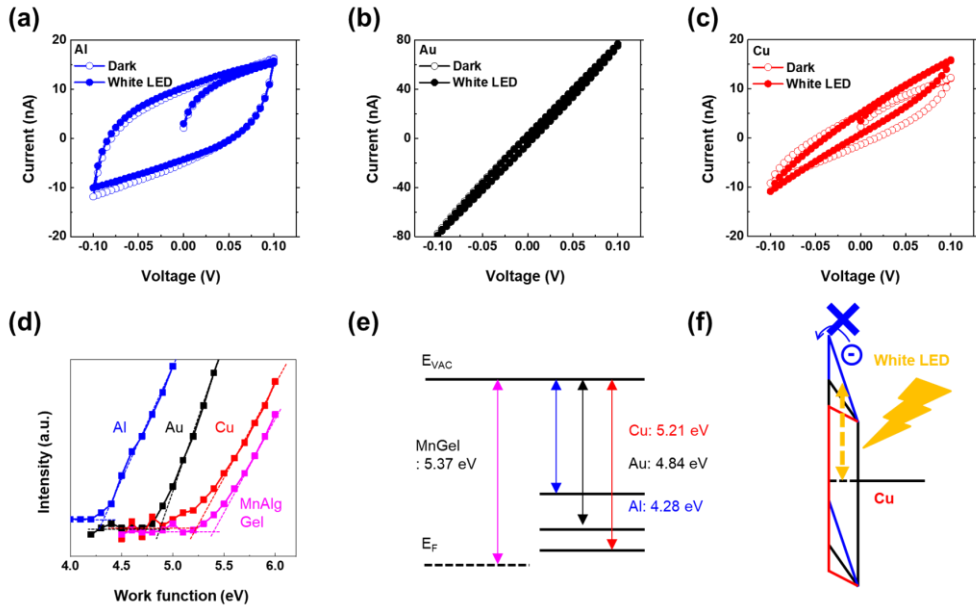


Figure P1_S8. Photoresponse of the MnAlgGel photodetectors with (a) Al, (b) Au, and (c) Cu electrodes. (d) Secondary-electron cutoff of Al (blue circles), Au (black), Cu (red), and MnAlgGel (pink). (e) Band diagram of MnAlgGel and contact electrodes: Al, Au, and Cu before the junction formation. (f) Band diagrams of the MnAlgGel/electrode junction.

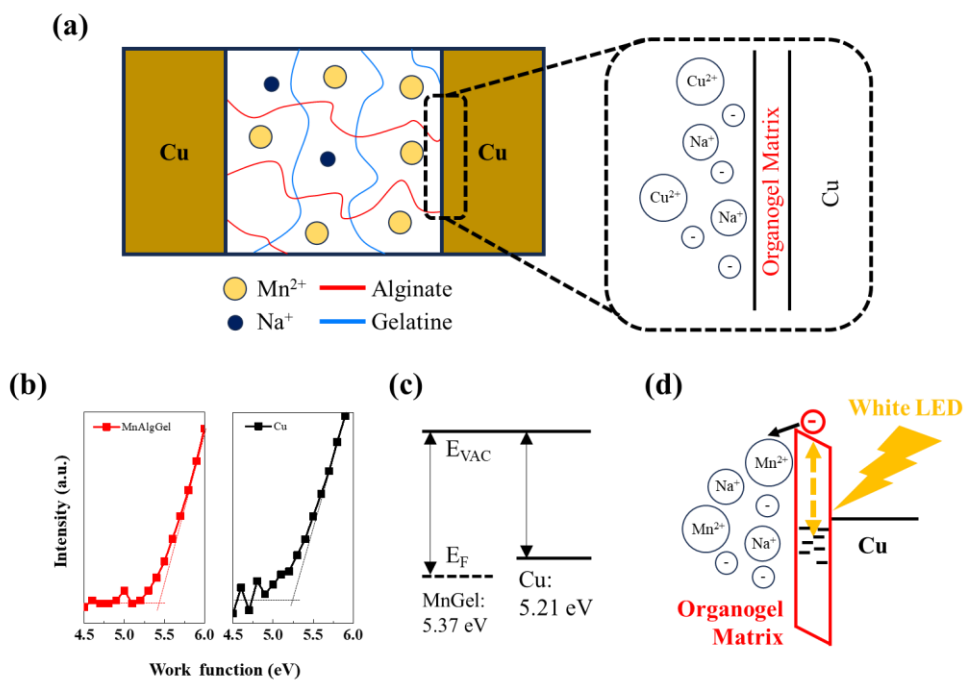


Figure P1_S9. (a) Illustration of the MnAlgGel photodetector with Cu electrodes. (b) Photoelectron Yield Spectroscopy in Air estimation of the secondary-electron cutoff of MnAlgGel (red squares) and Cu (black). (c) Band diagram of MnAlgGel and Cu before contact. (d) Band diagrams specifically illustrating the MnAlgGel/Cu interface. Trapped electrons at interface defect states can be excited by white LED illumination.

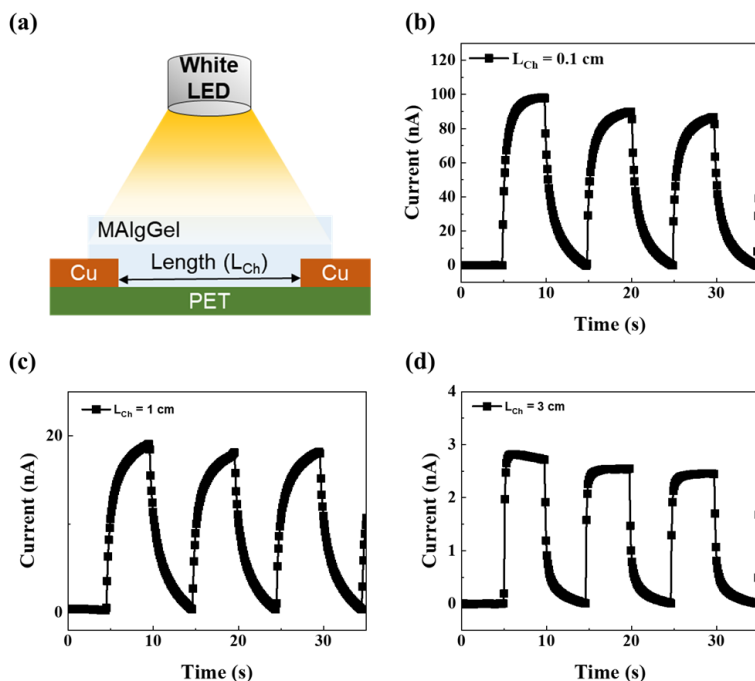


Figure P1_S10. (a) Side-view scheme of a MnAlgGel photodetector with Cu electrodes. Time-resolved photoresponse of the MnAlgGel photodetector with different channel length, L_{Ch} = (b) 0.1 cm, (c) 1 cm, and (d) 3 cm.

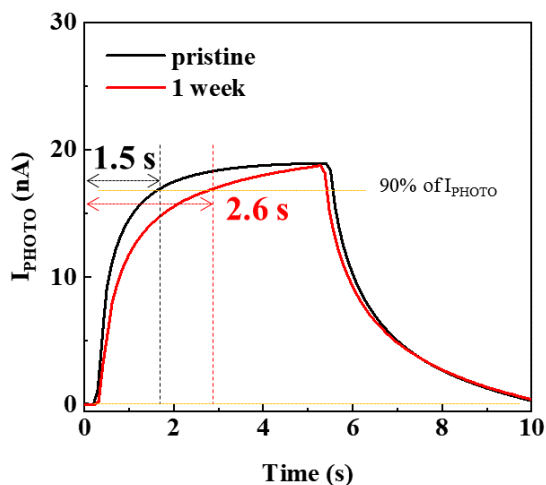


Figure P1_S11. Time resolved photoresponse of the MnAlgGel photodetector in its pristine state (black) and after one week of storage under ambient conditions (red). The unchanged maximum I_{PHOTO} value confirms the excellent long-term stability of our hydrogel. However, the change in photoswitching speed (from 1.5 s to 2.6 s) can be attributed to the degradation of metal/hydrogel interface quality due to Cu oxidation.

7. Strain sensitivity

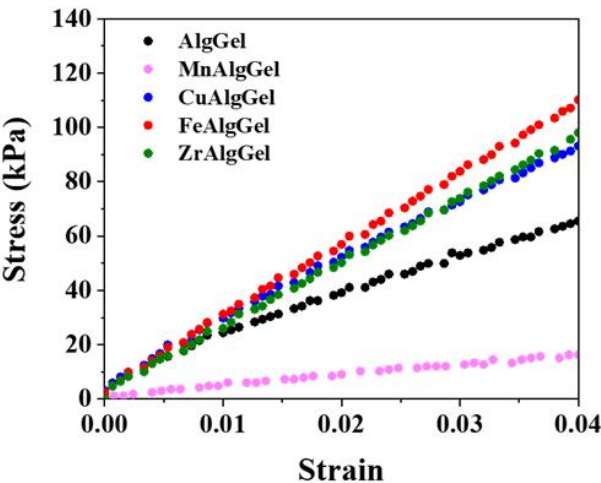


Figure P1_S12. Stress vs strain curves for the MAAlgGel samples in the 0.00-0.04 strain region, used for the determination of the Young’s modulus (YM).

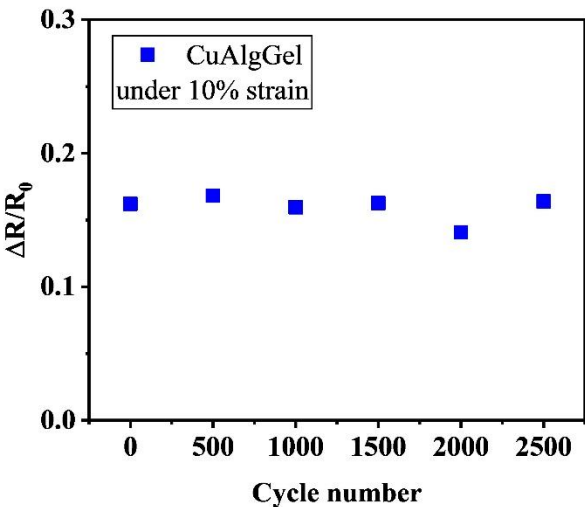


Figure P1_S13. Durability test of CuAlgGel for 2500 cycles under 10% strain.

8. References P1_S

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Table P2_S1. Preparation conditions of MXAlgGel polymer electrolytes. Steps 1, 2, and 3 last for 1 hour, 1.5 hours, and 1.5 hours, respectively.

<i>Step 1 (pure H₂O)</i>			<i>Step 2 (gly 1:4 in H₂O)</i>			<i>Step 3 (gly 1:4 in H₂O)</i>	<i>Sample</i>
MnCl ₂	CuCl ₂	LiCl	MnCl ₂	CuCl ₂	LiCl		
1.00 M		0.00	1.00 M		0.00		Mn100AlgGel
0.75 M		0.25	0.75 M		0.25		Mn075AlgGel
0.50 M		0.50	0.50 M		0.50		Mn050AlgGel
0.25 M		0.75	0.25 M		0.75		Mn025AlgGel
0.00 M		1.00	0.00 M		1.00		LiAlgGel
1.00 M		0.00	1.00 M		0.00		Cu100AlgGel
0.75 M		0.25	0.75 M		0.25		Cu075AlgGel
0.50 M		0.50	0.50 M		0.50		Cu050AlgGel
0.25 M		0.75	0.25 M		0.75		Cu025AlgGel
-	-		0.00 M		0.00		AlgGel

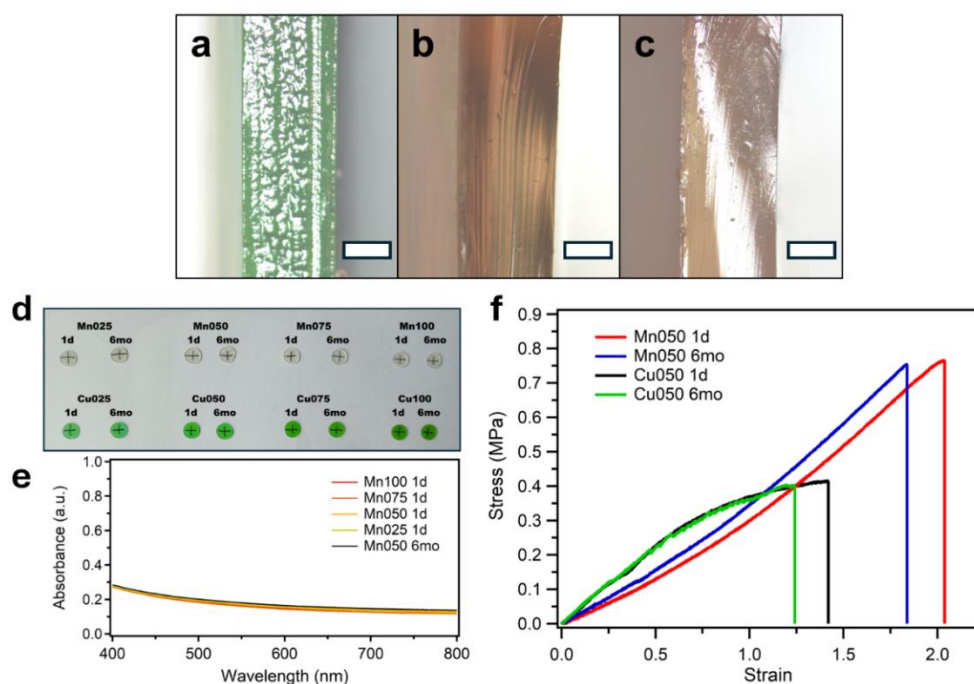


Figure P2_S1. Optical microscopy side-view of a) Cu050AlgGel, b) LiAlgGel, and c) Mn050AlgGel for thickness evaluation. The lateral scale bar corresponds to 300 μm. d) Photographs of Mn- and Cu-crosslinked AlgGel samples after 1 day and 6 months of storage under ambient conditions, showing stable macroscopic appearance and minimal visual changes

over time. A higher lithium concentration reduces the green colour intensity in CuXAlgGel, while MnXAlgGel remain visually unchanged. e) UV-vis absorbance spectra of Mn-crosslinked AlgGel samples after 1 day and 6 months, indicating excellent optical stability and the absence of significant aging-related changes in light transmittance. f) Stress-strain traction curves of Mn050AlgGel and Cu050AlgGel samples recorded after 1 day and 6 months, demonstrating retained mechanical properties with negligible degradation. Young's modulus (YM) and Ultimate tensile strength (UTS) obtained are reported in **Table P2_S2**.

Table P2_S2. Young's modulus (YM) and Ultimate tensile strength (UTS) of Mn050AlgGel 1d/6mo and Cu050AlgGel 1d/6mo. YM was evaluated in the 0.0 - 0.2 strain range.

<i>Sample</i>	<i>Young's modulus (MPa)</i>	<i>Ultimate tensile strength (MPa)</i>
Mn050 1d	0.24 ± 0.05	0.80 ± 0.06
Mn050 6mo	0.30 ± 0.04	0.75 ± 0.09
Cu050 1d	0.42 ± 0.07	0.43 ± 0.02
Cu050 6mo	0.50 ± 0.04	0.42 ± 0.02

Table P2_S3. General properties of the AlgGel-based organohydrogels: thickness; water, salt, glycerol (Gly) and alginate-gelatin polymer (Polym) content; Thermal degradation onset (T_{deg}). The error associated with T_{deg} is ± 2 °C. Further information on salt composition is reported in **Table P2_S4**.

<i>Sample</i>	<i>Thickness (μm)</i>	<i>Water (wt/wt%)</i>	<i>Salt (wt/wt%)</i>	<i>Gly (wt/wt%)</i>	<i>Polym (wt/wt%)</i>	<i>T_{deg} (°C)</i>
Mn100	600 ± 25	18.1 ± 0.5	5.2 ± 0.1	~ 58	~ 20	193
Mn075	626 ± 35	17.4 ± 0.5	3.9 ± 0.2	~ 60	~ 20	192
Mn050	608 ± 32	17.5 ± 0.5	3.0 ± 0.2	~ 61	~ 20	196
Mn025	624 ± 15	16.7 ± 0.5	2.4 ± 0.1	~ 61	~ 20	195
Li	619 ± 22	15.1 ± 0.5	0.8 ± 0.1	~ 64	~ 20	199
Cu100	610 ± 31	16.7 ± 0.5	5.2 ± 0.1	~ 58	~ 20	179
Cu075	597 ± 19	17.8 ± 0.5	4.3 ± 0.3	~ 58	~ 20	183
Cu050	604 ± 28	17.9 ± 0.5	2.6 ± 0.2	~ 58	~ 20	187
Cu025	616 ± 20	19.6 ± 0.5	1.9 ± 0.1	~ 58	~ 20	190
AlgGel	592 ± 36	14.5 ± 0.5	-	~ 65	~ 20	195

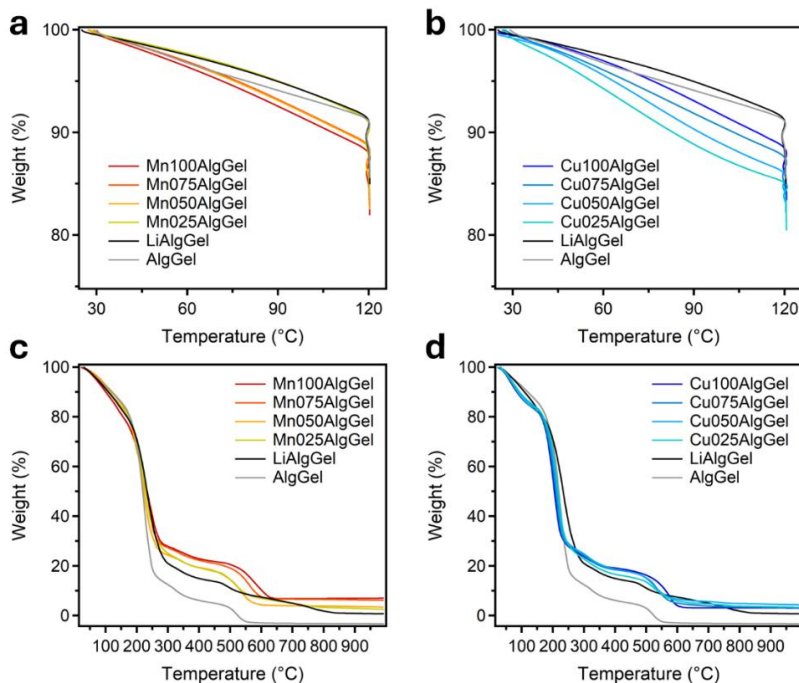


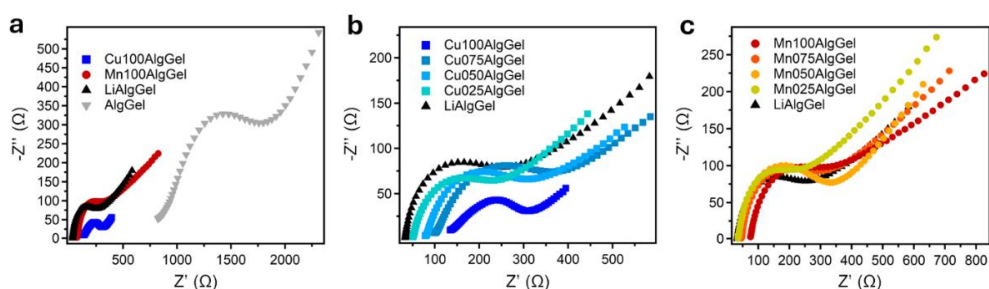
Figure P2_S2. a, b) TGA thermograms for AlgGel-based organohydrogels' water content determination. c, d) TGA thermograms for degradative profile evaluation.

Table P2_S4. Experimental metal ions' content of the AlgGel-based organohydrogels determined through ICP-AES.

<i>Sample</i>	<i>Na⁺</i> (wt/wt%)	<i>Cu²⁺</i> (wt/wt%)	<i>Mn²⁺</i> (wt/wt%)	<i>Li⁺</i> (wt/wt%)	<i>nLi+/nM2+</i>
Mn100AlgGel	-	-	5.2 ± 0.1	-	0
Mn075AlgGel	-	-	3.8 ± 0.1	0.11 ± 0.1	0.24 ± 0.02
Mn050AlgGel	-	-	2.8 ± 0.1	0.27 ± 0.1	0.77 ± 0.02
Mn025AlgGel	-	-	1.9 ± 0.1	0.49 ± 0.1	2.09 ± 0.02
LiAlgGel	-	-	-	0.75 ± 0.1	-
Cu100AlgGel	-	5.2 ± 0.1	-	-	0
Cu075AlgGel	-	4.2 ± 0.1	-	0.11 ± 0.1	0.25 ± 0.02
Cu050AlgGel	-	2.5 ± 0.1	-	0.15 ± 0.1	0.56 ± 0.02
Cu025AlgGel	-	1.7 ± 0.1	-	0.23 ± 0.1	1.28 ± 0.02
AlgGel	0.10 ± 0.1	-	-	-	-

Table P2_S5. SAXS fitting parameters for the investigated AlgGel-based organohydrogels.

<i>Sample</i>	<i>Scale</i>	<i>bkg</i>	<i>A</i>	<i>B</i>	ζ (nm)	<i>n</i>	<i>m</i>
Mn100	0.82	0.0205	$9.67 \cdot 10^{-7}$	1.50	6.3	3.29	3.27
Mn075	0.83	0.0213	$3.47 \cdot 10^{-6}$	1.72	5.9	3.06	3.28
Mn050	0.82	0.0179	$3.53 \cdot 10^{-6}$	4.69	9.4	3.04	3.01
Mn025	0.83	0.0117	$1.01 \cdot 10^{-5}$	6.48	14.7	2.87	3.07
Li	-	-	-	-	-	-	-
Cu100	0.83	0.0102	$8.24 \cdot 10^{-6}$	0.70	3.9	2.26	2.91
Cu075	0.82	0.0059	$1.62 \cdot 10^{-5}$	0.52	3.8	2.13	2.79
Cu050	0.82	0.0082	$3.74 \cdot 10^{-5}$	0.73	3.6	2.01	2.64
Cu025	0.80	0.0051	$4.17 \cdot 10^{-5}$	0.63	3.5	2.01	2.61
AlgGel	-	-	-	-	-	-	-

**Figure P2_S3.** a) Nyquist plots of Cu100AlgGel, Mn100AlgGel, LiAlgGel and AlgGel. Nyquist plots of b) Cu100AlgGel, Cu075AlgGel, Cu050AlgGel, Cu025AlgGel and LiAlgGel and c) Mn100AlgGel, Mn075AlgGel, Mn050AlgGel, Mn025AlgGel and LiAlgGel.**Table P2_S6.** Bulk resistance (R_b) and charge transfer resistance (R_{ct}) values for Mn100AlgGel, Mn075AlgGel, Mn050AlgGel, Mn025AlgGel, LiAlgGel, Cu100AlgGel, Cu075AlgGel, Cu050AlgGel, Cu025AlgGel and AlgGel.

<i>Sample</i>	<i>R_b</i> (Ω)	<i>R_{ct}</i> (Ω)	σ (S/m)
Mn100AlgGel	73.3	296.4	1.64
Mn075AlgGel	46.0	289.7	2.72
Mn050AlgGel	40.2	282.3	3.02
Mn025AlgGel	36.8	243.1	3.39
LiAlgGel	32.7	238.1	3.79
Cu100AlgGel	119.0	239.9	1.03
Cu075AlgGel	94.1	299.8	1.27
Cu050AlgGel	82.8	242.4	1.46

Cu025AlgGel	52.5	186.7	2.35
AlgGel	836.4	1138.5	0.14

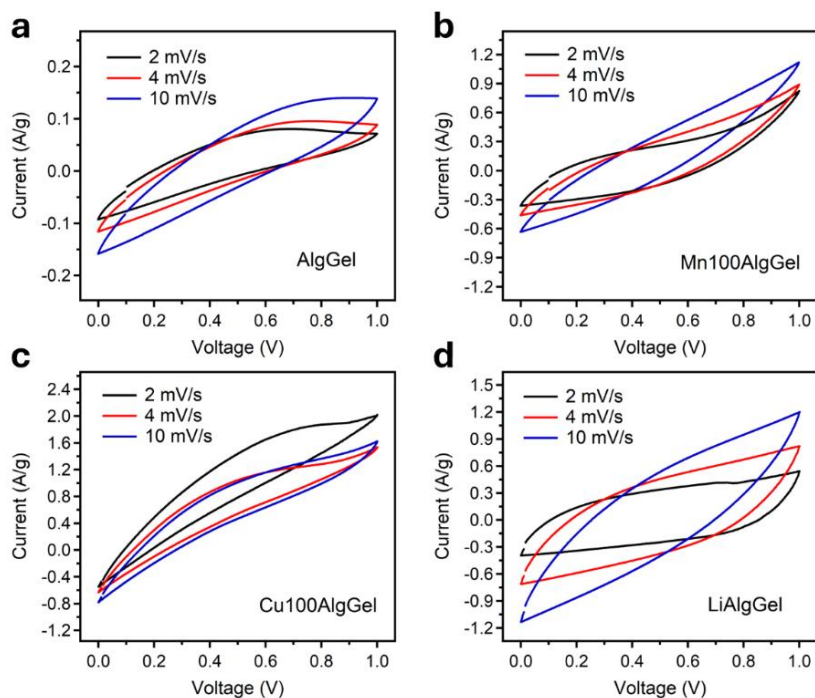


Figure P2_S4. CV curves of a) AlgGel, b) Mn100AlgGel, c) Cu100AlgGel, and d) LiAlgGel in supercapacitors at different scan rates (*i.e.*, 2 mV/s, 4 mV/s and 10 mV/s).

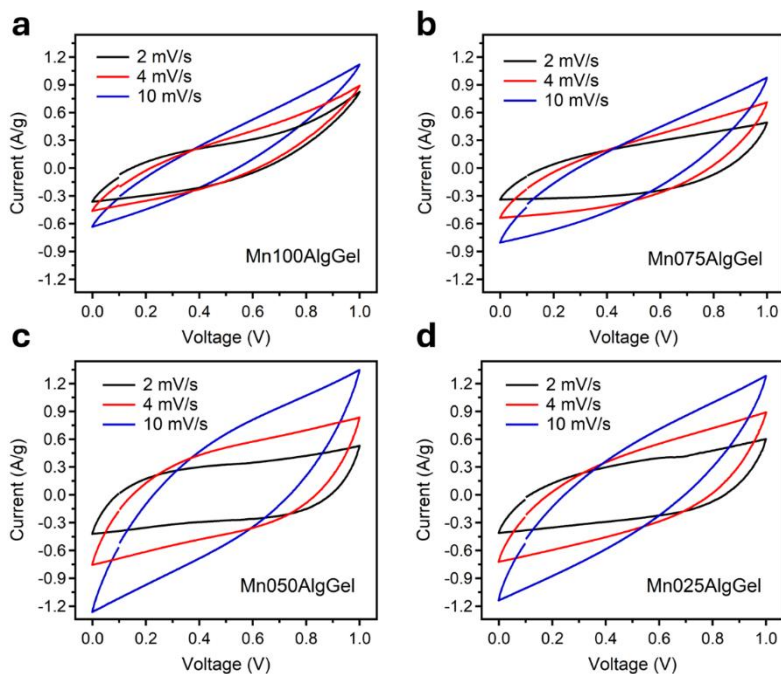


Figure P2_S5. CV curves of a) Mn100AlgGel, b) Mn075AlgGel, c) Mn050AlgGel, and d) Mn025AlgGel in supercapacitors at different scan rates (*i.e.*, 2 mV/s, 4 mV/s and 10 mV/s).

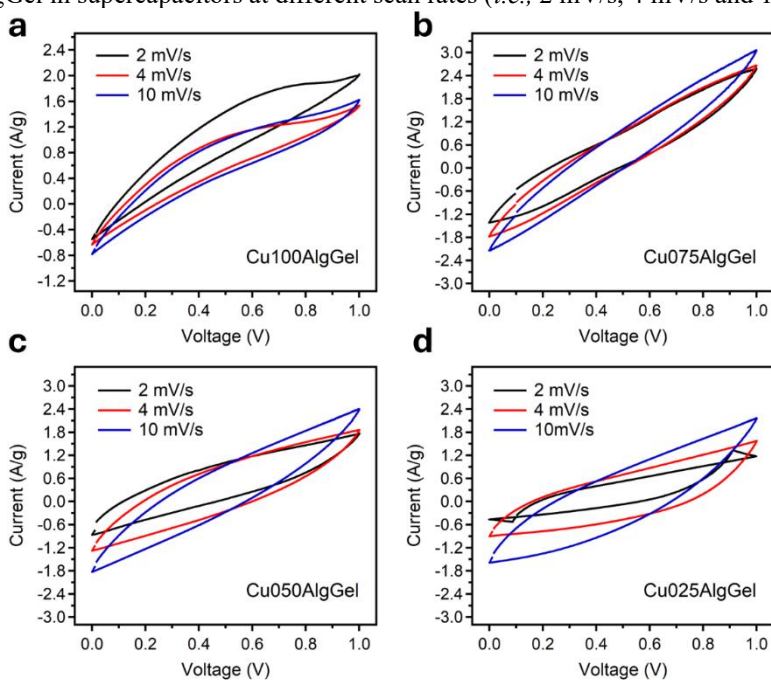


Figure P2_S6. CV curves of a) Cu100AlgGel, b) Cu075AlgGel, c) Cu050AlgGel, and d) Cu025AlgGel in supercapacitors at different scan rates (*i.e.*, 2 mV/s, 4 mV/s, 10 mV/s).

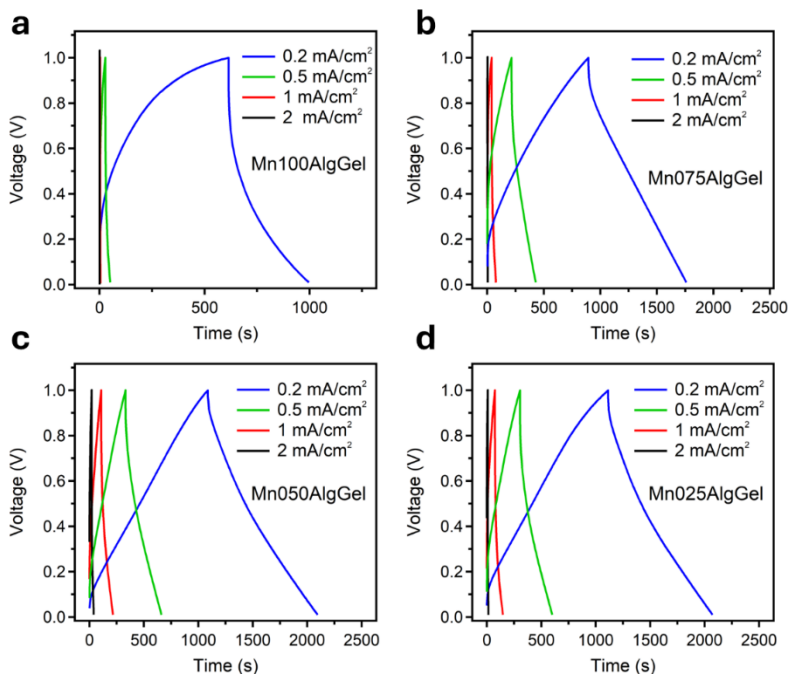


Figure P2_S7. GCD curves of a) Mn100AlgGel, b) Mn075AlgGel, c) Mn050AlgGel, and d) Mn025AlgGel at different current densities (*i.e.*, 0.2 mA/cm², 0.5 mA/cm², 1.0 mA/cm², 2.0 mA/cm²).

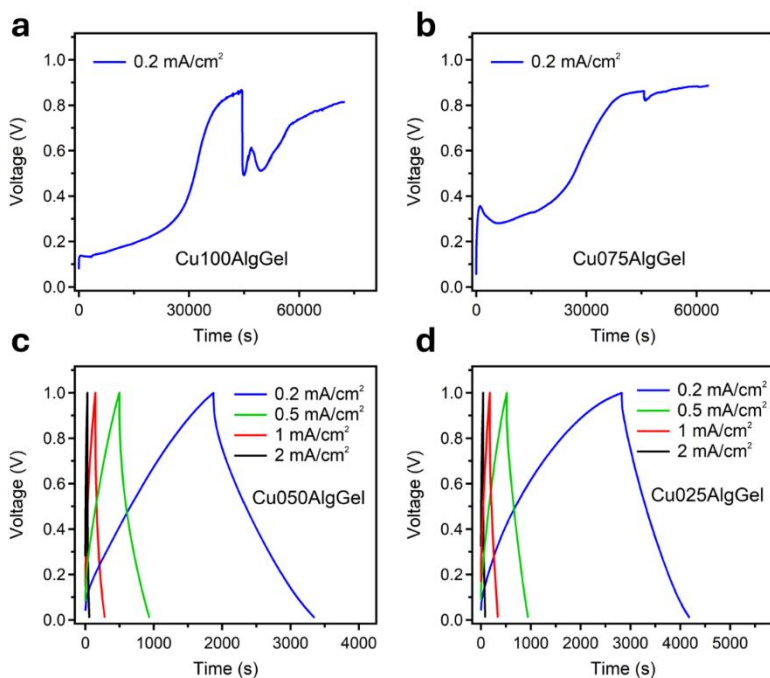


Figure P2_S8. GCD curves of a) Cu100AlgGel, b) Cu075AlgGel, c) Cu050AlgGel, and d) Cu025AlgGel at different current densities (*i.e.*, 0.2 mA/cm², 0.5 mA/cm², 1.0 mA/cm², 2.0 mA/cm²).

Cu025AlgGel at different current densities (*i.e.*, 0.2 mA/cm², 0.5 mA/cm², 1.0 mA/cm², 2.0 mA/cm²).

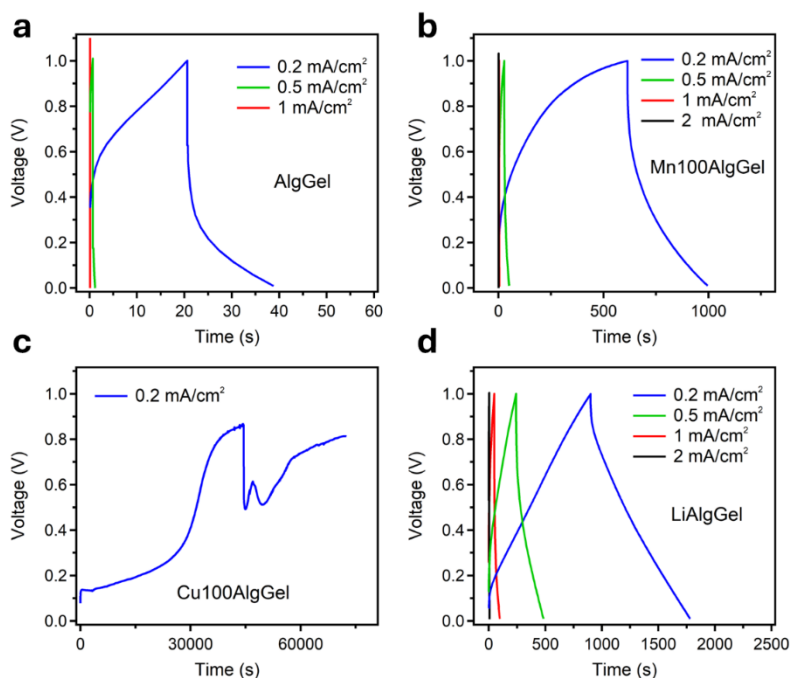


Figure P2_S9. GCD curves of a) AlgGel, b) Mn100AlgGel, c) Cu100AlgGel, and d) LiAlgGel at different current densities (*i.e.*, 0.2 mA/cm², 0.5 mA/cm², 1.0 mA/cm², 2.0 mA/cm²).

Table P2_S7. Areal and specific capacitances of Mn050AlgGel, Cu050AlgGel and LiAlgGel at different current densities.

	<i>Mn050AlgGel</i>	<i>Cu050AlgGel</i>	<i>LiAlgGel</i>
Areal capacitance (mF/cm²) at:			
0.2 mA/cm ²	394.2 ± 18.4	591.8 ± 1.8	339.3 ± 8.4
0.5 mA/cm ²	329.8 ± 0.4	441.5 ± 1.3	240.7 ± 0.3
1.0 mA/cm ²	215.0 ± 0.7	274.8 ± 3.0	96.8 ± 1.5
2.0 mA/cm ²	78.2 ± 1.6	107.6 ± 3.8	12.8 ± 0.5
Specific capacitance (F/g) at:			
0.10 A/g	39.4 ± 1.8	59.2 ± 0.2	33.9 ± 0.9
0.25 A/g	33.0 ± 0.1	44.2 ± 0.2	24.1 ± 0.1
0.50 A/g	21.5 ± 0.1	27.5 ± 0.3	9.7 ± 0.2
1.00 A/g	7.9 ± 0.2	10.8 ± 0.4	1.3 ± 0.1

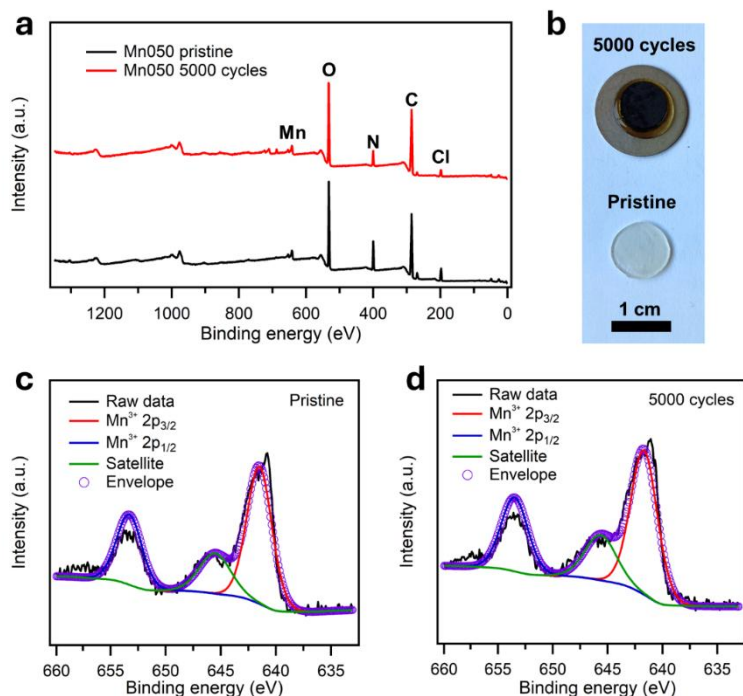


Figure P2_S10. a) XPS survey spectra of Mn050AlgGel in the pristine state and after 5000 charge/discharge cycles show no significant change in elemental composition. b) Photographs of the gels before and after cycling indicate that the macroscopic structure and appearance remain intact, with minor darkening due to electrode contact. High-resolution Mn 2p spectra of the pristine (c) and cycled (d) Mn050AlgGel samples reveal signals characteristic of Mn³⁺, suggesting partial surface oxidation of Mn³⁺ during sample preparation or measurement. The near-identical profiles before and after cycling confirm that the Mn oxidation state remains stable and no additional redox changes occur during operation. These findings, supported by quantitative XPS data presented in Table S8, confirm the chemical and structural stability of the Mn²⁺-crosslinked network during electrochemical operation.

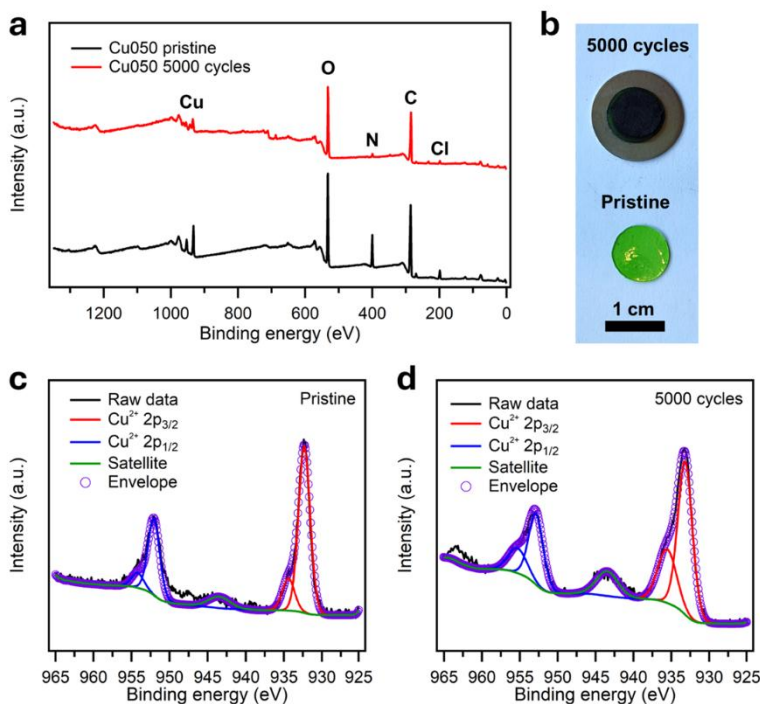


Figure P2_S11. a) XPS survey spectra of Cu050AlgGel in the pristine state and after 5000 charge/discharge cycles reveal no significant changes in elemental composition. b) Photographs of the gels before and after cycling show preserved macroscopic appearance, with minor darkening due to electrode contact. High-resolution Cu 2p spectra of pristine (c) and cycled (d) gels confirm the retention of Cu oxidation state, as evidenced by the consistent shape and intensity of Cu 2p_{3/2}, Cu 2p_{1/2}, and satellite features. The oxidation state and coordination environment remain unaltered after cycling. These findings, supported by quantitative XPS data presented in Table S8, confirm the chemical and structural stability of the Cu²⁺-crosslinked network during electrochemical operation.

Table P2_S8. Elemental composition of Mn050AlgGel and Cu050AlgGel before and after 5000 charge–discharge cycles. Results (with the related reference peak) are presented in atomic percentage.

Peak	Mn050 Pristine	Mn050 5000 cycles	Cu050 Pristine	Cu050 5000 cycles
Cl1s	(56.4 ± 0.1) %	(62.2 ± 0.2) %	(57.3 ± 0.2) %	(61.5 ± 0.2) %
O1s	(26.5 ± 0.2) %	(28.1 ± 0.2) %	(27.6 ± 0.1) %	(31.5 ± 0.1) %
N1s	(12.2 ± 0.2) %	(6.3 ± 0.1) %	(10.5 ± 0.2) %	(2.7 ± 0.1) %
Cl2p	(3.5 ± 0.3) %	(1.9 ± 0.2) %	(2.4 ± 0.2) %	(1.2 ± 0.1) %
Mn2p	(1.4 ± 0.1) %	(1.5 ± 0.1) %	-	-
Cu2p	-	-	(2.2 ± 0.1) %	(3.0 ± 0.1) %

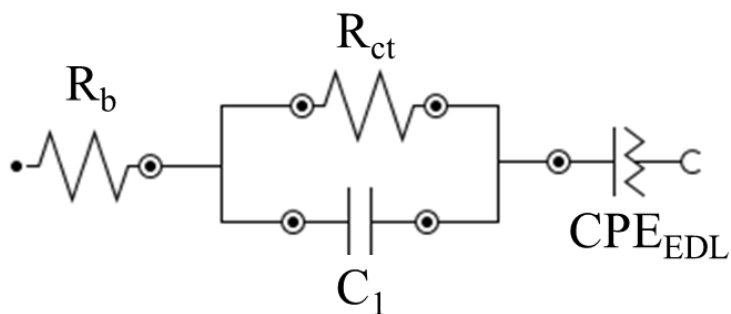


Figure P2_S12. The equivalent electric circuit models used for fitting the Nyquist plots. R_b : bulk resistance; R_{ct} : charge transfer resistance; C_1 : capacitance element; CPE_{EDL} : constant phase element representing the electrical double layer capacitance (EDLC).

Table P2_S9. Summary of the state-of-the-art electrochemical performance of organohydrogel electrolytes for energy storage applications.

<i>Ref</i>	<i>Electrodes</i>	<i>Electrolyte</i>	<i>Capacitance</i>	<i>Energy density</i>	<i>Power density</i>	<i>Capacitance retention (%)</i>
This work	AC//AC	Mn050AlgGel	394.2 mF/cm ² at 0.2 mA/cm ² 39.4 F/g at 0.1 A/g	54.8 μ Wh/cm ² 5.5 Wh/kg	1994.9 μ W/cm ² 192.7 W/kg	88.3 (5000 cycles)
This work	AC//AC	Cu050AlgGel	591.8 mF/cm ² at 0.2 mA/cm ² 59.2 F/g at 0.1 A/g	82.2 μ Wh/cm ² 8.2 Wh/kg	1957.8 μ W/cm ² 196.5 W/kg	85.9 (5000 cycles)
1	Gr//Gr	SA/PAAm/ DMSO/KCl	10.61 mF/cm ² at 2 mV/s	$\sim$ 0.36 μ Wh/cm ²	$\sim$ 6 μ W/cm ²	98.66 (10000 cycles)
2	AC//AC	Starch/PVA/ DMSO/CaCl ₂	156.50 mF/cm ² at 1 mA/cm ²	21.74 μ Wh/cm ²	526.29 μ W/cm ²	82.2 (8000 cycles)
3	AC//AC	Starch/PVA/ Gly/CaCl ₂	107.2 mF/cm ² at 1 mA/cm ²	14.9 mWh/cm ²	0.25 mW/cm ²	84.5 (3000 cycles)
4	AC//AC	PVA/SA/ PEG/NaCl	103.6 mF/cm ² at 2 mA/cm ²	14.39 μ Wh/cm ²	1 mW/cm ²	84.3 (6000 cycles)
5	AC-CNT// AC-CNT	PVA/P(AM-AMPS)/ Gly/Laponite/N a ₂ SO ₄	186.1 mF/cm ² at 1 mA/cm ²	Not provided	Not provided	Not provided
6	Gly-Mo-PVA-PPy// Gly-Mo-PVA-PPy	PVA/(Gly-Mo)/ PPy/ H ₂ SO ₄	140.75 mF/cm ² at 1 mA/cm ²	Not provided	Not provided	Not provided
7	CC-PANI// CC-PANI	Amylopectin (AP)/Acrylic acid (AA)/acrylamide (AM)/PEG/Gly/ KCl	14.30 mF/cm ² at 0.2 mA/cm ²	Not provided	Not provided	Not provided

8	PANI// PANI	PVA/Alg/CaCl ₂ / Gly/(EG/sorbito l)	140.75 mF/cm ² at 1 mA/cm ²	Not provided	Not provided	Not provided
9	Ag@SWCNT // Ag@SWCNT	Regenerated cellulose/ EG/NaCl	66.7 mF/cm ² at 0.67 mA/cm ²	9.3 μWh/cm ²	334.8 mW/cm ²	~ 80 (1000 cycles)
10	CNTs//CNTs	PVA/EG/LiCl	~ 17 mF/cm ² at ~ 0.5 mA/cm ²	Not provided	Not provided	88.3 (5000 cycles)
11	AC//AC	PAMPS/PAAm/ EG/LiCl	43 F/g at 1 A/g	6.11 Wh/kg	999.6 W/kg	100 (10000 cycles)
12	AC//AC	HPC/PVA/ Gly/LiClO ₄	194.7 F/g at 2 A/g	23.3 Wh/kg	177.2 W/kg	90.6 (5000 cycles)
13	CNTs//CNTs	MX-GO/ CNFs/SA/PVA	5.4 F/g at 0.2 A/g	Not provided	Not provided	98.2 (1500 cycles)
14	AC//AC	Gelatin/oxidized starch (OST)/Gly/ZnCl 2	28.1 F/g at 0.5 A/g	4.89 Wh/kg	709 W/kg	90.6 (2000 cycles)
15	AC//AC	PVA/PI/DMSO/ LiCl	~114 mF/cm ² at 1.67 mA/cm ²	16.7 μWh/cm ²	410.0 μW/cm ²	95.3
16	AC//AC	SPI/PVA/EG/ MgCl ₂ /Na ₃ Cit	113.76 mF/cm ² at 1 mA/cm ²	15.80 μWh/cm ²	500 μW/cm ²	81.6 (1000 cycles)

Abbreviations: AC = activated carbon; Gr = graphene; SA = sodium alginate; CC = carbon cloth; poly(2-acrylamido-2-methylpropanesulfonic acid) = PAMPS; polyacrylamide = PAAm; PVA = Polyvinyl alcohol; Gly = glycerol; EG = ethylene glycol; PEG = polyethylene glycol; CNFs = cellulose nanofibrils; HPC = Hydroxypropylcellulose; SPI = soy protein isolate; PPY = polypyrrole; CNT = carbon nanotubes; PANI = polyaniline; CNTs = carbon nanotubes.

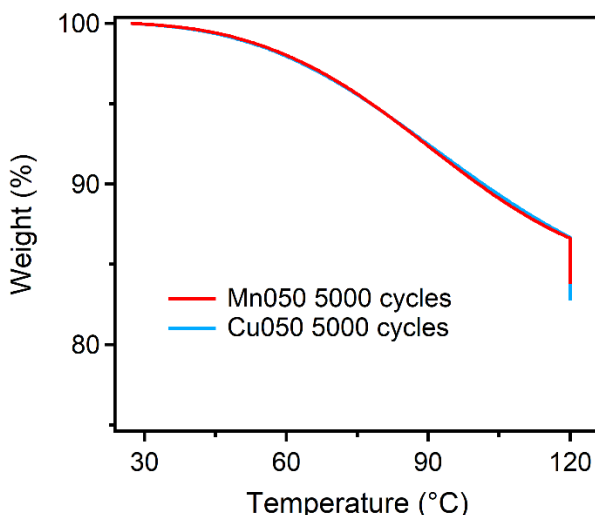


Figure P2_S13. Thermogravimetric analysis (TGA) of Mn050AlgGel and Cu050AlgGel samples after 5000 charge/discharge cycles. The observed weight loss up to 120 °C, attributed to residual water content, shows a difference of less than 1.5% compared to their pristine counterparts. These results confirm the retention of water content after extended cycling. See also **Figure P2_S2** and **Table P2_S10** for comparison with pristine samples.

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4.3_P3_S_Project 3

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Table P3_S1. General properties of GELTGXXX.

Figure P3_S1. Scalability of GELTGXXX organohydrogels fabrication.

Figure P3_S2. Thermogravimetric analysis (TGA) of GELTGXXX organohydrogels.

Figure P3_S3. Humidity-dependent resistance measurements of GELTGXXX organohydrogels.

Figure P3_S4. Small-angle X-ray scattering (SAXS) profiles of GELTGXXX organohydrogels

Figure P3_S5. Swelling behavior of GELTGXXX organohydrogels over time

Table P3_S2. Comparative overview of polymer gel-based strain sensors reported in the literature.

Figure P3_S6. Schematic illustration of the setup used to assess the thermoresponsive conductivity of GELTGXXX

Table P3_S1. Thickness, water and TG formulation content, onset of the first matrix degradation (T_{deg}), glass transition temperature (T_g) and electrical conductivity (σ) of GELTGXXX.

Sample	Thickness (μm)	Water (wt/wt%)	TG (wt/wt%)	T_{deg} ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)	σ (mS/m)*
GELTG000	641 ± 15	13.4	0	181	41.2	0.81 ± 0.25
GELTG025	633 ± 22	14.7	0.7	180	42.5	0.71 ± 0.24
GELTG125	632 ± 29	14.5	3.6	179	40.5	0.50 ± 0.21
GELTG250	637 ± 17	14.2	7.2	180	43.1	0.38 ± 0.18

*At 20 $^{\circ}\text{C}$ and 40 % RH



Figure P3_S1. Scalability of GELTGXXX organohydrogels fabrication. a) Comparison between a standard lab-scale sample (top left, 9.5 cm $\times$ 3.0 cm) and a large-area hydrogel prepared using a custom silicone mold (bottom right, 25 cm $\times$ 15 cm). b, c) Manual handling of the scaled-up hydrogel sheet demonstrates its mechanical integrity, homogeneity, and ease of processing.

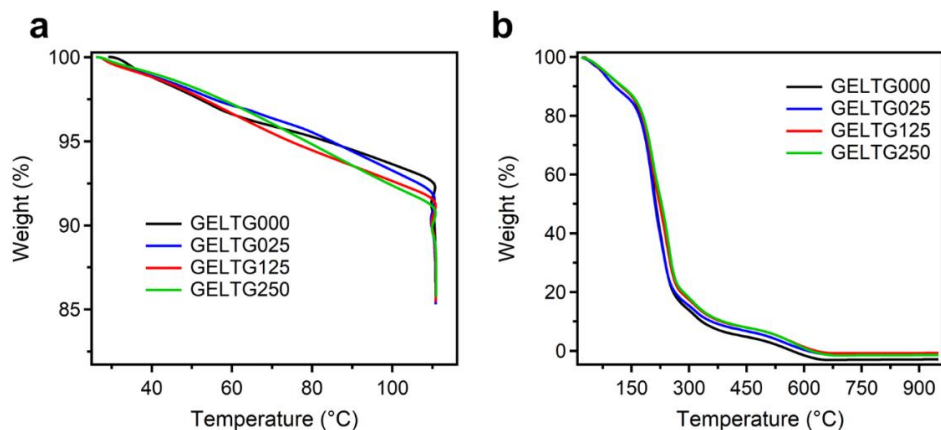


Figure P3_S2. Thermogravimetric analysis (TGA) of GELTGXXX organohydrogels. a) TGA ramp from room temperature to 120 °C followed by a 20-minute isothermal step under nitrogen, used to determine the water content of the gels. All formulations exhibit similar water content (~14 wt%), indicating that differences in material properties are not due to hydration level. b) Thermal degradation profiles acquired from room temperature to 900 °C under air, showing comparable decomposition behavior across all samples, with the onset near 180 °C attributed to glycerol degradation.

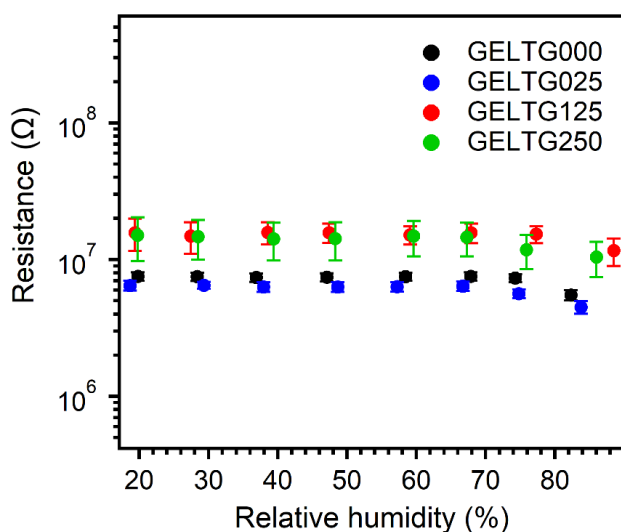


Figure P3_S3. Humidity-dependent resistance measurements of GELTGXXX organohydrogels. Electrical resistance of GELTG000, GELTG025, GELTG125, and GELTG250 as a function of relative humidity (RH). All formulations maintain stable resistance from 20% to 80% RH, with only a minor decrease above 80% RH—likely due to the formation of a superficial water layer without significant impact on the bulk conductive properties.

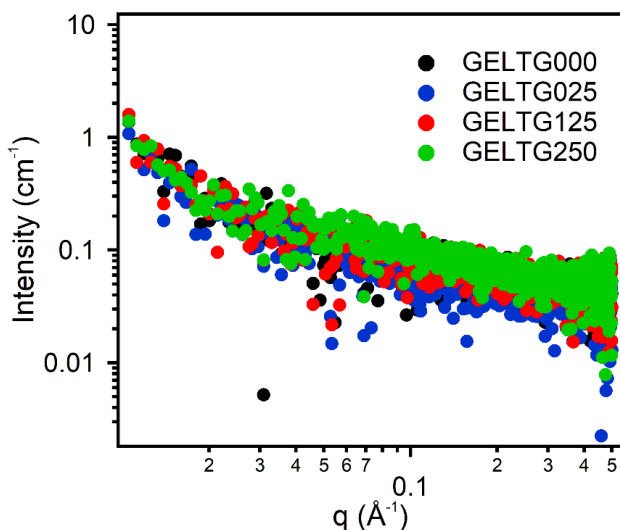


Figure P3_S4. Small-angle X-ray scattering (SAXS) profiles of GELTGXXX organohydrogels. Scattering intensity as a function of the scattering vector q for GELTG000, GELTG025, GELTG125, and GELTG250. The nearly overlapping profiles indicate that the nanoscale structure of the polymer network remains largely unchanged across different TG concentrations, suggesting that enzymatic crosslinking primarily affects mesoscale organization rather than local chain packing.

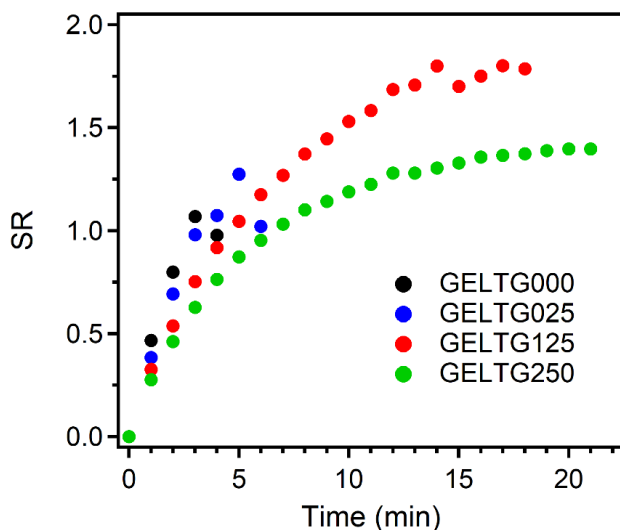


Figure P3_S5. Swelling behavior of GELTGXXX organohydrogels over time. Swelling ratio (SR) as a function of time for GELTG000, GELTG025, GELTG125, and GELTG250 in deionized water. GELTG125 exhibits the highest swelling capacity ($SR_{\max}: 1.76 \pm 0.18$), indicating an optimal balance between crosslink density and network flexibility. In contrast, the uncrosslinked (GELTG000) and lightly crosslinked (GELTG025) samples display limited swelling due to structural fragility ($SR_{\max}: 1.13 \pm 0.09$ and 1.21 ± 0.08 , respectively), while

GELTG250 shows restricted expansion as a result of excessive crosslinking ($SR_{\max}$: 1.39 ± 0.11). Details of the test procedure are provided in the Experimental Section

Table P3_S2. Comparative overview of polymer gel-based strain sensors reported in the literature. Key parameters include the polymeric matrix, type of dopants or fillers, working strain range, gauge factor (GF), responsiveness to temperature (T) and relative humidity (RH), and transparency (Transp.).

Ref	Polym	Doping	Strain	GF	T sensing	RH sensing	Transp.
This work	Gelatin	None	0-300%	2.86	Yes	No	Yes
1	Xhantan gum, PAAm	FeCl ₃	0-100%	2.41	-	-	Yes
2	PVA	PEDOT/PSS, MXene	0-100%	1.29	-	-	No
3	PVA, Chitosan, Cellulose nanofibers	PBFDO, FeCl ₃ , Tannic acid	0-100%	1.46	-	-	No
4	PAAm, Chitosan, Polypyrrole	FeCl ₃ , Phytic acid	0-400%	2.45	-	-	No
5	PVA	PEDOT/PSS, H ₂ SO ₄	0-300%	2.18	-	-	No
6	PVA, Aramid nanofibers	KCl, KOH	0-120%	1.30	-	-	No
7	PAAm, CMC	FeCl ₃	0-30%	1.40	-	-	Partial
8	PVA, CMCS	Tannic acid, NaCl	0-150%	1.55	-	-	No
9	PVA, Starch	Tannic acid, CaCl ₂	0-100%	1.76	-	-	No
10	Acyl gellan gum, gelatin	None	0-300%	2.37	-	-	No
11	PAAm	Phytic acid, Carboxylated cellulose nanofibers (CCNF), Carboxylic carbon nanotubes (C-CNTs)	0-400%	1.5	Yes	Yes	No
12	PVA, Acrylic acid (AAc)	NaCl	0-55%	0.85	Yes	Yes	Partial
13	PVA	Tetraaniline (TANI)	0-80%	2.70	-	Yes	No
14	PVA, Carrageenan	MXenes, CaCl ₂	0-130%	0.77	-	-	No
15	PVA, Acrylic acid (AAc)	AlCl ₃ , Ammonium persulfate (APS)	0-200%	~2	-	-	Partial
16	PAAm, Collagen	AgNPs, LiCl	0-25%	~2.38	-	No	No

17	Hydroxypropylacrilate (HPA)	Ammonium persulfate (APS), AlCl_3	0-75%	1.12	-	-	No
18	PAAm, Gelatin	LiCl	0-50%	1.26	Yes	-	Yes
19	PVA, Cellulose nanofibers (CNF)	AlCl_3	0-100%	0.96	Yes	-	No
20	PAAm, Silk fibroin, PAAc, poly(ethylene glycol) diacrylate (PEGDA)	MgCl_2	0-100%	1.29	-	-	No
21	Agar, Gellan gum, k-Carrageenan	NaCl	0-50%	0.57	Yes	-	Yes
22	PVA, Cellulose nanofibrils	MXene nanosheets	0-160%	0.77	-	-	No
23	PVA	$\text{Zn}(\text{NO}_3)_2$	0-300%	1.25	-	-	Yes
24	PAAm, PEGDA, Hydroxyethylcellulose	NaCl	0-100%	2.28	-	-	No

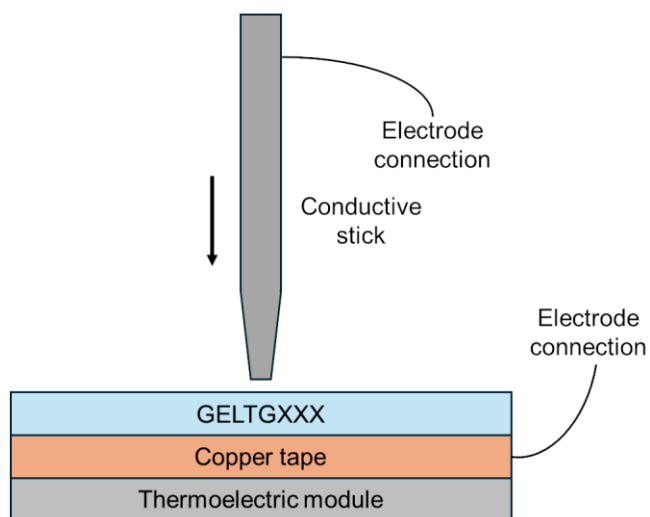


Figure P3_S6. Schematic illustration of the probe penetration test setup used to assess the thermoresponsive conductivity of GELTGXXX. As the hydrogel softens upon heating, the conductive stick progressively penetrates the material until it gets in contact with the underlying copper tape, completing the circuit and enabling electrical readout.

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4.4_P4_S_Project 4

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1. MCas general properties

Table P4_S1. Shrinking ratio during the crosslinking and M^{X+} content (determined through ICP-AES) for the MCas hydrogels.

<i>Sample</i>	<i>Shrinking ratio</i>	<i>M^{X+} content (mmol/g of</i>
NaCas	0.98	0.79
CaCas	1.05	0.86
SrCas	0.98	0.95
BaCas	1.01	0.52
MnCas	0.93	1.48
ZnCas	0.66	0.80
FeCas	0.97	0.49
AlCas	0.56	0.38
ZrCas	1.03	0.65

2. FTIR analysis

Table P4_S2. Peak assignment of the spectra reported in **Figure P4_1b**. The error associated with the values is $\pm 2 \text{ cm}^{-1}$

Sample	δ (NH-CO) O.O.P.	δ (NH-CO) I.P.	$\nu(\text{COO-})$ sym	$\delta(\text{N-H})/\nu(\text{C-N})$ amide I	$\nu(\text{COO-})$ asym	$\nu(\text{C=O})$ amide I	$\nu(\text{NH})$ amide I and II
NaCas	975	1082	1398	1448	1538	1640	3291
CaCas	994	1092	1419	1447	1539	1635	3278
SrCas	988	1101	1419	1446	1540	1635	3281
BaCas	980	1096	1406	1446	1538	1635	3284
MnCas	996	1084	1419	1447	1539	1635	3283
CuCas	998	1081	/	1447	1517	1635	3283
ZnCas	1033	1082	/	1446	1529	1633	3252
FeCas	1014	1082	/	1445	1529	1634	3281
AlCas	1032	1107	/	1453	1530	1633	3275

3. XPS analysis

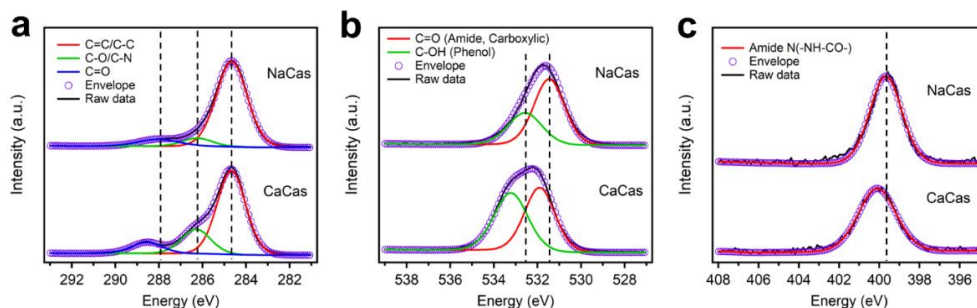


Figure P4_S1. High-resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of NaCas and CaCas gels. The centers of the deconvolution bands are the following. **C 1s NaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.08 eV (C=O). **C 1s CaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.58 eV (C=O). **O 1s NaCas:** 531.48 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **O 1s CaCas:** 531.88 eV (C=O, Amide, Carboxylic); 533.18 eV (C-OH, Phenol). **N 1s NaCas:** 399.68 eV (Amide N(-NH-CO-)). **N 1s CaCas:** 400.08 eV (Amide N(-NH-CO-)).

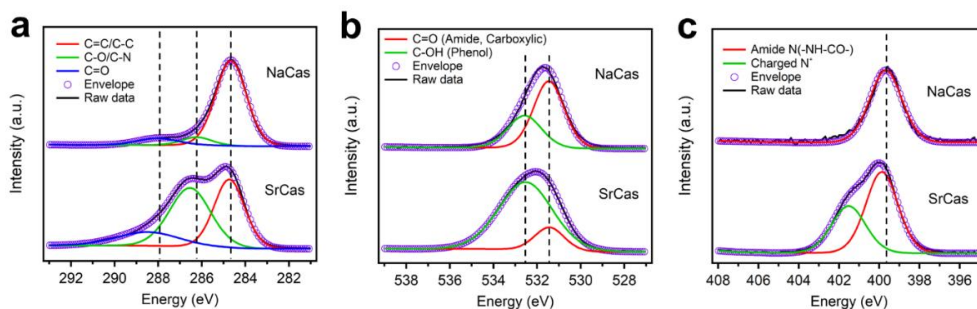


Figure P4_S2. High-resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of NaCas and SrCas gels. The centers of the deconvolution bands are the following. **C 1s NaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.08 eV (C=O). **C 1s SrCas:** 284.68 eV (C=C/C-C); 286.58 eV (C-O/C-N); 288.48 eV (C=O). **O 1s NaCas:** 531.48 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **O 1s SrCas:** 531.38 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **N 1s NaCas:** 399.68 eV (Amide N(-NH-CO-)). **N 1s SrCas:** 400.08 eV (Amide N(-NH-CO-)); 401.48 eV (Charged N⁺).

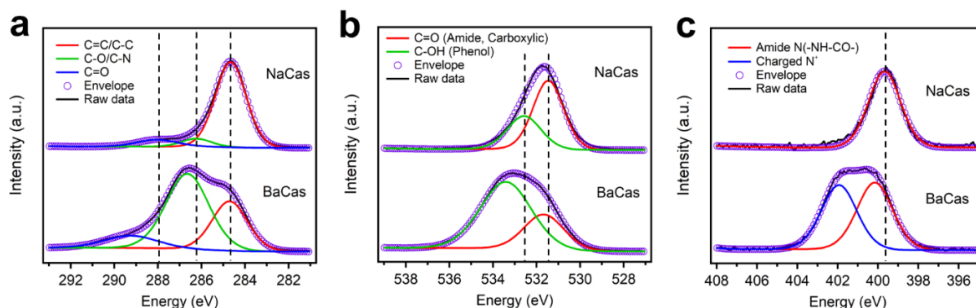


Figure P4_S3. High-resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of NaCas and BaCas gels. The centers of the deconvolution bands are the following. **C 1s NaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.08 eV (C=O). **C 1s BaCas:** 284.68 eV (C=C/C-C); 286.68 eV (C-O/C-N); 289.28 eV (C=O). **O 1s NaCas:** 531.48 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **O 1s BaCas:** 531.68 eV (C=O, Amide, Carboxylic); 533.38 eV (C-OH, Phenol). **N 1s NaCas:** 399.68 eV (Amide N(-NH-CO-)). **N 1s BaCas:** 400.18 eV (Amide N(-NH-CO-)); 401.88 eV (Charged N⁺).

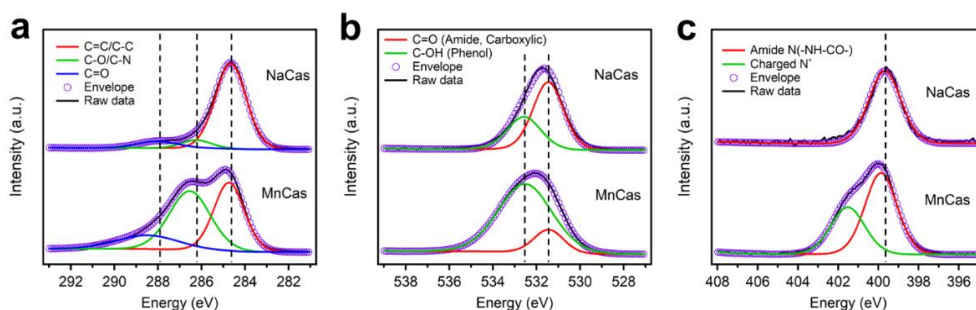


Figure P4_S4. High-resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of NaCas and MnCas gels. The centers of the deconvolution bands are the following. **C 1s NaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.08 eV (C=O). **C 1s MnCas:** 284.68 eV (C=C/C-C); 286.58 eV (C-O/C-N); 288.48 eV (C=O). **O 1s NaCas:** 531.48 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **O 1s MnCas:** 531.38 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **N 1s NaCas:** 399.68 eV (Amide N(-NH-CO-)). **N 1s MnCas:** 399.88 eV (Amide N(-NH-CO-)); 401.48 eV (Charged N⁺).

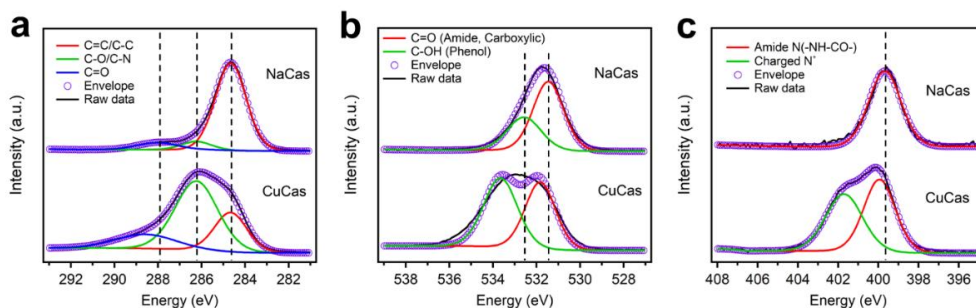


Figure P4_S5. High-resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of NaCas and CuCas gels. The centers of the deconvolution bands are the following. **C 1s NaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.08 eV (C=O). **C 1s CuCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.58 eV (C=O). **O 1s NaCas:** 531.48 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **O 1s CuCas:** 531.78 eV (C=O, Amide, Carboxylic); 533.68 eV (C-OH, Phenol). **N 1s NaCas:** 399.68 eV (Amide N(-NH-CO-)). **N 1s CuCas:** 399.88 eV (Amide N(-NH-CO-)); 401.68 eV (Charged N⁺).

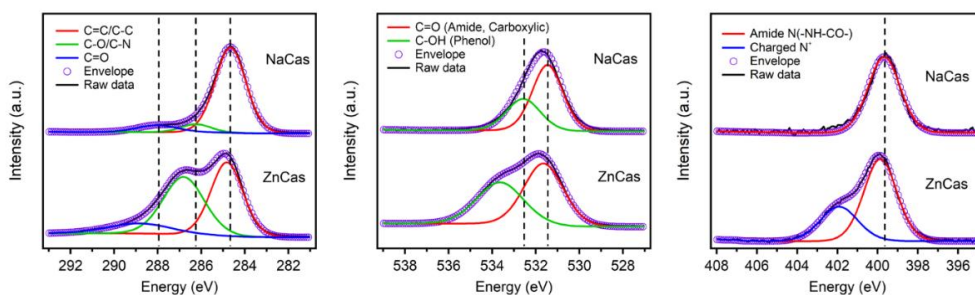


Figure P4_S6. High-resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of NaCas and ZnCas gels. The centers of the deconvolution bands are the following. **C 1s NaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.08 eV (C=O). **C 1s ZnCas:** 284.78 eV (C=C/C-C); 286.78 eV (C-O/C-N); 288.88 eV (C=O). **O 1s NaCas:** 531.48 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **O 1s ZnCas:** 531.58 eV (C=O, Amide, Carboxylic); 533.58 eV (C-OH, Phenol). **N 1s NaCas:** 399.68 eV (Amide N(-NH-CO-)). **N 1s ZnCas:** 399.88 eV (Amide N(-NH-CO-)); 401.88 eV (Charged N⁺).

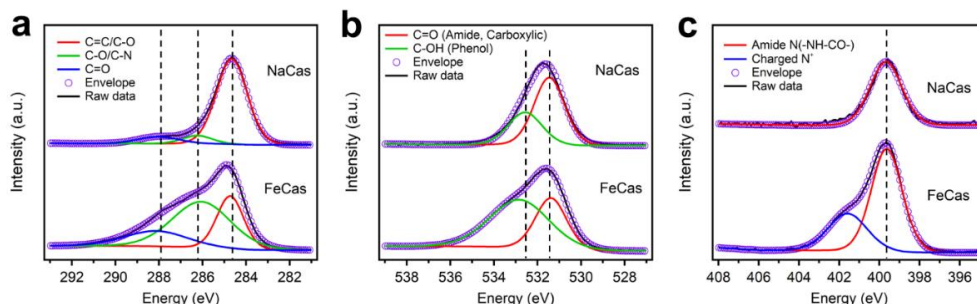


Figure P4_S7. High-resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of NaCas and FeCas gels. The centers of the deconvolution bands are the following. **C 1s NaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.08 eV (C=O). **C 1s FeCas:** 284.68 eV (C=C/C-C); 286.08 eV (C-O/C-N); 288.18 eV (C=O). **O 1s NaCas:** 531.48 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **O 1s FeCas:** 531.38 eV (C=O, Amide, Carboxylic); 532.88 eV (C-OH, Phenol). **N 1s NaCas:** 399.68 eV (Amide N(-NH-CO-)). **N 1s FeCas:** 399.58 eV (Amide N(-NH-CO-)); 401.58 eV (Charged N⁺).

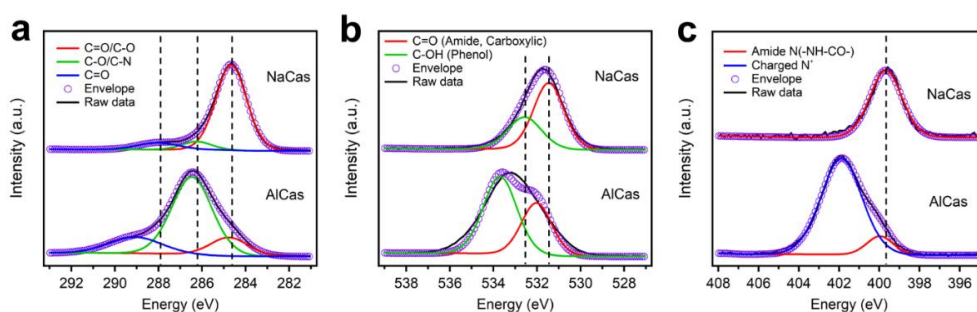


Figure P4_S8. High-resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of NaCas and AlCas gels. The centers of the deconvolution bands are the following. **C 1s NaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.08 eV (C=O). **C 1s AlCas:** 284.68 eV (C=C/C-C); 286.48 eV (C-O/C-N); 289.08 eV (C=O). **O 1s NaCas:** 531.48 eV (C=O, Amide, Carboxylic); 532.58 eV (C-OH, Phenol). **O 1s AlCas:** 531.98 eV (C=O, Amide, Carboxylic); 533.68 eV (C-OH, Phenol). **N 1s NaCas:** 399.68 eV (Amide N(-NH-CO-)). **N 1s AlCas:** 399.98 eV (Amide N(-NH-CO-)); 401.88 eV (Charged N⁺).

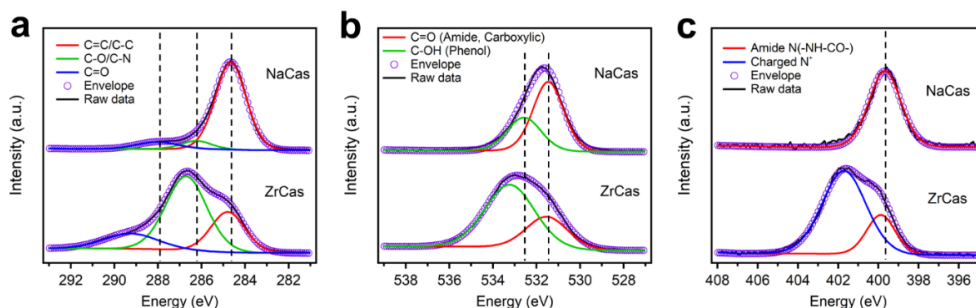


Figure P4_S9. High-resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of NaCas and AlCas gels. The centers of the deconvolution bands are the following. **C 1s NaCas:** 284.68 eV (C=C/C-C); 286.28 eV (C-O/C-N); 288.08 eV (C=O). **C 1s AlCas:** 284.78 eV (C=C/C-C); 286.68 eV (C-O/C-N); 289.18 eV (C=O). **O 1s NaCas:** 531.48 eV (C=O, Amide, Carboxylic); 533.18 eV (C-OH, Phenol). **O 1s AlCas:** 531.48 eV (C=O, Amide, Carboxylic); 533.68 eV (C-OH, Phenol). **N 1s NaCas:** 399.68 eV (Amide N(-NH-CO-)). **N 1s AlCas:** 399.88 eV (Amide N(-NH-CO-)); 401.68 eV (Charged N⁺).

4. DSC analysis

Table P4_S3. Glass transition temperatures (T_g) of the MCas sample, extracted from the thermograms in Figure 2a. The error associated with the given values is ± 1.0 °C

<i>NaCas</i>	<i>CaCas</i>	<i>SrCas</i>	<i>BaCas</i>	<i>MnCas</i>	<i>CuCas</i>	<i>ZnCas</i>	<i>FeCas</i>	<i>AlCas</i>	<i>ZrCas</i>
72.2 °C	73.3 °C	71.7 °C	72.2 °C	75.1 °C	74.6 °C	75.0 °C	74.3 °C	76.6 °C	75.6 °C

5. SAXS analysis

The SAXS curves presented in **Figure P4_2b** were fitted using the following equation within the q -range of $0.02 - 0.5 \text{ \AA}^{-1}$. For the ZrCas sample, the fitting range was extended to $0.01 \text{ \AA}^{-1}$ to enhance the quality of the fit, as the slope undergoes a significant change around $0.02 \text{ \AA}^{-1}$, potentially affecting the accuracy of the fitting. For the NaCas curve, the following equation was employed to fit the peak associated with the presence of micelles within the viscous polymeric solution:

$$I(q) = \frac{A}{\left(1 + \left(\frac{q - q_0}{B}\right)^2\right)} + bkg \quad (\text{Eq. P4_S1})$$

where A is a scale factor, B represents the half-width at half-maximum of the peak, and bkg is the background signal. The peak observed at $q = 0.031 \text{ \AA}^{-1}$ indicates that the micelles are $\sim 20.3 \text{ nm}$ apart. In contrast, the presence of crosslinking significantly

alters the micellar assembly, leading to smoother SAXS curves. These curves were best fitted using the following model [1-6]:

$$I(q) = \frac{A}{q^k} + \frac{B}{1+(q\xi_1)^m} + \frac{C}{1+(q\xi_2)^n} + bkg \quad (\text{Eq. P4_S2})$$

where bkg is the background signal, A is the Porod scale factor, and k is the corresponding Porod exponent. B and C are Lorentzian scale factors, while ξ_1 and ξ_2 denote the respective correlation lengths. The parameters m and n correspond to the associated power-law exponents. The extracted long-distance (ξ_1) and short-distance (ξ_2) correlation lengths are summarized in **Table P4_S4**, along with the other fitting parameters. For consistency, the primary correlation length, ξ_1 (associated with the low- q Lorentzian term and obtainable for every sample) is used for all cross-sample comparisons in the main text, as it reflects the dominant average spacing between crosslinked domains.

Table P4_S4. SAXS fitting parameters (Eq. S2) for the MCas curves illustrated in **Figure P4_2b**.

	<i>CaCas</i>	<i>SrCas</i>	<i>BaCas</i>	<i>MnCas</i>	<i>CuCas</i>	<i>ZnCas</i>	<i>FeCas</i>	<i>AlCas</i>	<i>ZrCas</i>
<i>bkg</i>	0.038	0.031	0.049	0.063	0.034	0.032	0.072	0.060	0.081
<i>A</i>	-	-	-	-	-	$8.1 \cdot 10^{-5}$	-	-	$9.8 \cdot 10^{-6}$
<i>k</i>	-	-	-	-	-	3.24	-	-	3.50
<i>B</i>	20.5	35.7	31.5	20.7	10.17	0.47	8.43	12.4	4.43
<i>C</i>	0.56	0.39	0.56	0.74	0.10	-	-	-	-
ξ_1 (nm)	4.7±0.2	5.4±0.3	6.4±0.3	5.1±0.3	2.9±0.2	1.0±0.1	2.6±0.1	2.6±0.1	2.3±0.1
ξ_2 (nm)	1.0±0.1	0.9±0.1	0.8±0.1	1.0±0.1	0.4±0.1	-	-	-	-
<i>m</i>	3.94	3.89	3.29	3.28	3.38	1.50	3.00	3.28	2.06
<i>n</i>	2.86	2.43	2.51	2.55	4.70	-	-	-	-

6. Scanning electron microscopy (SEM)

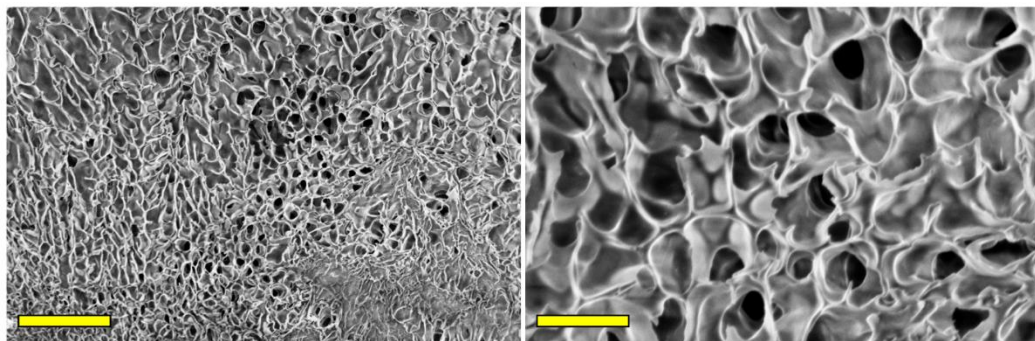


Figure P4_S10. SEM micrographs of NaCas at different magnifications. The scale bars represent 8 μm (left panel) and 2 μm (right panel).

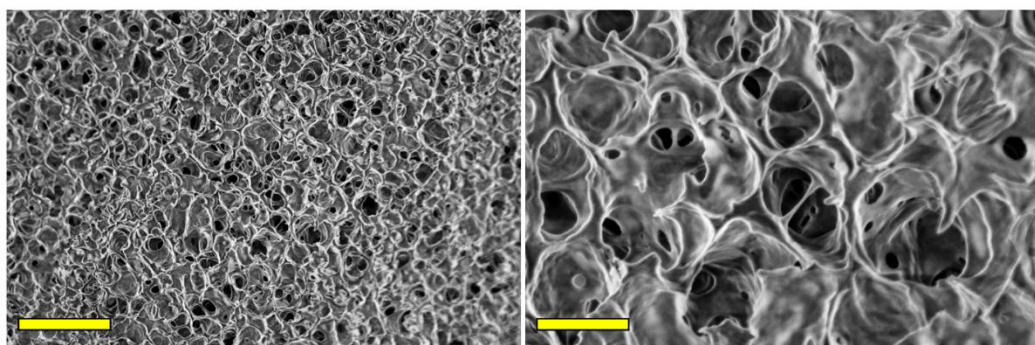


Figure P4_S11. SEM micrographs of CaCas at different magnifications. The scale bars represent 8 μm (left panel) and 2 μm (right panel).

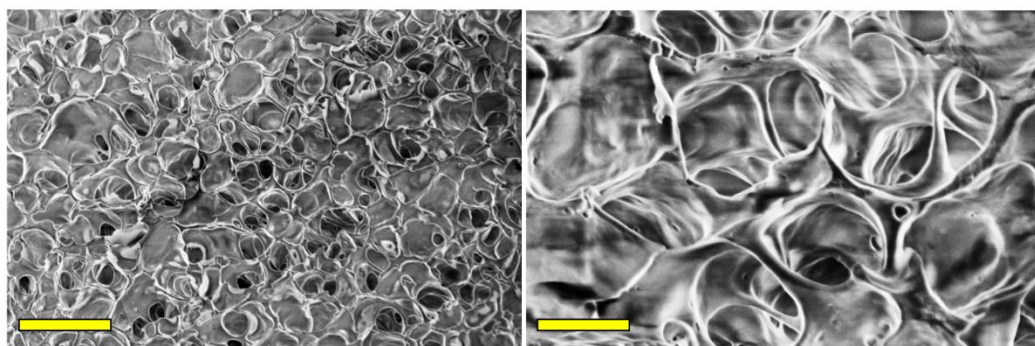


Figure P4_S12. SEM micrographs of SrCas at different magnifications. The scale bars represent 8 μm (left panel) and 2 μm (right panel).

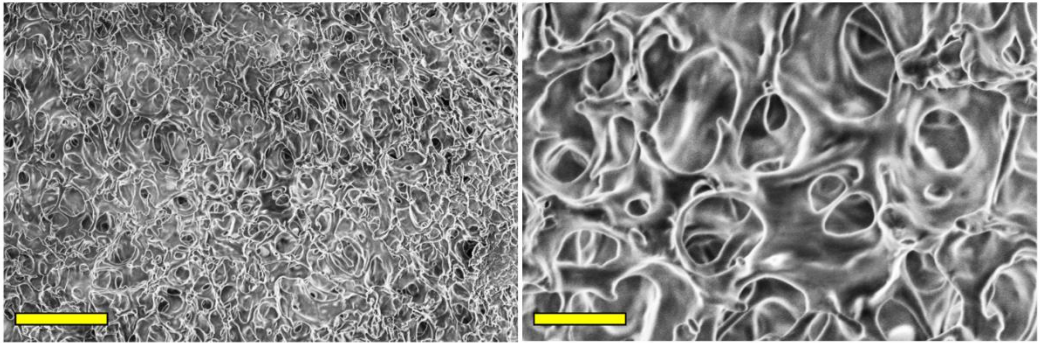


Figure P4_S13. SEM micrographs of BaCas at different magnifications. The scale bars represent 8 μm (left panel) and 2 μm (right panel).

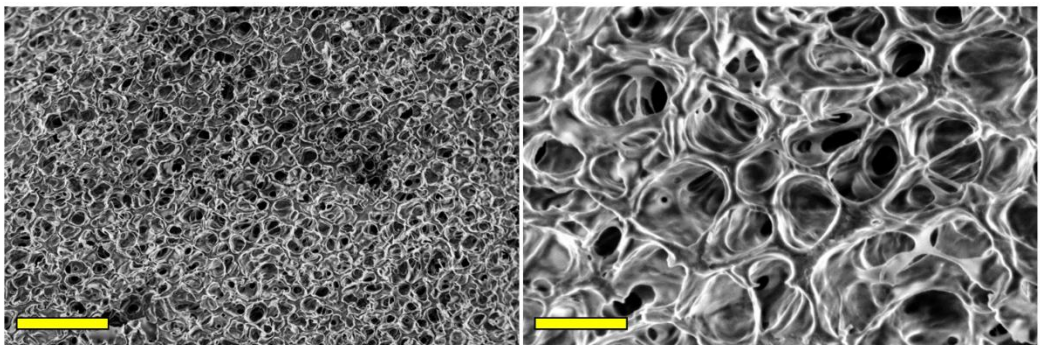


Figure P4_S14. SEM micrographs of MnCas at different magnifications. The scale bars represent 8 μm (left panel) and 2 μm (right panel).

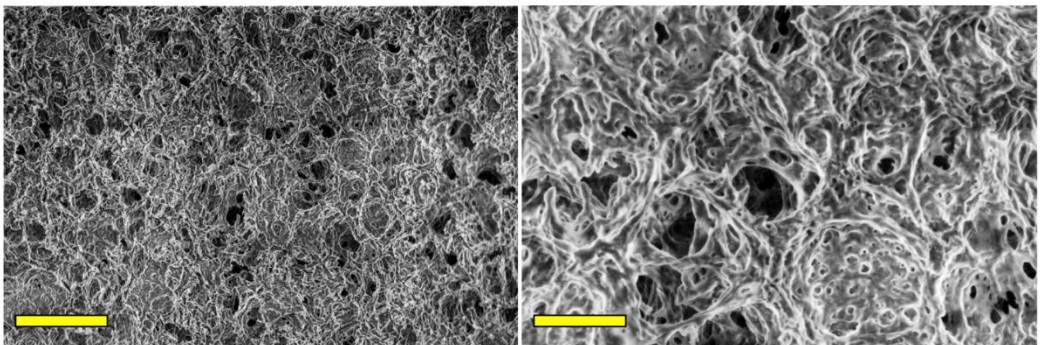


Figure P4_S15. SEM micrographs of CuCas at different magnifications. The scale bars represent 8 μm (left panel) and 2 μm (right panel)

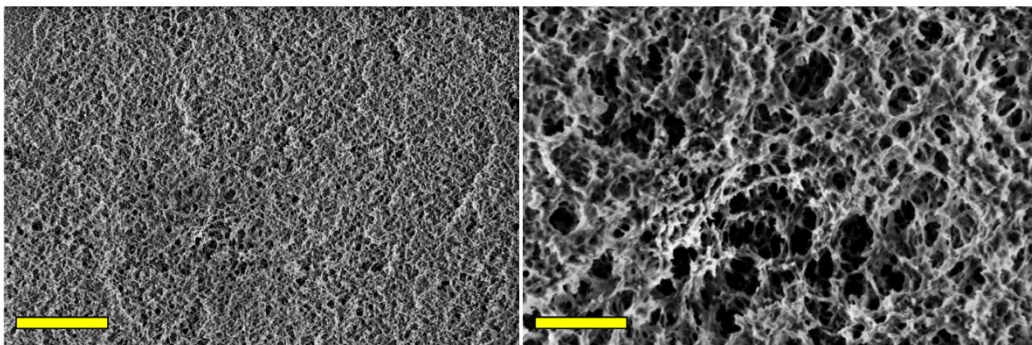


Figure P4_S16. SEM micrographs of ZnCas at different magnifications. The scale bars represent 8 μm (left panel) and 2 μm (right panel).

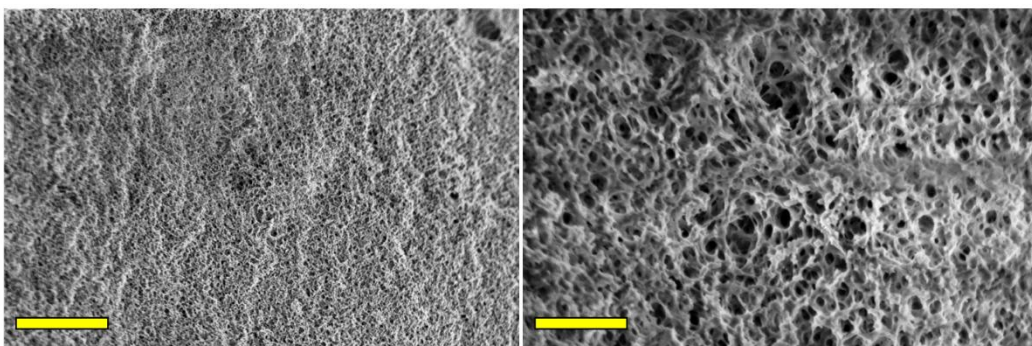


Figure P4_S17. SEM micrographs of FeCas at different magnifications. The scale bars represent 8 μm (left panel) and 2 μm (right panel).

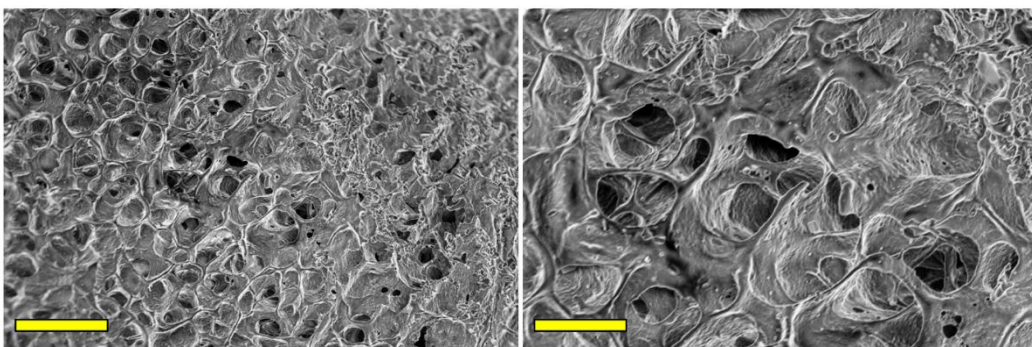


Figure P4_S18. SEM micrographs of AlCas at different magnifications. The scale bars represent 20 μm (left panel) and 8 μm (right panel).

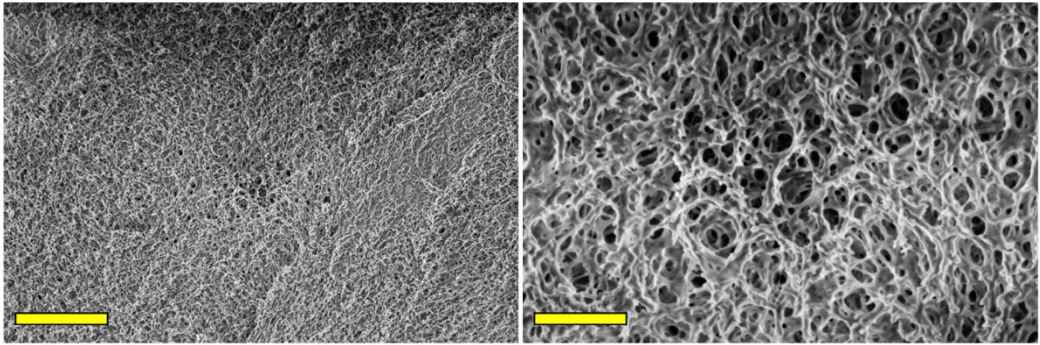


Figure P4_S19. SEM micrographs of ZrCas at different magnifications. The scale bars represent 8 μm (left panel) and 2 μm (right panel)

7. MCas response to compression

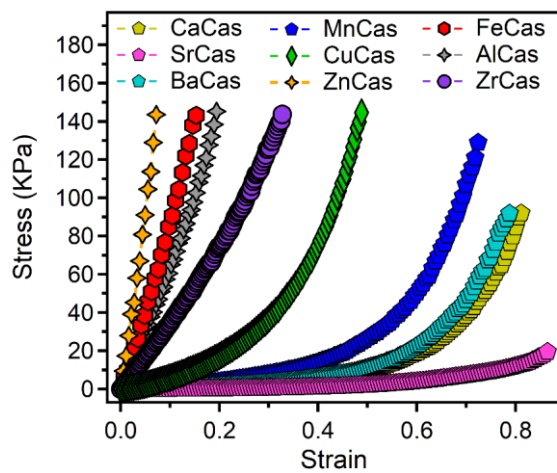


Figure P4_S20. Full-range compressive stress-strain curves of the MCas samples, illustrating their mechanical response under compression.

Table P4_S5. Compressive moduli of the MCas samples, extracted from the stress-strain curves in **Figure P4_S20** over the 0.00–0.07 strain range.

<i>Sample</i>	<i>Compressive modulus (kPa)</i>
CaCas	8.3 ± 0.2
SrCas	1.6 ± 0.3
BaCas	8.2 ± 0.8
MnCas	11.4 ± 0.5
CuCas	75.9 ± 2.9
ZnCas	1792 ± 170
FeCas	844 ± 36
AlCas	557 ± 61
ZrCas	359 ± 34

8. MCas conductivity evaluation

Table P4_S6. Conductivity of the MCas samples.

<i>Sample</i>	<i>Conductivity (mS/m)</i>
CaCas	0.234 ± 0.012
SrCas	0.011 ± 0.001
BaCas	0.013 ± 0.001
MnCas	0.020 ± 0.001
CuCas	13.5 ± 0.7
ZnCas	0.023 ± 0.001
FeCas	5.91 ± 0.31
AlCas	0.095 ± 0.005
ZrCas	0.052 ± 0.003

9. TGA analysis

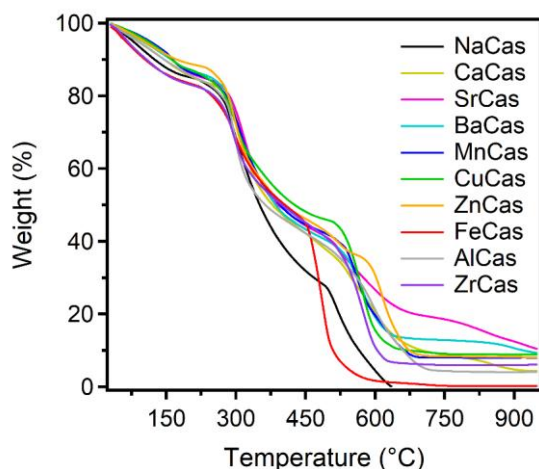


Figure P4_S21. TGA thermograms of the MCas samples

Table P4_S7. TGA mass losses for the samples illustrated in **Figure P4_S21**. Region I (RT - 130 °C), Region II (130 °C - 380 °C), Region III (RT 380 °C - 720 °C), Region IV (720 °C - 950 °C). Data normalized for the water content of the samples are also reported (N. mass loss (%)). Also the onset of the Ist and IInd degradation of the protein matrix are reported. The error on the Weight loss associated with each sample never exceeds 1.0 %.

<i>Sample</i>	<i>Region</i>	<i>Mass loss</i>	<i>N. mass loss</i>	<i>Onset Ist deg.</i>	<i>Onset IInd deg.</i>
NaCas	I	10.6	0		
	II	45.0	50.3	271	
	III	45.1	50.4		500
	IV	~ 0	~ 0		
CaCas	I	8.6	0		
	II	41.6	45.5	285	
	III	40.4	44.2		526
	IV	5.2	5.7		
SrCas	I	6.7	0		
	II	42.1	45.1	286	
	III	32.0	34.3		508
	IV	8.9	9.5		
BaCas	I	7.5	0		
	II	41.7	45.1	276	
	III	37.4	40.4		537

	IV	3.7	4.0		
MnCas	I	6.3	0		
	II	41.5	44.3	275	
	III	44.2	47.2		535
	IV	~ 0	~ 0		
CuCas	I	6.7	0		
	II	38.0	41.0	275	
	III	45.9	49.5		530
	IV	~ 0	~ 0		
ZnCas	I	7.2	0		
	II	39.9	43.0		
	III	44.5	48.0	272	
	IV	0.4	0.4		592
FeCas	I	12.5	0		
	II	34.6	39.5	257	
	III	52.4	59.9		457
	IV	0.3	0.3		
AlCas	I	8.6	0		
	II	43.2	47.3	280	
	III	43.5	47.6		547
	IV	0.6	0.7		
ZrCas	I	12.4	0		
	II	35.5	40.5	269	
	III	46.0	52.5		535
	IV	~ 0	~ 0		

10. Energy storage performance

Table P4_S8. Bulk resistance (R_b) and charge transfer resistance (R_{ct}) values for CuCas and ZnCas.

Sample	R_b (Ω)	R_{ct} (Ω)
CuCas	14.9	31.5
ZnCas	4.7	92.5

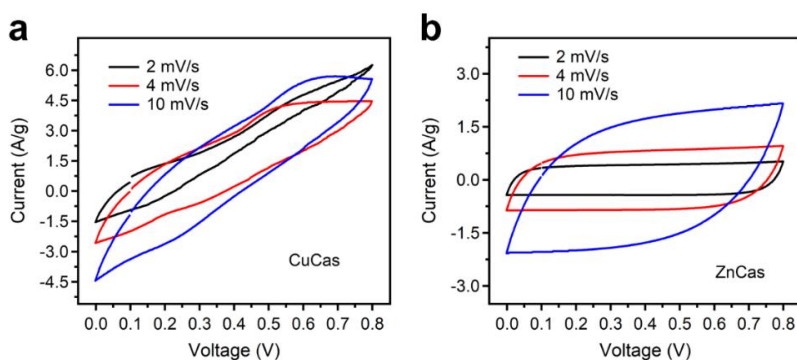


Figure P4_S22. CV curves of a) CuCas and b) ZnCas in symmetric supercapacitors at different scan rates (*i.e.*, 2 mV/s, 4 mV/s, 10 mV/s).

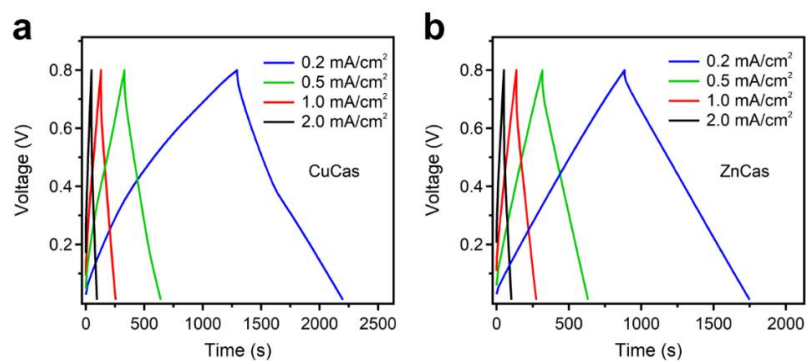


Figure P4_S23. GCD curves of a) CuCas and b) ZnCas at different current densities (*i.e.*, 0.2 mA/cm², 0.5 mA/cm², 1.0 mA/cm², 2.0 mA/cm²).

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Figure P5_S17. Magnified time-resolved photoresponse of the Janus MoS₂.

Table P5 S1. Comparison table of 2D TMD-based artificial synapses.

Material	Synapse type	Mechanism	Program	Erase	Wavelength (nm)	No. of states	Reten. time	Ref
SA/MoS ₂ /P (VDF-TrFE)	LTP, STP	Photo-induced ionic gating	Optical	Voltage off (natural)	455-940	60	>120 s	This work
Ferrocene /MoS ₂ /Azo	LTP, STP	Electro-chemical	Electrical, optical	Electrical	365	16	>800 s	[1]
CdSe/ZnS/MoS ₂	LTP	Charge trapping	Optical	Electrical	532	50	70 s	[2]
MoS ₂	LTP, STP	Charge trapping, ionic gating	Electrical, optical	Electrical, optical	445	6	> 2000 s	[3]
MoS ₂ /h-BN	LTP, STP	Charge trapping	Optical	Electrical	520	4	>350 s	[4]
MoS ₂ /h-BN	LTP	Charge trapping	Electrical, optical	Electrical, optical	365	100	>21 days	[5]
MoS ₂ /P(VDF-TrFE)	LTP	Ferroelectric gating	Electrical	Electrical	-	128	1800 s	[6]
Graphdiyne /MoS ₂	LTP	Ion-gating	Electrical	Electrical	-	200	>10000 s	[7]

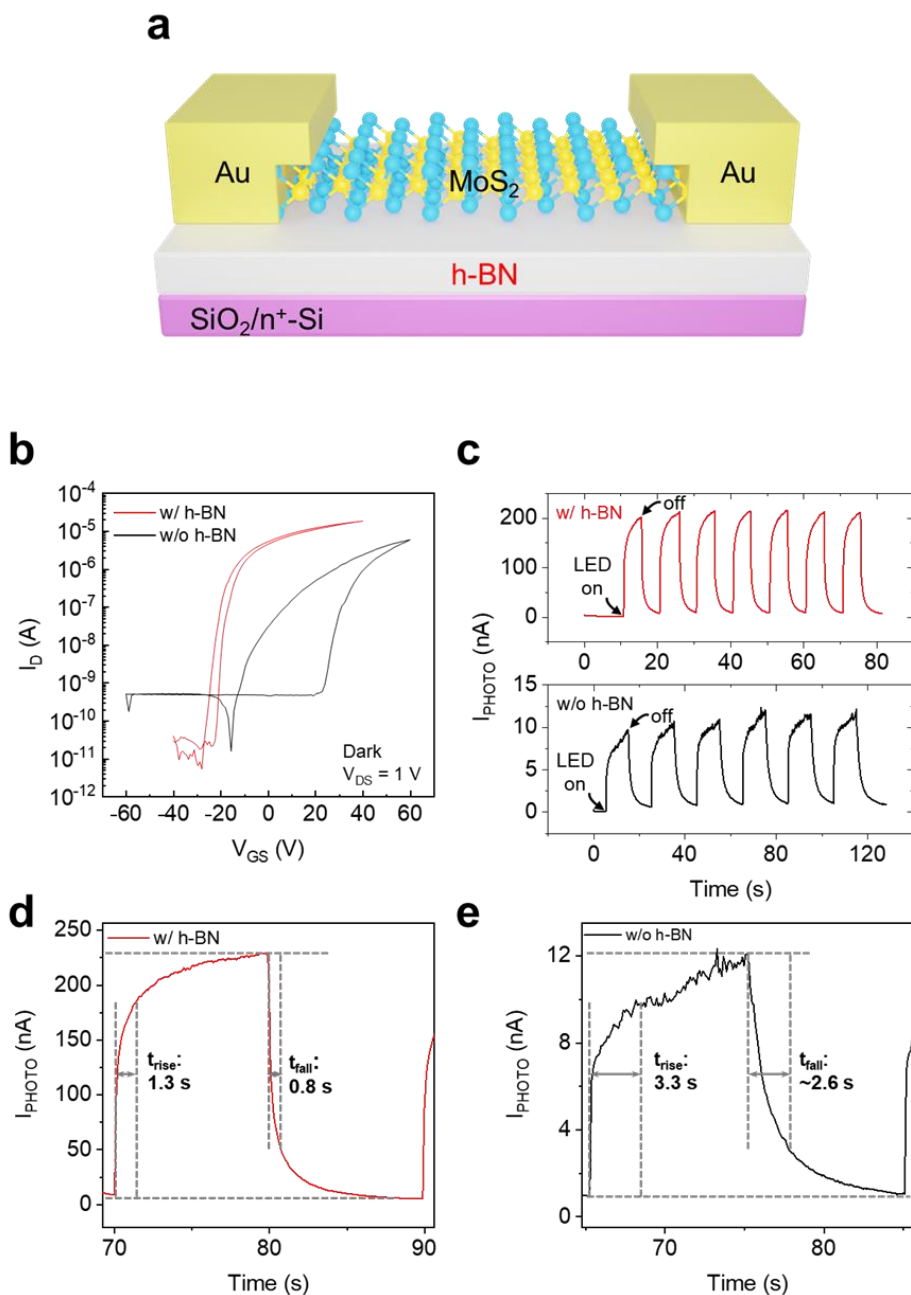


Figure P5_S1. Optoelectrical characteristics of MoS₂ FETs with and without h-BN layer. (a) 3D schematic device view of a MoS₂ channel FET with h-BN layer. (b) Transfer curves of a h-BN supported MoS₂ FET (red) and a control device without h-BN (black) under dark conditions. (c-e) Time-resolved photoresponse of MoS₂ FET with h-BN and the control device under 680 nm LED (0.03 mW cm⁻²) illumination

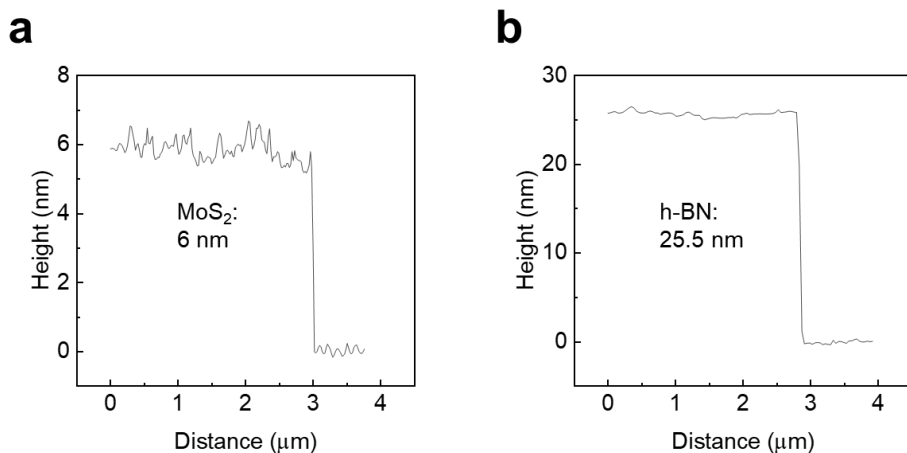


Figure P5_S2. AFM height profiles of (a) MoS₂ and (b) h-BN flakes.

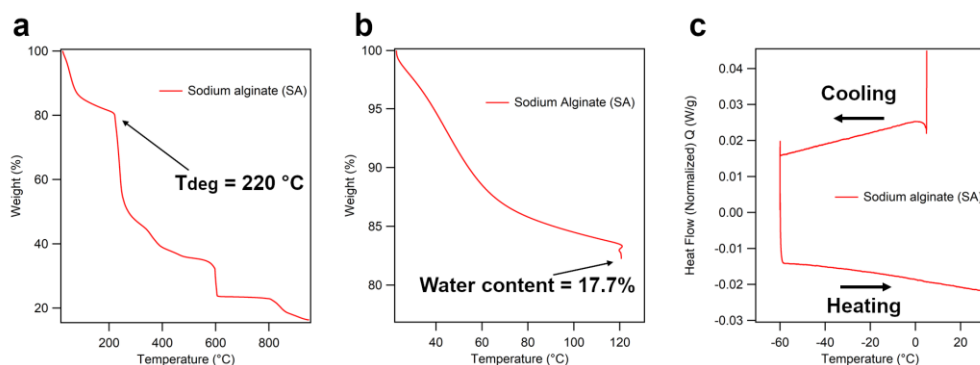


Figure P5_S3. (a) TGA degradation profile of sodium alginate (SA) under air flux, highlighting the onset of the first degradation of the polymer chains (T_{deg}) at 220 °C. (b) SA water content determination (at RH = 40%) by TGA. (c) DSC cooling and heating thermograms for freezable water investigation in SA. The absence of peaks highlights the non-freezable state of the 17.7% of water contained, attributable to its strong interaction with SA's ions and functional groups.

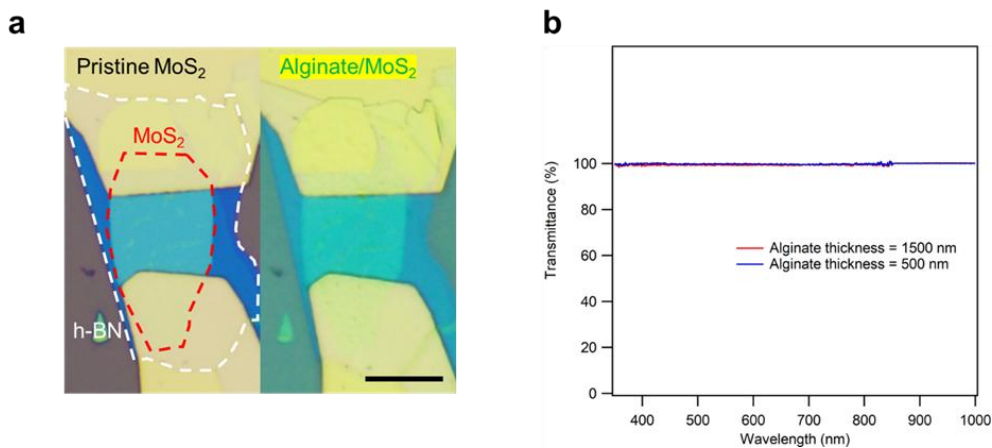


Figure P5_S4. (a) Optical microscopy image of a SA/MoS₂ synaptic device. Scale bar = 10 μ m. (b) UV-Vis spectra of the SA deposited on quartz substrates.

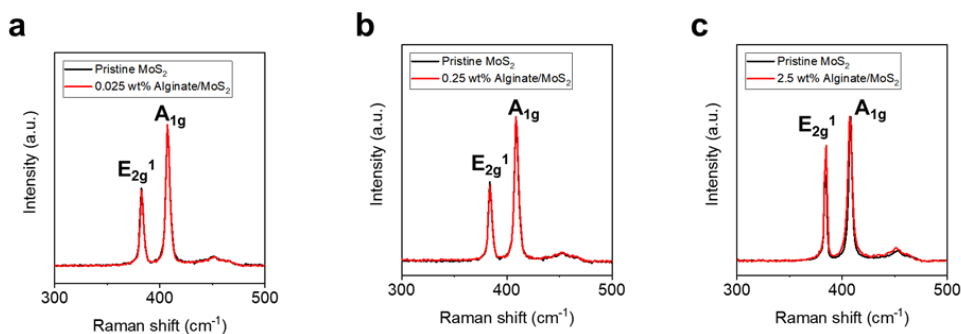


Figure P5_S5. Raman spectra of pristine MoS₂ and SA/MoS₂ with different concentrations of SA solution: (a) 0.025 wt%, (b) 0.25 wt%, and (c) 2.5 wt%. When the 2.5 wt% SA was deposited on MoS₂, the E_{2g}¹/A_{1g} ratio increased from 0.6 (pristine) to 0.8. Such change in the Raman ratio means that cations in SA intercalated into MoS₂. [8,9]

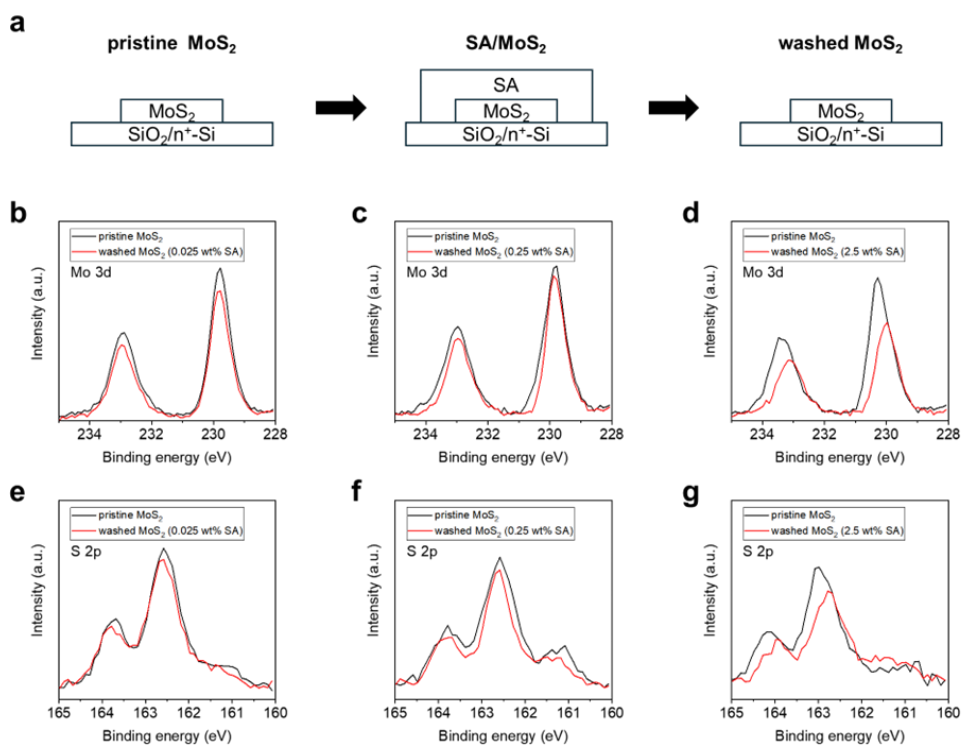


Figure P5_S6. High-resolution XPS analysis of pristine (black) and distilled water-washed MoS_2 (red) after SA deposition. (a) Sample preparation steps. See the experimental section for details. Mo 3d and S 2p spectra of (b) pristine and (e) washed MoS_2 after 0.025 wt% SA deposition, (c) pristine and (f) washed MoS_2 after 0.25 wt% SA deposition, and (d) pristine and (g) washed MoS_2 after 2.5 wt% SA deposition. When MoS_2 was treated by 2.5 wt% SA, Mo 3d doublet peaks and 2p peaks shifted to lower binding energies by ~ 0.3 eV. Such shift in XPS peaks corresponds to sodium intercalation, as Raman analysis indicated similar results when utilizing 2.5 wt% SA solution.[9]

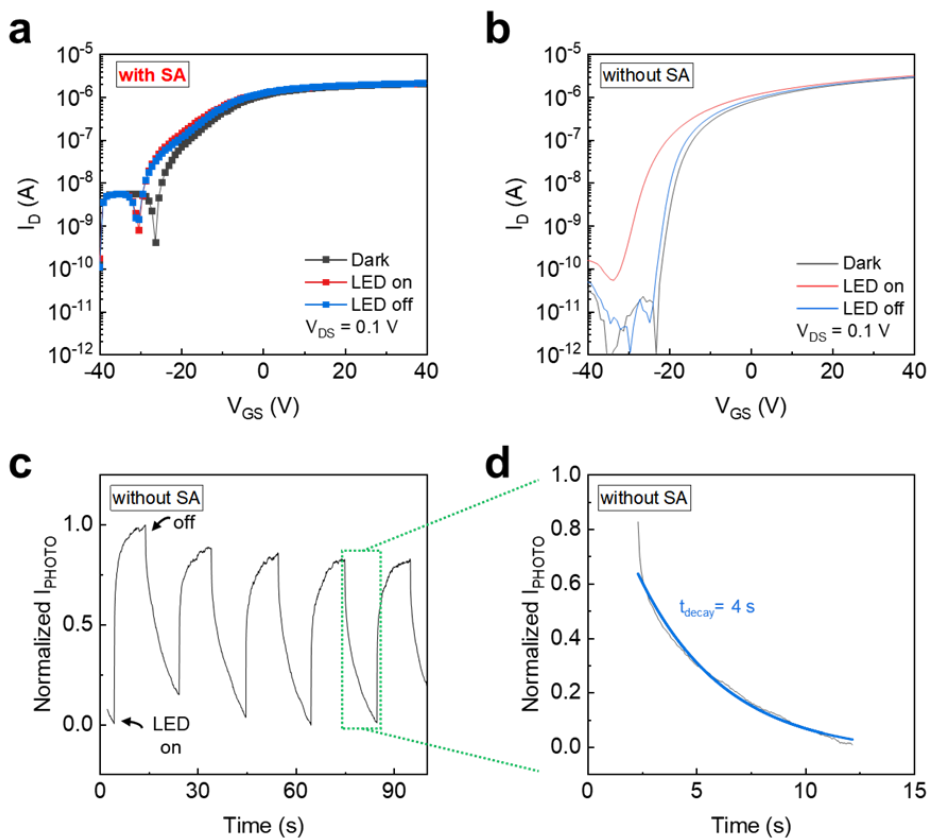


Figure P5_S7. Optoelectrical characteristics of pristine MoS₂ FET without SA. Transfer curves of a MoS₂ channel FET (a) with and (b) without SA. (c) and (d) Time-resolved photoresponse of MoS₂ FET without SA, which demonstrating photodetector with 4 s of fast decay time constant under 680 nm LED (0.5 mW cm^{-2}) illumination.

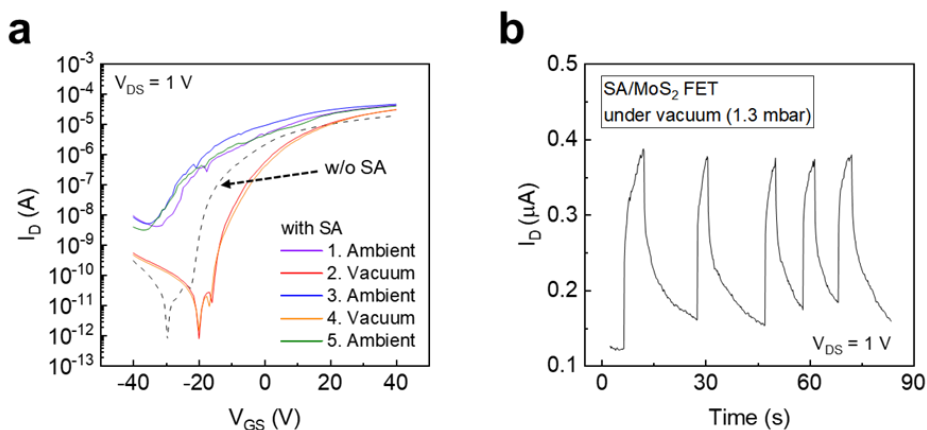


Figure P5_S8. Optoelectrical characteristics of SA/MoS₂ FET under vacuum. (a) Cyclic transfer characteristics of the SA/MoS₂ channel FET under ambient and 1.3 mbar of low vacuum condition. (b) Time-resolved photoresponse of MoS₂ FET under the vacuum, losing PPC effect due to immobilized cations in SA.

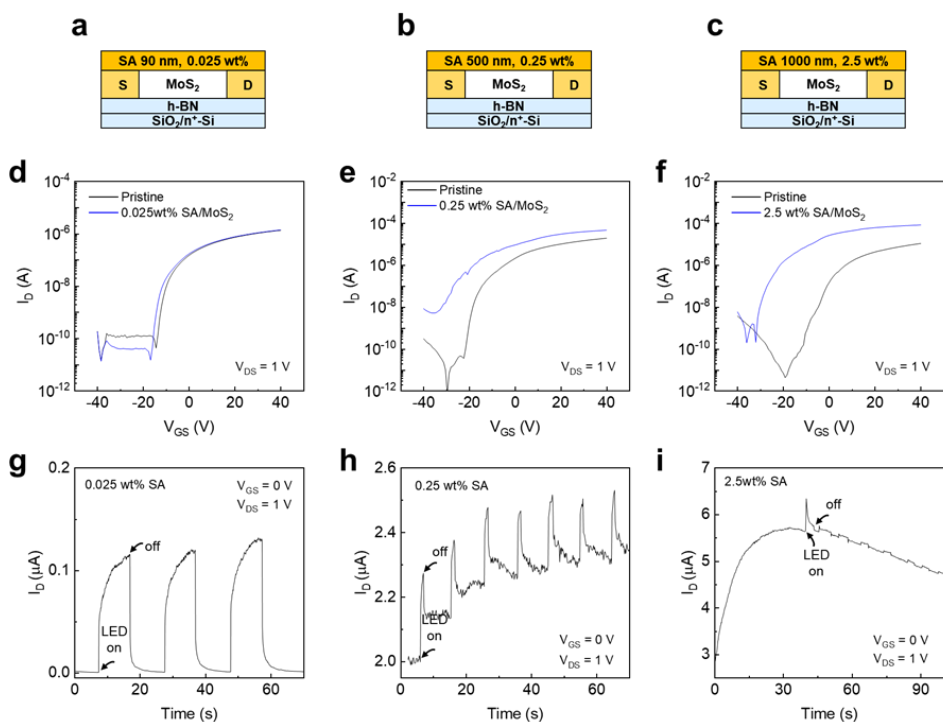


Figure P5_S9. (a-c) 2D schematic structures, (d-f) transfer curves, and (g-i) time-resolved photoresponse of SA/MoS₂ FETs at varying SA concentrations.

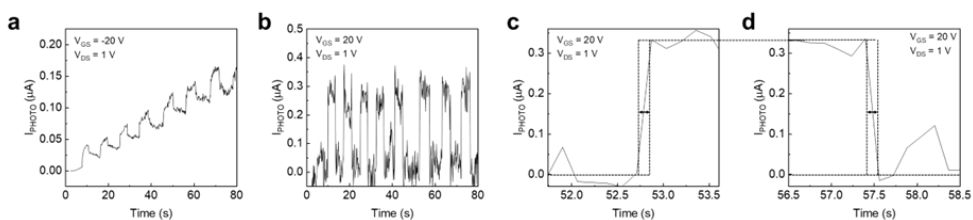


Figure P5_S10. Time-resolved photoresponse of SA/MoS₂ FET under different V_{GS}: (a) V_{GS} = -20 V and (b-d) V_{GS} = 20 V.

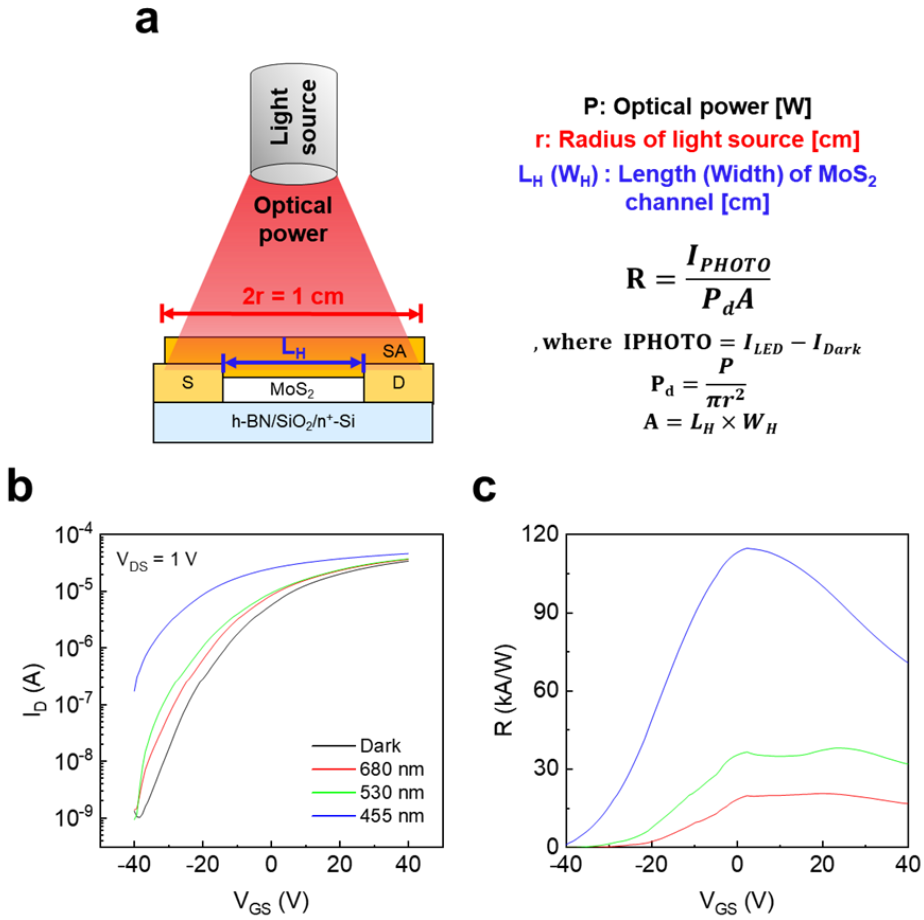


Figure P5_S11. (a) Schematic cross section of SA/MoS₂/h-BN FET and calculation details for photoresponsivity (R) estimation. (b) I_{DS} vs. V_{GS} and (c) R vs. V_{GS} of SA/MoS₂/h-BN FET. At $V_{GS} = 20$ V, R under 680 nm, 530 nm, and 455 nm LED illumination is estimated to be 20, 37, and 100 kA W⁻¹, respectively.

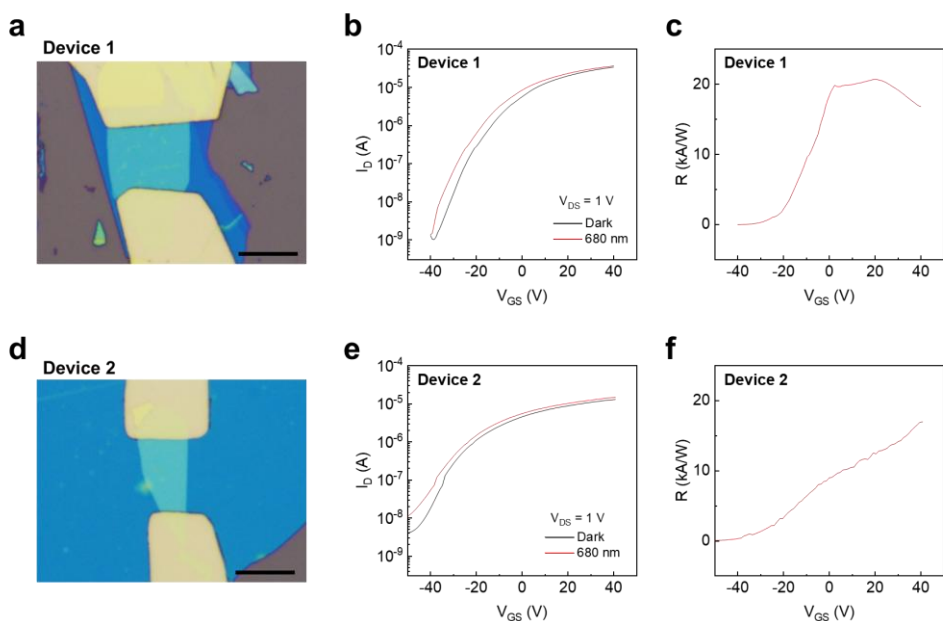


Figure P5_S12. Optical microscopy images and photoresponse characteristics of two devices: Device 1, used in Figures 3a–c and Device 2, used in Figures 3d and 3e. (a, d) Optical microscopy images of Device 1 and Device 2 before SA deposition. The scale bars are 10 μm . (b, c) Optoelectric characteristics and corresponding photoresponsivity of Device 1 after SA deposition under 680 nm LED illumination at 0.5 mW cm^{-2} . (e, f) Optoelectric characteristics and corresponding photoresponsivity of Device 2 after SA deposition under the same illumination conditions. The similar order of estimated responsivity values between the two devices supports the reproducibility of the observed photoresponse.

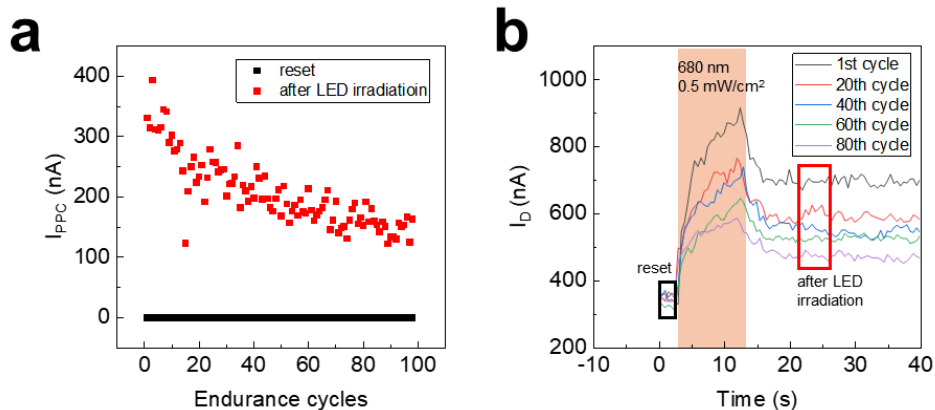


Figure P5_S13. Endurance test of SA/MoS₂/h-BN FET. (a) Plot of I_{PPC} after LED irradiation and subsequent reset operations over multiple cycles. (b) Time-resolved I_D after 10 s of LED illumination (680 nm, 0.5 mW/cm²) for the 1st, 20th, 40th, 60th, and 80th cycles. Although a gradual decrease in I_{PPC} is observed over repeated cycles, I_{PPC} remains stably above 100 nA, confirming robust synaptic operation and reliable reset functionality.

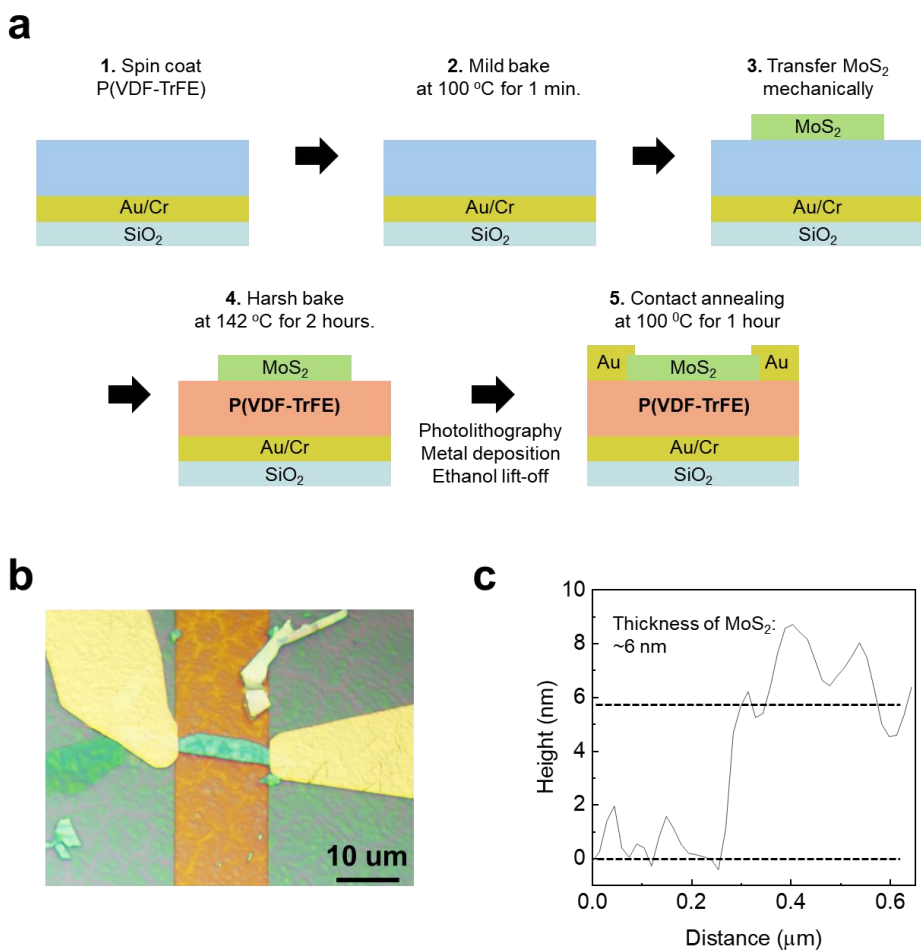


Figure P5_S14. (a) Fabrication process and (b) optical microscopy image of MoS₂ FeFET. (c) Thickness profile of MoS₂ on polymer before crystallization.

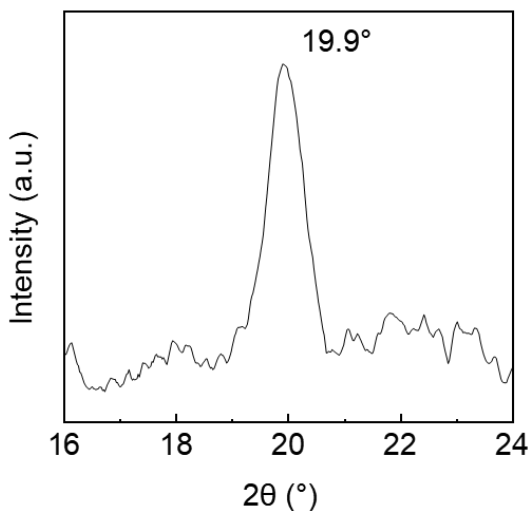


Figure P5_S15. XRD patterns of P(VDF-TrFE). (200) peaks at $2\theta = 19.9^\circ$ confirms the crystalline β -phase of P(VDF-TrFE) polymer.

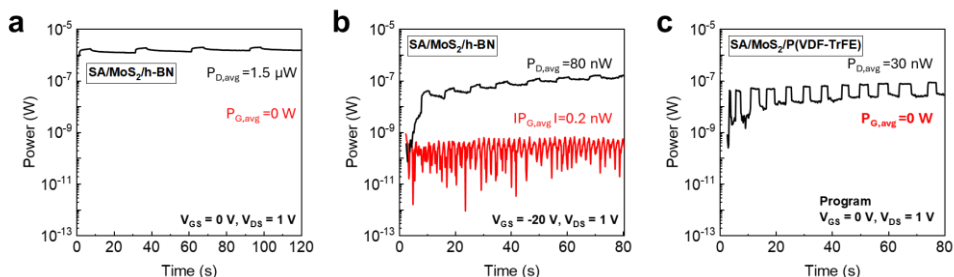


Figure P5_S16. Power consumption of SA/MoS₂/h-BN FET at $V_{GS} = 0$ V (a) and $V_{GS} = -20$ V (b), and power consumption of SA/MoS₂/P(VDF-TrFE) FET at $V_{GS} = 0$ V (c) under the Program state, where $P_G = V_{GS}I_G$ and $P_D = V_{DS}I_D$. The SA/MoS₂/h-BN FET exhibits a power consumption 50 times larger than that of the SA/MoS₂/P(VDF-TrFE) FET (with $P_{D,avg} = 30$ nW) under the same operating conditions of $V_{GS} = 0$ V and $V_{DS} = 1$ V. A comparable $P_{D,avg}$ in the SA/MoS₂/P(VDF-TrFE) FET can be achieved under a high gate bias of $V_{GS} = -20$ V, which unavoidably leads to the generation of P_G . However, by leveraging ferroelectric polarization, the SA/MoS₂/P(VDF-TrFE) Janus FET enables energy efficient operation, maintaining low P_D and negligible P_G at the same time.

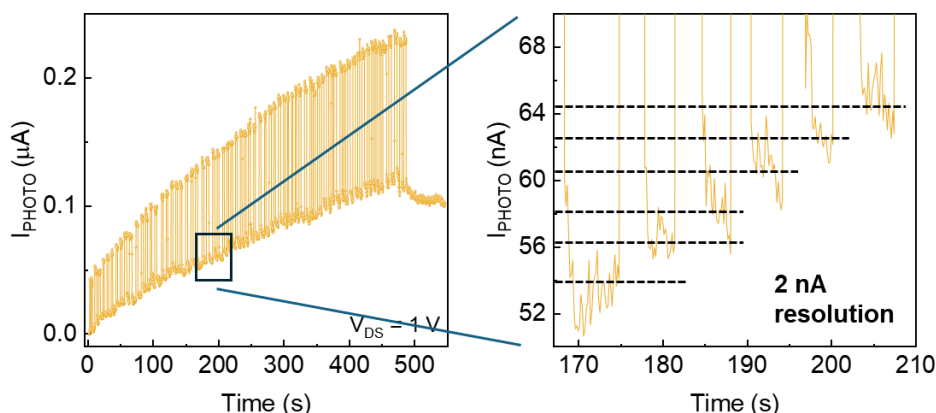


Figure P5_S17. Magnified time-resolved photoresponse of the Janus MoS₂.

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Appendix I. Characterization Methods

1. Project 1

Glycerol Content Determination: The points below were followed, assuming that the amount of ions is not relevant:

- 1) The gels, in their pre-glycerol treatment stage, were dried under fume hood and then under vacuum. Their weight before and after the dehydration was recorded. 2) In this way, the ratio between the dry polymer content and the initial hydrogel mass was determined.
- 3) Were-glycerol gels were weighted before undergoing the glycerol addition step. In their post-glycerol treatment stage, the gels were dried under fume hood and then under vacuum. Their weight after the de hydration was recorded.
- 4) The mass of dry polymer in the tested samples derives from point 2.
- 5) The glycerol amount is obtained by subtracting the dry polymer mass and the water content (determined by TGA) from the weight of the dried organohydrogels recorded at point 3.

UV-Vis Spectrophotometry: UV-Vis absorbance spectra of the gels were collected with a Cary UV-Vis multi-cell spectrometer (Agilent) in the 200–1000 nm range, simply sticking the gels to the wall of a quartz cuvette perpendicular to the light path.

Thermogravimetric Analysis (TGA): Discovery SDT650 (TA Instruments) was used to perform Thermogravimetric analysis. All the analyzed samples were previously equilibrated at RH = 33%. A heating ramp from room temperature (RT) to 1000°C, with a rate of 10 °C min⁻¹, was applied to determine the degradation profile of the samples. Measurements were performed under air flux (100 mL min⁻¹), using aluminum pans. For the water content determination, a heating ramp from RT to 120 °C (rate of 10 °C min⁻¹), followed by a 10 min isotherm was applied. Measurements were performed under N₂ flux (100 mL min⁻¹), using aluminum pans. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Measurements were performed in duplicate.

Differential Scanning Calorimetry (DSC): DSC analysis was carried out by means of Discovery DSC 2500 (TA Instruments). Tzero aluminum hermetic pans (TA

Instruments) were used for all the measurements. For the determination of the glass transition temperature (T_g), the samples were analyzed by applying a heating ramp from 5°C to 80°C, with a heating rate of 10 °C min⁻¹. In order to define the state of the water in the samples, the latter were subjected to a cooling ramp from 5 °C to -60 °C, followed by a heating ramp from -60 °C to 25°C (in both cases with an heating rate of 1 °C min⁻¹). Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Measurements were performed in duplicate.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES): The content of crosslinking ions (Mn²⁺, Cu²⁺, Fe³⁺, Zr⁴⁺) in the MAIgGel samples was determined using an Agilent 720-ES Inductively coupled plasma-atomic emission spectrometer (ICP-AES) equipped with a pneumatic nebulizer and a cyclonic spray chamber. Prior to the analysis, approximately 10 mg of each sample was kept in 2 mL of a Na₂EDTA 0.05 M + NaOH 10% (w/v) water solution (2.00 mL and 0.100 mL respectively) for 1 h at 80°C, under magnetic stirring. After dissolution, 1 mL of the solution was diluted 6 times with MilliQ water. The calibration lines were obtained by preparing the standard solutions starting from commercial standards certified at 1000 ppm. After each measurement, the system was washed with a 2% HNO₃ solution. Measurements were performed in triplicate.

Scanning Electron Microscopy (SEM): The morphology of the gels (prior to the glycerol addition) was assessed using a FEI Quanta FEG 650 scanning electron microscope. Samples were lyophilized at the end of the washing step of the preparation procedure. A 20 nm thick gold layer was sputtered on the samples. The micrographs were acquired with an accelerating voltage of 30 kV, sample-detector distance around 9.5 mm and using a detector for secondary electrons.

Small-Angle X-Ray Scattering (SAXS): Small-angle X-ray scattering analysis was carried out using Xeuss 3.0 (Xenocs). Cu K α radiation with a wavelength (λ) of 1.542 Å at a power of 30 W was obtained using an ultra-brilliant point microfocus X-ray source (GENIX-Fox 3D, Xenocs, Grenoble). Two sample-to-detector distances of 450 and 1800 mm (calibrated using silver behenate) provided a measurable q-range between 0.006 and 0.6 Å⁻¹ (where q, the scattering vector, is given by $q = 4\pi\sin\theta/\lambda$, and 2θ is the scattering angle). Measurements were performed under vacuum using

hermetic gel holders. Data were analyzed using Sasview software (<https://www.sasview.org/>). Mechanical Properties: The mechanical properties of the organohydrogels were assessed using a Mark-10 M7-025E digital force gauge mounted on a Mark-10 ESM-303E motorized test stand. Samples were clamped at the edges: the length of the stretchable region was equal to 3 cm.

Temperature Sensitivity Test: The temperature sensitivity measurements were carried out using rectangular hydrogel stripes of 33 mm (length) $\times$ 10 mm (width) that were first connected with conductive copper tape on top of the Kapton/ Al_2O_3 cylinder. Subsequently, the samples were transferred to a home-made temperature test chamber, and the cylinder was filled with water at different temperatures. Finally, the samples were connected to the probe workstation (Keithley 2636B). The sensitivity of the samples was tested increasing the temperature from 10 °C to 50 °C. The related I versus t curves were recorded applying a direct voltage of 1 V. For the sensitivity evaluation, conductivity versus temperature was plotted to obtain linear correlation. For each hydrogel sensor, three samples were tested and one of them was measured three times to assess the stability of the samples.

Humidity Sensitivity Test: The humidity sensitivity measurements were carried out using rectangular hydrogel stripes of 36 mm (length) $\times$ 2 mm (width), connected with iron crocodiles on a PCB board. A homemade humidity chamber was employed for the RH sensing test at room temperature. Finally, the samples were connected to the probe workstation (Keithley 2636B). During the testing, the RH was changed by adding either wet or dry air from a commercial humidifier. The humidity inside the chamber was monitored using a commercial humidity sensor (Sensirion SMART). The relative humidity of the test chamber was increased from 20% to 80% and the related I-t curves were recorded applying a direct voltage of 1 V. For the sensitivity evaluation, the resistivity versus relative humidity was plotted to obtain linear correlation. For each hydrogel sensor, three samples were tested and one of them was measured three times to assess the self-stability of the samples.

Photoresponsivity: Optoelectrical measurements of all organohydrogel-based photodetectors were performed using a Keithley dual-channel 2636B sourcemeter at room temperature under dark and white LED, with an intensity of 3.47 mW cm^{-2}

(ambient condition). Photoelectron Yield Spectroscopy: The work function (WF) was measured by photoelectron yield spectroscopy in air (PYSA), using a AC-2 photoelectron spectrometer (Riken-Keiki Co.). The ambient photoelectron yield measurements were performed onto an Au/glass pattern substrate for the organohydrogels, which was prepared by photolithograph and thermal evaporation, and placing the gel directly on the metal electrodes. The ultraviolet (UV) incident light powers were 300 nW for the metal electrodes, and 1000 nW for the organohydrogels with a counting time of 10 s per point.

Strain Sensitivity Tests: The sensitivity of the MAIgGel samples to strain was assessed using a Mark-10M7-025E digital force gauge mounted on a Mark-10 ESM-303E motorized test stand. Samples were clamped at the edges (the length of the stretchable region was equal to 3 cm) and then connected to the probe workstation (Keithley 2636B) to measure current variations. The related I–t curves were recorded applying a direct voltage of 1 V. For the sensitivity evaluation, the normalized change in resistance versus strain to obtain a linear correlation was plotted. The experimental setup is illustrated in **Figure P1_4a**.

2. Project 2

Small Angle X-ray Scattering (SAXS): Small angle scattering measurements were performed using a Xeuss 3HR system with a scatterless collimation camera and a hybrid detector (Eiger 1M, Dectris). Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) was produced by an ultra-brilliant point microfocus X-ray source (GENIX-Fox 3D, Xenocs, Grenoble) operating at 30 W. Measurements were taken at two sample-to detector distances (375 mm and 1750 mm) to cover a q-range of $0.004 \text{ \AA}^{-1}$ to $0.6 \text{ \AA}^{-1}$. Data analysis was conducted using SasView software. (<http://www.sasview.org/>).

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES): The Li⁺, Na⁺, Mn²⁺, and Cu²⁺ content in the AlgGel-based samples was quantified using an Agilent 720-ES ICP-AES instrument equipped with a pneumatic nebulizer. Approximately 10 mg of each sample was dissolved in 2 mL of 0.05 M Na₂EDTA and 10% (w/v) NaOH solution at 80 °C for 1 hour with magnetic stirring. After dilution, measurements were performed in triplicate using calibration lines from certified standards.

Thermogravimetric Analysis (TGA): A Discovery SDT650 (TA Instruments) was used. Samples were analyzed under air flow (100 mL min^{-1}) with a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $950 \text{ }^{\circ}\text{C}$ and using aluminum pans. For the water content determination, a heating ramp from RT to $120 \text{ }^{\circ}\text{C}$ (rate of $10 \text{ }^{\circ}\text{C min}^{-1}$), followed by a 10 minutes isotherm. Measurements were performed under N_2 flux (100 mL min^{-1}), using aluminum pans. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Samples were all equilibrated at $\text{RH} = 40\%$ prior the measurement.

Differential Scanning Calorimetry (DSC): DSC measurements were performed using a Discovery DSC 2500 instrument. Samples equilibrated at $40\% \text{ RH}$ were hermetically sealed within Tzero Aluminum Hermetic pans (TA Instruments) and then investigated by cooling from $5 \text{ }^{\circ}\text{C}$ to $-60 \text{ }^{\circ}\text{C}$, then heated from $-60 \text{ }^{\circ}\text{C}$ to $25 \text{ }^{\circ}\text{C}$, in both cases using a heating rate of $1 \text{ }^{\circ}\text{C min}^{-1}$ under nitrogen (N_2) flow. Data were processed with Trios v5.1.1.46572 software (TA Instruments).

Mechanical Properties: Compressive properties AlgGel-based electrolyte disks (1 cm of diameter) were measured using a DiscoveryDHR-3 rheometer, using a head plate with 2 cm of diameter. The compression speed was $2 \text{ } \mu\text{m s}^{-1}$. The compressive modulus (CM) of the samples was determined from the slope of the linear fit to the stress– strain curves shown in Figure 1e, within the 0.00– 0.05 strain range. Traction tests on Mn050AlgGel and Cu050AlgGel samples, before and after storage, were performed using a Mark-10 M7-025E digital force gauge mounted on a Mark-10 ESM-303E motorized test stand. Samples were cut into stripes (1 cm width), clamped at the edges and stretched at a constant rate of 30 mm/min . The Young's modulus (YM) was determined by linear fitting of the stress vs. strain curves shown in **Figure P2_S1f**, within the 0.0–0.2 strain range.

Electrochemical Characterization: Before characterization, samples were cut into disk shapes or stripes (1 cm diameter and width, respectively). Coin-Cell Assembly: Working electrodes were prepared by mixing AC (80 wt%, 16 mg), Super P (10 wt%, 2 mg), and PVDF (10 wt%, 2 mg) in an agate mortar with several drops of NMP to form a homogeneous paste. The paste was coated onto carbon paper electrodes (0.8 cm diameter) and dried overnight under vacuum at $80 \text{ }^{\circ}\text{C}$. The mass loading of active

carbon on each electrode was $\approx 2 \text{ mg cm}^{-2}$. Two electrodes were assembled in CR2032 stainless steel coin cells with the AlgGel-based organohydrogels (1.0 cm diameter) serving as the electrolyte. The electrochemical performance of the AlgGel-based organohydrogels was studied using cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) on Autolab PG STAT128N Potentiostat / Galvanostat instruments with a Metrohm Autolab DuoCoin Cell Holder (Metrohm AG) at room temperature. CV was performed at scan rates of $2\text{--}10 \text{ mV s}^{-1}$ in the voltage range between 0 and 1.8 V or 0 and 1.0 V. EIS measurement was recorded with a frequency range of 0.01 Hz to 1 MHz, with data fitted to an equivalent circuit model (**Figure P2_S12**) to extract key electrochemical parameters. The galvanostatic charge-discharge (GCD) tests were carried out on Neware Battery Tester (BTS-4008T-5V/10mA, Neware Technology Company, Guangdong, China). GCD curves were tested at current densities ranging from 0.2 to 2 mA cm^{-2} . Calculation of ionic conductivity (σ):

$$\sigma = \frac{l}{R_b \cdot A}$$

Being l the gel thickness (**Table P2_S3**), A the gel area (0.50 cm^2) and R_b the bulk resistance

X-ray Photoelectron Spectroscopy: X-ray Photoelectron Spectroscopy (XPS) (Thermo Scientific K-Alpha X-ray photoelectron spectrometer) equipped with an aluminum X-ray source (energy 1.4866 keV) at a vacuum level of $10^{-8}\text{--}10^{-9}$ mbar in the main chamber. The spot size of the X-ray beam was fixed at $400 \text{ }\mu\text{m}$.

3. Project 3

UV-Vis Spectrophotometry: Absorbance spectra of the organohydrogels were acquired using a Cary UV-Vis multicell spectrometer (Agilent) across the 300-800 nm range.

Differential Scanning Calorimetry (DSC): DSC measurements were performed using a Discovery DSC 2500 (TA Instruments). All samples were sealed in Tzero aluminum hermetic pans and analyzed under two different protocols. To determine the glass transition temperature (T_g), samples were heated from $5 \text{ }^\circ\text{C}$ to $70 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$. To assess the water state, samples were first cooled from $5 \text{ }^\circ\text{C}$ to $-60 \text{ }^\circ\text{C}$ and then heated

from -60 °C to 25 °C at the same rate. All samples were pre-equilibrated at 40% relative humidity. Data were processed using Trios software (v5.1.1.46572, TA Instruments).

Thermogravimetric Analysis (TGA): TGA was carried out using a Discovery SDT650 (TA Instruments). For degradation profile analysis, samples equilibrated at 40% RH were heated from room temperature (RT) to 950 °C at 10 °C min⁻¹ under an air flow of 100 mL min⁻¹ in alumina crucibles. To quantify water content, a separate ramp from RT to 110 °C was applied (10 °C min⁻¹), followed by a 20-minute isothermal step, under nitrogen flow (100 mL min⁻¹) in aluminum pans. All results were processed with Trios v5.1.1.46572.

Small-Angle X-ray Scattering (SAXS): SAXS measurements were performed using a Xeuss 3HR system equipped with a GENIX-Fox 3D Cu K α microfocus source (λ = 1.542 Å, 30 W) and an Eiger 1M hybrid pixel detector (Dectris). Data were collected at sample-to-detector distances of 400 mm and 1800 mm, covering a 0.005-0.5 Å⁻¹ q -range.

Scanning Electron Microscopy (SEM): To assess gel morphology, samples were immersed in 100 mL deionized water for 6 h to remove glycerol, freeze-dried, and sputter-coated with a 10 nm gold layer. Micrographs were acquired using a FEI Quanta FEG 650 microscope with a 30 kV accelerating voltage, a sample–detector distance of ~10.2 mm, and secondary electron detection.

Swelling experiments: The swelling behavior of GELTGXXX was evaluated by immersing 4.5 × 1.0 cm strips in 100 mL of deionized water. At predefined time intervals, the samples were removed, gently blotted with a paper towel to eliminate surface moisture, and then weighed. The Swelling ratio (SR) was calculated using the following equation:

$$SR = \frac{W_t - W_0}{W_0}$$

where W_t and W_0 are the mass of the swollen gel at time t and at the beginning of the experiment (i.e., dry), respectively.

Mechanical Characterization: Tensile mechanical properties were evaluated using a Mark-10 M7-025E digital force gauge mounted on a Mark-10 ESM-303E motorized test stand. Gel strips were clamped at the edges, with a stretchable region of 3.5 cm.

Temperature Sensitivity Measurements: Temperature-dependent conductivity was assessed by placing gel samples on a Peltier heating plate connected to a Keithley 2636B source meter. The temperature gradually increased from 20 °C to 50 °C while recording I vs T curves under a constant 0.2 V bias. For each formulation, three independent samples were tested, and one was measured in triplicate to assess reproducibility.

Humidity Sensitivity Measurements: Humidity responsiveness was evaluated using 36 mm × 2 mm gel strips connected to a PCB board via iron crocodile clips. Samples were placed inside a custom-built humidity chamber, where RH was varied from 20% to 80% using wet or dry air from a commercial humidifier. Humidity was monitored with a Sensirion SMART sensor. Electrical response was measured with a Keithley 2636B under 0.2 V bias. Each formulation was tested on three samples, one of which was measured in triplicate.

Strain Sensitivity Measurements: Strain-sensing performance was measured using the same Mark-10 tensile setup. Gel samples (3.5 cm gauge length) were connected to the Keithley 2636B system, and current changes were recorded as I-t curves under an applied 1.0 V bias. Measurements were performed in triplicate.

Probe Penetration Test: GELTGXXX stripes (4.5 × 1.0 cm) were placed on copper tape attached to a thermoelectric module. A conductive probe was positioned on top of the gel. Upon heating, the gel softened, allowing the probe to penetrate and contact the copper tape, completing the circuit (see **Figure P3_S6**). The electrical signal was recorded to monitor the temperature-dependent conductivity response using a digital multimeter.

4. Project 4

Inductively coupled plasma-atomic emission spectrometry (ICP-AES): The content of Na⁺, Ca²⁺, Sr²⁺, Ba²⁺, Mn²⁺, Cu²⁺, Zn²⁺, Fe³⁺, Al³⁺, and Zr⁴⁺ in the MCas samples was quantified using an Agilent 720-ES ICP-AES instrument equipped with a pneumatic

nebulizer. Approximately 10 mg of each sample was dissolved in 2 mL of 0.05 M Na₂EDTA and 10% (w/v) NaOH solution at 80 °C for 1 hour with magnetic stirring. After dilution, measurements were performed in triplicate using calibration lines from certified standards.

Fourier-transform infrared spectroscopy (FTIR): FTIR spectra of the dried MCas samples were acquired in ATR (Attenuated Total Reflectance) mode with a Thermo Nicolet Nexus 870 FTIR spectrophotometer (Thermo Fisher Scientific, Waltham, MA, United States) equipped with a Golden Gate accessory. All the spectra were recorded with a resolution of 2 cm⁻¹, averaging 128 scans for measurement, in the range 4000–650 cm⁻¹.

X-ray photoelectron spectroscopy (XPS): X-ray Photoelectron Spectroscopy was performed on air-dried MCas samples by a Thermo Scientific K-Alpha X-ray photoelectron spectrometer, equipped with an aluminum X-ray source (energy 1.4866 keV) at a vacuum level of 10⁻⁸-10⁻⁹ mbar in the main chamber. The spot size of the X-ray beam was fixed at 400 μm.

Differential scanning calorimetry (DSC): DSC measurements were performed using a Discovery DSC 2500 instrument. Air-dried samples, equilibrated at 40% RH were heated from 5 °C to 110 °C with a rate of 10 °C/min. Tzero Aluminum Hermetic pans (TA Instruments) were used for all the measurements. Data were processed with Trios v5.1.1.46572 software (TA Instruments).

Small-angle X-ray scattering (SAXS): Small-angle scattering measurements were performed using a Xeuss 3HR system with a scatterless collimation camera and a hybrid detector (Eiger 1M, Dectris). Cu Kα radiation ($\lambda = 1.542 \text{ \AA}$) was produced by an ultra-brilliant point microfocus X-ray source (GENIX-Fox 3D, Xenocs, Grenoble) operating at 30 W. Measurements were taken at two sample-to-detector distances (400 mm and 1800 mm) to cover a q -range of 0.005 Å⁻¹ to 0.5 Å⁻¹. Data analysis was conducted using SasView software. (<http://www.sasview.org/>).

Field Emission-Scanning Electron Microscopy (FE-SEM): A Zeiss ΣIGMA FE-SEM (Oberkochen, Germany) was used to carry out the measurements. Samples prepared as described in section 1.2 (SI) were freeze-dried when in the wet state, immediately

after the washing step. The micrographs were acquired with an accelerating voltage of 2 kV, sample-detector distance 2-4 mm, aperture 10 μm and using the In-Lens detector.

Compressive tests: Compressive properties MCas hydrogels (1.3 cm of diameter) were measured using a Discovery DHR-3 rheometer, using a head plate with 2 cm diameter. The compression speed was 20 $\mu\text{m/s}$.

Electrical conductivity determination: MCas-based hydrogel disks (1.3 cm of diameter) were placed between two gold plates (2 x 2 cm) and then connected to a probe workstation (Keithley 2636B) to measure current variations. The related I-t curves were recorded applying a direct voltage of 0.2 V.

Thermogravimetric analysis (TGA): Discovery SDT650 (TA Instruments) was used to perform Thermogravimetric analysis. Samples were analyzed under air flow (100 mL min^{-1}) with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ from room temperature to 950 $^{\circ}\text{C}$ and using alumina pans. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Samples were all equilibrated at RH = 40% prior to the measurement.

Electrochemical characterization: Working electrodes were prepared by mixing AC (80 wt%, 16 mg), Super P (10 wt%, 2 mg), and PVDF (10 wt%, 2 mg) in an agate mortar with several drops of NMP to form a homogeneous paste. The paste was coated onto carbon paper electrodes (0.8 cm diameter) and dried overnight under vacuum at 80 $^{\circ}\text{C}$. The mass loading of active carbon on each electrode was $\sim 2 \text{ mg/cm}^2$. Two electrodes were assembled in CR2032 stainless steel coin cells with the MCas-based hydrogels (1.3 cm diameter) serving as the electrolyte. The electrochemical performance of the MCas hydrogels was studied using cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) on Autolab PGSTAT128N Potentiostat / Galvanostat instruments with a Metrohm Autolab DuoCoin Cell Holder (Metrohm AG) at room temperature. CV was performed at scan rates of 2-10 mV/s in the voltage range between 0 and 0.8 V. EIS measurement was recorded with a frequency range of 0.01 Hz to 1 MHz. The galvanostatic charge-discharge (GCD) tests were carried out on Neware Battery Tester (BTS-4008T-5V/10mA, Neware Technology Company, Guangdong, China). GCD curves were tested at current densities ranging from 0.2 to 2 mA/cm^2 .

5. Project 5

Optoelectronic Measurements: Electrical measurements were performed using a Keithley dual-channel 2636A and 4200A SCS semiconductor parameter analyzer under ambient atmosphere and dark conditions. Electrical transport characteristics in low vacuum (≈ 1.3 mbar) were measured using the 4200A SCS in a Lakeshore probe station. Photoresponse measurements of the transistors were conducted under the illumination of 740, 680, 530, and 455 nm LEDs.

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES): The amount of Na^+ contained in the used sodium alginate was determined by means of an Agilent 720-ES Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) equipped with a pneumatic nebulizer and a cyclonic spray chamber. Sodium alginate solutions 0.1% (w/v) in MilliQ were analyzed. The calibration lines were obtained by preparing the standard solutions starting from commercial standards certified at 1000 ppm. Sodium absorbance was evaluated at 589.592 nm. Measurements were performed in quadruplicate. After each measurement, the system was washed with a 2% HNO_3 solution.

Thermogravimetric Analysis (TGA): TGA was carried out with a Discovery SDT650 from TA Instruments, using an alumina pan under air flux (100 mL min^{-1}). A heating ramp from room temperature (RT) to 950°C , with a rate of $10^\circ\text{C min}^{-1}$, was applied. For water content determination, samples were heated to 120°C at the same rate, followed by a 10 min isotherm. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Samples were all equilibrated at $\text{RH} = 40\%$ prior to measurement.

Differential Scanning Calorimetry (DSC): DSC analysis was carried out by means of Discovery DSC 2500 (TA Instruments). In order to define the state of the water in the samples, the latter were subjected to a cooling ramp from 5 to -60°C , followed by a heating ramp from -60 to 25°C (in both cases with a heating rate of 1°C min^{-1}). Tzero Aluminum Hermetic pans (TA Instruments) were used. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Measurements were performed in duplicate. Samples were all equilibrated at $\text{RH} = 40\%$ prior the measurement.

X-Ray Photoelectron Spectroscopy (XPS): XPS measurements (Thermo Scientific K-Alpha) were performed at a base chamber pressure of $\sim 10^{-9}$ mbar using an Al K α X-ray source (1486 eV). Spot sizes of 400 μm and pass energies of 200 eV (for wide scans) and 10–20 eV (for high-resolution scans) were used. All XPS spectra were calibrated to the C 1s peak at 284.8 eV.

Atomic Force Microscopy (AFM): For AFM imaging, scan-assist mode atomic force microscopy was performed in the air using a Bruker Dimension Icon. The tip model was SCAN-ASSIST-AIR with a stiffness constant $K = 0.4 \text{ N m}^{-1}$.

UV-Vis Spectrophotometry: UV-Vis absorbance spectra of the gels were collected using a Cary UV-Vis multi-cell spectrometer (Agilent) in the 200–1000 nm range. Gels were adhered to the wall of a quartz cuvette, perpendicular to the light path.

Confocal Raman Microscopy: Confocal Raman microscopy was carried out using a Renishaw InVia Qontor confocal microRaman system equipped with a front-illuminated CCD camera and a research-grade Leica DM 2700 microscope. Spectra were collected by using a 100 $\times$ and a laser operating at 532 nm with a power of 100 mW and a grating of 2400 lines per mm. Spectra were processed with the Renishaw software WiRE 5.5, and corrected for cosmic rays, baseline, and noise.

X-Ray Diffraction Analysis: The crystallinity of ferroelectric P(VDF-TrFE) polymer was investigated by X-ray diffraction patterns (Bruker D8 X-ray diffractometer).

Appendix II

The following publications, directly arising from the research conducted during this doctoral work, are reported in the next pages in their Publisher's Main Text PDF version. All supporting information is already included in the thesis core (Section 4) and is therefore not reproduced here.

Paper I = Project 1; P. Tordi; A. Tamayo; Y. Jeong; M. Bonini; P. Samorì, Multiresponsive Ionic Conductive Alginate/Gelatin Organohydrogels with Tunable Functions, *Advanced Functional Materials*, **2024**, 34 (52), 2410663. (Featured in *Hot Topic: Organic Electronics*)

Paper II = Review Article; P. Tordi; F. Ridi; P. Samorì; M. Bonini, Cation–Alginate Complexes and Their Hydrogels: A Powerful Toolkit for the Development of Next-Generation Sustainable Functional Materials, *Advanced Functional Materials*, **2025**, 35 (9), 2416390.

Paper III = Project 2; P. Tordi; V. Montes-García; A. Tamayo; M. Bonini; P. Samorì; A. Ciesielski, Ionically Tunable Gel Electrolytes Based on Gelatin–Alginate Biopolymers for High-Performance Supercapacitors, *Small*, **2025**, 21 (33), 2503937. (Featured in *Hot Topic: Batteries and Supercapacitors*)

Paper IV = Project 3; P. Tordi; A. Tamayo; Y. Jeong; B. Han; T. Al Kayal; A. Cavallo; M. Bonini; P. Samorì, Fully Bio-Based Gelatin Organohydrogels via Enzymatic Crosslinking for Sustainable Soft Strain and Temperature Sensing, *Advanced Functional Materials*, **2025**, e20762. (Featured in *Hot Topic: Wearable Sensors*)

Paper V = Project 5; Y. Jeong*; **P. Tordi*;** A. Tamayo; B. Han; M. Bonini; P. Samorì, Mimicking Synaptic Plasticity: Optoionic MoS₂ Memory Powered by Biopolymer Hydrogels as a Dynamic Cation Reservoir, *Advanced Functional Materials*, **2025**, 35 (50), e09607. (*Equal contribution)

The ionically crosslinked caseinate system (Project 4) is fully documented within the thesis core (Section 2 and 4). Its corresponding manuscript (under submission) is not reproduced here.

Multiresponsive Ionic Conductive Alginate/Gelatin Organohydrogels with Tunable Functions

Pietro Tordi, Adrián Tamayo, Yeonsu Jeong, Massimo Bonini,* and Paolo Samorì*

Materials combining stretchability and sensitivity to external stimuli are key for wearable electronics applications to enable the emergence of disruptive technologies in biosensing, health monitoring, photodetection and human motion recognition. Conductive organohydrogels have gained significant attention due to their high sensitivity and cost-effective preparation. Biopolymers like gelatin and alginate offer unique opportunities for developing responsive wearable devices, owing to their biocompatibility and sensitivity toward environmental factors. Here sustainable bio-inspired method is presented to produce alginate/gelatin organohydrogels combining transparency in the visible range, ionic conductivity, high stretchability, and multiresponsiveness. The controlled alginate's crosslinking with various metal cations like Mn^{2+} , Cu^{2+} , Fe^{3+} , and Zr^{4+} enables modulating ionic conductivity as well as finely tuning the material's thermal and mechanical properties. These organohydrogels show responsiveness to temperature (from 10 to 50 degrees, with a sensitivity of $0.19\ K^{-1}$), relative humidity (from 20 to 80%, with a sensitivity of $0.022\ RH(\%)^{-1}$), and strain (gauge factor >1.6), enabling real-time monitoring of environmental and physiological parameters. Remarkably, they also exhibit photoresponsivity of $9.2\ \mu A\ W^{-1}$ under visible light, a feature rarely reported in literature. The ease of tuning responsiveness to the chosen stimuli and the high sensitivities open perspectives for applying these materials as wearable stretchable sensors.

1. Introduction

The immense application potential of wearable electronics has triggered intensified research efforts in the development of new multifunctional materials combining stretchability and

sensitivity to external stimuli paving the way for their applications in health monitoring, biosensing, photoresponsivity, and human motion recognition.^[1–7] Among flexible and stretchable materials, conductive hydrogels have gained a great research interest during the last decade because of their superior mechanical properties when compared to inorganic conductors.^[8–13] The use of ionic conductivity for sensing is recently emerging as a powerful strategy enabling the use of polymeric matrices that are not intrinsically conductive, without the addition of carbon-based electron conductive fillers that affect the transparency of the final products.^[14–16] Ionically conductive hydrogels operate on the basis of the movement of ions within their 3D structure, in analogy to the ionic conduction observed in biological tissues.^[17–20] This characteristic, together with the high sensitive and stable conductivity, make ionic conductive hydrogels exceptionally well-suited as wearable sensors for health monitoring.

The use of ionic conductivity opens the door to the design of stretchable sensors employing biopolymeric compounds,

which are notorious for their poor electrical conductivity. Biopolymers offer in fact interesting opportunities for the development of responsive wearable devices, since they are sustainable, usually biocompatible/biodegradable and often particularly sensitive to the surrounding environment. Among biopolymers, gelatin and alginate are well-suited to this purpose, when properly processed. Gelatin is a polypeptide obtained from the hydrolysis of collagen, capable of forming hydrogels extremely sensitive to temperature.^[21,22] Alginate, on the other hand, is an exopolysaccharide extracted from brown algae that possesses high reactivity and selectivity towards metal cations with various oxidation states;^[23–30] in fact, cations interact with both the hydroxyl and carboxylate groups on the polymer backbone, producing crosslinked hydrogel structures with characteristic porosities and mechanical properties. Gelatin and alginate hydrogels are well known for their compatibility with human tissues, making them commonly used as scaffolds for cell proliferation and as materials for wound dressings.^[31–34]

Among hydrogels, those able to absorb a large amount of organic molecules retaining their structural integrity are attracting more and more interest in the last few years;^[35,36] in fact, compared to conventional hydrogels, they can be endowed with

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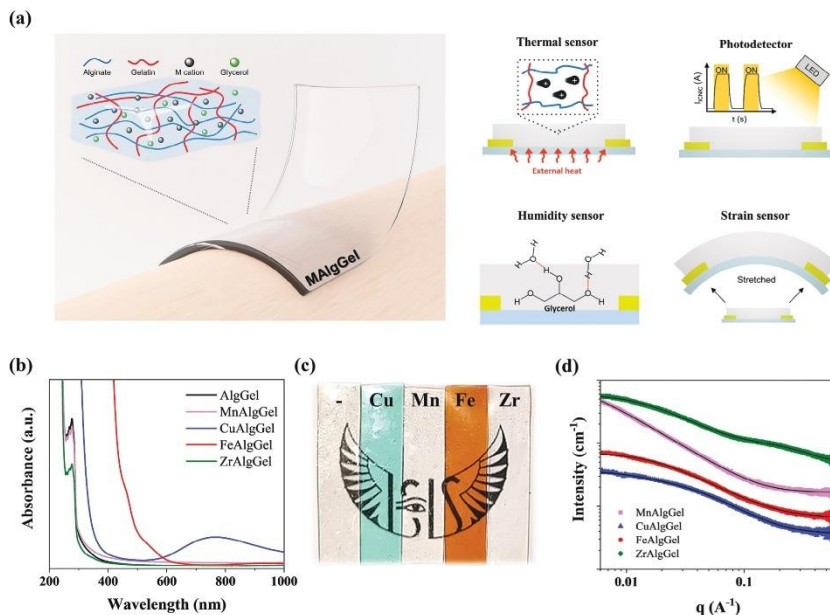


Figure 1. a) 3D cartoon of the multiresponsive alginate/gelatin organohydrogel crosslinked with a metal cation (MAIgGel), placed on human skin. The scheme shows the potential applications of MAIgGel, as thermal sensor, photodetector, humidity sensor and strain sensor. b) UV-Vis spectra, c) optical image of the prepared MAIgGel samples placed on top of a printed ISIS Strasbourg logo, and d) small angle X-ray scattering curves. Samples' coding: – = AlgGel = black; Mn = MnAlgGel = pink; Cu = CuAlgGel = blue; Fe = FeAlgGel = red; Zr = ZrAlgGel = green. SAXS curves were offset for clarity.

additional functionalities while retaining extremely high stability against stresses and enhanced sensitivity to environmental conditions. These emerging materials, known as organohydrogels, have recently found application as carriers for drug delivery or sensors (e.g., temperature, strain, and humidity).^[37,38] The introduction of molecules such as glycerol^[39] or ethylene glycol^[40] is commonly exploited to impart high flexibility to the gel structure and to enhance its sensitivity (e.g., to strain) in a dehydrated environment. In this regard, You et al. developed gelatin/polypyrrole/reduced graphene oxide porous organohydrogel for pressure and strain sensing.^[41] The sensitivity in this case relied on changes in the electrical conductivity of the matrix resulting from structural changes involving the porous architecture. Highly stretchable ionic conductive organohydrogels were also realized, with good sensitivities and durabilities.^[42,43] Interestingly, Feng et al. developed ionic conductive strain sensors that can function as supercapacitors by doping the polymeric scaffold with alizarin red S.^[44] It is worth mentioning that the introduction of light sensitive and conductive polymer fillers, such as polypyrrole, enables UV detection. However, it unfortunately de-

termines a loss of transparency and results in a high magnitude of dark state current, which is undesirable for practical device applications.^[45,46] The organohydrogel responsiveness to multiple stimuli usually arises from the presence of fillers which however strongly hampers the reproducibility of the preparation and the tuning of the performances.

Aiming at fostering the use of biopolymer-based stretchable sensors for application in wearable electronics (e.g., e-skins) and environmental monitoring, here we report an unprecedented sustainable and reproducible preparation method for the development of alginate-gelatin organohydrogels simultaneously displaying ionic conductivity, stretchability and transparency in the visible range. Gelatin was used to impart stretchability and thermal responsiveness, whereas alginate was crosslinked with di-, tri- and tetravalent cations (namely Mn^{2+} , Cu^{2+} , Fe^{3+} , Zr^{4+}) to modulate both the mechanical properties and the ionic conductivity of the material. The possibility to compare between different ions (going beyond the common Ca^{2+} -mediated crosslinking of alginate) adds novelty to our study, since no similar approaches have been reported in the literature. **Figure 1a** portrays

Table 1. Physicochemical properties of the MAlGgel organohydrogels.

	AlgGel	MnAlgGel	CuAlgGel	FeAlgGel	ZrAlgGel
Thickness [μm]	511 $\pm$ 15	817 $\pm$ 24	805 $\pm$ 24	829 $\pm$ 25	847 $\pm$ 26
Polymer content [w/w%]	18.3 $\pm$ 1.0	28.4 $\pm$ 1.5	24.7 $\pm$ 1.0	21.9 $\pm$ 0.6	21.4 $\pm$ 1.1
Glycerol content [w/w%]	74.3 $\pm$ 0.8	57.9 $\pm$ 1.2	60.7 $\pm$ 0.7	63.2 $\pm$ 0.3	63.7 $\pm$ 0.8
Water content [w/w%]	7.4 $\pm$ 0.2	13.7 $\pm$ 0.3	14.6 $\pm$ 0.3	14.9 $\pm$ 0.3	14.9 $\pm$ 0.3
Degradation onset [$^{\circ}\text{C}$]	148.9	171.3	168.7	167.8	169.6
M^{X+} content [$\times 10^{-2}$ mmol g^{-1}]	–	7.1 $\pm$ 0.4	5.9 $\pm$ 0.3	7.5 $\pm$ 0.4	6.3 $\pm$ 0.3
T_g [$^{\circ}\text{C}$]	41.7 (57.1) ^{a)}	42.4	42.5	52.5	62.8
YM [MPa]	1.87 $\pm$ 0.14	0.52 $\pm$ 0.08	2.44 $\pm$ 0.06	2.57 $\pm$ 0.16	2.46 $\pm$ 0.06
UTS [MPa]	1.45 $\pm$ 0.06	0.64 $\pm$ 0.02	1.88 $\pm$ 0.04	1.17 $\pm$ 0.11	1.42 $\pm$ 0.05

^{a)} Second peak resulting from the re-assembling of the chains during the first thermal event. T_g , YM, and UTS stand for glass transition temperature, Young's modulus, and ultimate tensile strength, respectively.

a schematic illustration of the multi-responsive alginate-gelatin organohydrogel (AlgGel) crosslinked with a generic metal cation (M), applied on human skin. These matrices proved responsiveness to temperature, humidity and strain, thus endowing our gels with a huge potential for real-time monitoring of multiple stimuli related to the environment and the human body (e.g., solar irradiation, tissue inflammation and motion). Significantly, the electrical properties of bottom-contacted two-terminals organohydrogel devices exhibited a markedly high photocurrent (I_{PHOTO}) (ca. 20 nA) in response to visible light, a feature scarcely reported in the literature. When considering the incident light intensities, ranging from few $\mu\text{W cm}^{-2}$ to tens of mW cm^{-2} in common polymer-based wearable photodetectors,^[45–47] our device demonstrated fast and sensitive photoswitching behavior, with response and recovery times amounting to 2.23 s and 3.13 s, respectively, under 3.47 mW cm^{-2} of white LED illumination. This unique photosensitivity is attributed to the light sensitivity of gelatin,^[45] and the efficient charge injection from metal electrodes to hydrogel upon exposure to white LED. The possibility to easily tune the responsive nature as a function of the chosen crosslinker and the demonstrated high sensitivities to multiple stimuli suggest promising perspectives for the use of our devices as wearable stretchable sensors.

2. Results and Discussion

2.1. Physicochemical Characterization of the MAlGgel Organohydrogels

The results of the analysis on the compositional, structural and optical properties of the effect of crosslinking of AlgGel samples upon addition of specific cationic species are reported in Figure 1b–d, Table 1, and Figure S1 (Supporting Information). They reveal that crosslinked samples possess comparable thickness (i.e., around 800 μm , see Table 1 and Figure S1, Supporting Information) exceeding that of AlgGel. Importantly, the sample's crosslinking endows robustness to the hydrogel structure, hindering its collapse during the drying process through a strong modification of the gel's structure, by enhancing its packing density (see Figure S2, Supporting Information). Figure 1b,c provide unambiguous evidence of the high transparency of MAlGgel

to visible light. The crosslinking ion does not particularly affect the amount of glycerol loaded by the gels during the last step of the preparation (between 58 and 64 (w/w%), Table 1). Likewise, Table 1 and Figure S3 (Supporting Information, TGA water evaporation thermogram) reveal that the water content inside the organohydrogels is constant at values of around 14% (w/w%) upon crosslinking. The polymer content of the samples is also reported in Table 1 and clearly varies as a function of the ion. This finding derives from the different shrinkage experienced by the polymer network upon the final dehydration step and strongly influences the light responsiveness of our materials (see Section 2.4). The absence of peaks in the DSC thermograms displayed in Figure S4a (Supporting Information) testifies that only non-freezable water is present in the samples,^[48,49] suggesting that our materials can retain their flexibility below 0 $^{\circ}\text{C}$, thereby extending their applicability beyond the limit of common hydrogels. TGA analysis (Figure S5 and Table S1, Supporting Information) highlights that the addition of glycerol to the uncrosslinked polymer matrix lowers the degradation onset of the polymer (corresponding to the first massive mass loss in Figure S5, Supporting Information, AlgGel thermogram) to approximately 150 $^{\circ}\text{C}$, while the crosslinking increases the stability of the latter. The MAlGgel samples also display similar thermal stability, undergoing the first degradation around 170 $^{\circ}\text{C}$. DSC curves reported in Figure S4b (Supporting Information) show that the addition of glycerol lowers the glass transition temperature (T_g) of the polymer, increasing the chain's degrees of freedom. Interestingly, AlgGel shows two inflection points that can be ascribed to T_g (at 41.7 $^{\circ}\text{C}$ and 57.1 $^{\circ}\text{C}$, respectively); in fact, the absence of a crosslinker may lead to an easier reorganization of the polymer chains during the heating, resulting in a second glass transition. In the case of both MnAlgGel and CuAlgGel only one T_g can be identified at 42.5 $^{\circ}\text{C}$, in accordance with the previously hypothesized role of the crosslinker. In the case of FeAlgGel and ZrAlgGel the T_g shifts to higher temperatures (i.e., 52.5 $^{\circ}\text{C}$ and 62.8 $^{\circ}\text{C}$, respectively) evidencing that the freedom of the polymer chains is reduced by the crosslinking, probably due to the protonation that occurs in the acid Fe^{3+} and Zr^{4+} crosslinking bath. Such a reduced freedom leads to a higher rigidity of FeAlgGel and ZrAlgGel. The different mechanical properties of the MAlGgel samples arise from the different strength of the interactions between the M^{X+} ions

Table 2. Conductivity, mechanical response, thermal-response, humidity and photoresponse of AlgGel and MAlGel samples. The sensitivity parameters are averaged from three different measurements.

	AlgGel	MnAlgGel	CuAlgGel	FeAlgGel	ZrAlgGel
Conductivity [mS m^{-1}] ^{a)}	0.17 ± 0.06	1.3 ± 0.3	3.7 ± 0.5	6.0 ± 1.4	6.1 ± 0.9
Temperature response [K^{-1}]	— ^{b)}	0.19 ± 0.02	0.16 ± 0.03	0.06 ± 0.01	0.13 ± 0.02
B [kJ mol^{-1}] ^{c)}	6.4 ± 0.7	2.7 ± 0.2	2.2 ± 0.3	2.3 ± 0.6	2.2 ± 0.2
Humidity response [$\times 10^{-2} \text{ RH}(\%)^{-1}$]	(2.1 ± 0.2)	2.2 ± 0.3	2.1 ± 0.3	1.8 ± 0.1	1.5 ± 0.1
RH sensitivity range [%]	20–60	20–60	20–60	20–70	20–80
Photo-responsivity [$\mu\text{A W}^{-1}$]	0.6	9.2	5.1	4.3	5.8
Photo switching speed [s]	3.42/4.35	2.23/3.13	3.31/3.61	4.00/4.28	3.76/3.92
GF1 [Region I]	2.80 ± 1.15	2.25 ± 0.57	1.67 ± 0.19	2.29 ± 0.22	2.38 ± 0.26
GF2 [Region II]	2.18 ± 0.38	2.02 ± 0.40	1.73 ± 0.18	2.15 ± 0.07	2.27 ± 0.18

^{a)} Extracted using Cu electrode; ^{b)} Nonlinear temperature responsiveness; ^{c)} Activation energy of the ionic movement.

and the polymer network, as also highlighted by the correlation lengths (ξ) extracted by small angle X-ray scattering (SAXS) investigation (Figure 1d and Table S2, Supporting Information). These aspects are discussed in greater detail in the next sections. As shown in Table 1, the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis reveals that the amount of crosslinking ions in the MAlGel samples is particularly low, yet sufficient to guarantee an easily detectable ionic conductivity and provide an excellent structural integrity under stress. The samples prepared using different cations (Mn^{2+} , Cu^{2+} , Fe^{3+} and Zr^{4+}) and the non-crosslinked AlgGel exhibit significantly different conductivities, which can be attributed to the different ionic density, retention in the gel matrix and kinetic energy. The AlgGel sample exhibits the lowest conductivity ($0.17 \pm 0.06 \text{ mS m}^{-1}$), being one order of magnitude lower than that of MnAlgGel ($1.3 \pm 0.3 \text{ mS m}^{-1}$). The conductivity is even superior in the case of CuAlgGel ($3.7 \pm 0.5 \text{ mS m}^{-1}$), FeAlgGel ($6.0 \pm 1.4 \text{ mS m}^{-1}$) and ZrAlgGel ($6.1 \pm 0.9 \text{ mS m}^{-1}$) (Table 2). The higher glycerol content can contribute to generate the particularly low conductivity of AlgGel. However, differences in conductivity are not determined simply by the glycerol content within the samples (see Table 1), but they are rather related to the ions interaction with the polymer matrix (which is dependent on charge and dimension of the M^{X+} species⁵⁰) and usually involves electrostatic forces). The ionic conductivity values of the MAlGel samples are comparable with state-of-the-art ionic conductive hydrogel sensors ($1\text{--}1000 \text{ mS m}^{-1}$).^{51–54}

2.2. MAlGel Organohydrogels Sensitivity to Thermal Variations

Our gels possess thermoresponsive properties that arise from factors such as ionic mobility and viscosity of the polymer network, which are highly dependent on the temperature.^{33,56} The thermo-responsivity of the organohydrogels can be profitably used for environmental monitoring or biomedical application such as the real time observation of temperature variations induced by various external phenomena (e.g., sun exposition or water evaporation) or monitoring infection and inflammation evolution.

The temperature-dependence of the conductivity (σ) was extracted between 283 and 323 K, which are regarded as the optimal

range for electronic skins and generic wearable electronics.^{37–39} The MAlGel samples were connected to a home-made heater, equipped with two copper electrodes. As shown in Figure 2a and Figure S6 (Supporting Information), the electrical conductivity of the MAlGel samples is highly dependent on the temperature. The charge transport mechanism in the hydrogel arises from the free diffusion of ions and their interaction with the hydrogel matrix: the ionic conductivity of the sample increases with the temperature. At low temperature, protons and ions tend to interact via dipole–dipole forces with the carboxylate and hydroxyl groups of the alginate/gelatin matrix, yielding low ionic conductivity for all the different MAlGels. On the other hand, at higher temperatures, the interaction between ions and matrix is weakened and the water molecules are less prone to interact with glycerol: the resulting increase in ion mobility combined with the decrease of viscosity determines an enhancement in the ionic conductivity. The temperature sensitivity of the organohydrogels was extracted from the slope of the $\Delta\sigma/\sigma$ versus T curves reported in Figure 2b (see values in Table 2). MnAlgGel, CuAlgGel and ZrAlgGel provided thermal sensitivity values of 0.19, 0.16, and 0.13 K^{-1} , respectively, while FeAlgGel exhibited the lowest thermal sensitivity (i.e., 0.06 K^{-1}). This evidence may indicate that, in this specific case, the interaction between the crosslinking ions and the polymer matrix is the strongest among the tested samples, significantly hampering the ionic movement. The “long-distance” correlation lengths (ξ_1) of FeAlgGel (i.e., $\approx 6.3 \text{ nm}$, see Section S3 and Table S2, Supporting Information), which is determined by small angle X-ray scattering, is the smallest among the investigated samples, and it supports our hypothesis. Interestingly MnAlgGel exhibited a change of the thermal sensitivity above 307 K, which can be attributed to a phase transition of the gelatin component in the polymeric matrix.⁶⁰ The weak interaction between Mn^{2+} and alginate (already reported in literature^{25,26,61}) is sufficient to maintain the structural integrity of the material during the heating, over the examined temperature range: the net change in the ionic conductivity may arise from nonlinear variations of the polymer chains’ mobility as the temperature increases. AlgGel displayed a nonlinear dependence with high thermal sensitivity ($>0.2 \text{ K}^{-1}$). It is worth mentioning that the onset of AlgGel samples melting was observed at ca. 300 K, which was accompanied by a drastic increase of the ionic conductivity (Figure S6a, Supporting Information). By and large, because of its

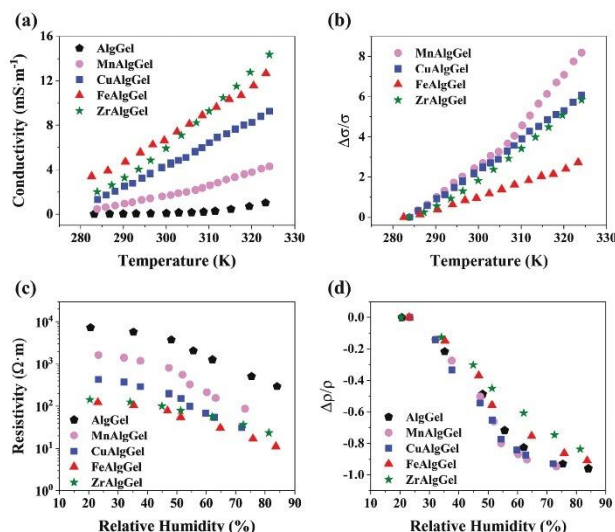


Figure 2. The influence of the temperature on a) conductivity and b) relative change of conductivity of AlgGel and the MAlGels. The influence of relative humidity on c) resistivity and d) relative change of resistivity of AlgGel and the MAlGels. All the measurements were conducted on three different batches for each sample (Figures S6 and S8, Supporting Information, full dots), demonstrating excellent reproducibility in terms of fabrication and temperature/humidity sensitivity.

low linearity of the electrical response and the drastic change in the physicochemical properties over the thermal region of interest, AlgGel was therefore not considered as a promising platform for temperature monitoring. The crosslinked samples were subjected to multiple cycles of heating and cooling, to check their robustness to cyclability. We found a high reversibility in the range of temperature from 283 to 323 K (Figure S6, Supporting Information, empty dots) for all of them. Conversely, AlgGel did not recover its original performances after the melting at 300 K. In order to study in depth the ion conduction mechanism of the alginate/gelatin organohydrogels, the conductivity of the samples as a function of the temperature was fitted according to the typical Arrhenius plot (Figure S7, Supporting Information). The temperature dependence on the MAlGel conductivity could not be accurately fitted using the aforementioned model: the Vogel-Tamman-Fulcher (VTF) approach, incorporating the influence of various physical parameters, (e.g., viscosity, temperature, ion charge) on the conductivity,^[62,63] provided better results. The obtained B parameters (activation energy of the ionic movement, reported in Table 2), obtained using the VTF equation described in Section S4 (Supporting Information) (Equation S2, Supporting Information), are similar for all the crosslinked matrices (between 2.7 and 2.2 kJ mol^{-1}), while AlgGel reaches the highest value among the analyzed samples (i.e., 6.4 kJ mol^{-1}): this behavior

can be attributed to the lower amount of ions in the AlgGel matrix.

2.3. MAlGel Organohydrogels Sensitivity to Relative Humidity Variations

The MAlGel organohydrogels are able to reversibly absorb water due to the hydrophilic nature of both the polymeric matrix and the glycerol molecules, the latter being the main component of our materials ($\approx 60\%$ w/w, see Table 1). This characteristic makes our products an ideal platform for the development of high performance wearable humidity sensors.^[64–66] The response to humidity changes was measured inside a home-made box, supplying air at different relative humidity (RH) levels inside the samples' chamber. The resistivity (ρ) of the samples was recorded in the RH range between 20% to 80% (see Figure 2c), which is considered being the optimal range for their use in the field of wearable electronics.^[64,66,67] Figure 2d portrays relative changes of resistivity ($\Delta\rho/\rho$) of the samples at different RH. It shows that AlgGel, MnAlgGel, and CuAlgGel are characterized by identical humidity responses ($\approx 0.020 \text{ RH}(\%)^{-1}$) in the range from 20% to 60% RH, reaching a plateau of the electrical response for RH exceeding 60%. In contrast, FeAlgGel and

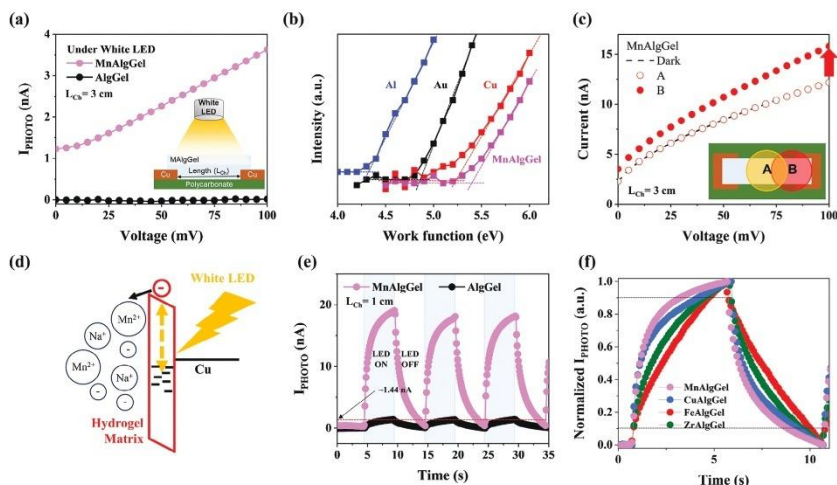


Figure 3. a) Photoreponse of MnAlgGel and AlgGel upon exposure to white LED. Schematic inset image displaying a side-view of MnAlgGel photodetector. b) Secondary-electron cutoff of Al (blue squares), Au (black), Cu (red), and MnAlgGel (pink). c) Current versus voltage characteristics of the MnAlgGel photodetector with a channel length of 3 cm, receiving the photons focused on the local area: a center of hydrogel (Position A) and a metal/hydrogel interface (Position B). d) Band diagram of the MnAlgGel/Cu interface. e) Time-resolved photoresponse of the MnAlgGel and AlgGel photodetector with a channel length of 1 cm. f) Normalized I_{photo} versus time plots of MnAlgGel. All the illuminated area by the LED in this experiment was fixed as a circle with a 1 cm radius.

ZrAlgGel exhibited similar humidity-sensitivity ($0.018 \text{ RH}(\%)^{-1}$ and $0.015 \text{ RH}(\%)^{-1}$, respectively) in a wide range of RH values corresponding to 20–70% and 20–80%, respectively. The broadening of the sensing range can be ascribed to the different water retention capacities among the samples resulting from the higher glycerol content (+3%, w/w) and stiffness of the FeAlgGel and ZrAlgGel samples with respect to the other M^{2+} -crosslinked samples. In general, MnAlgGel samples exhibited humidity sensitivity in the same order of magnitude (0.022 – $0.015 \text{ RH}(\%)^{-1}$, see Table 2), which suggests that glycerol is ruling the sensing process by imparting high hydrophilicity to the matrix. The mechanism behind the sensing comprises the absorption of water into the structure that triggers an increase in the conductivity^[68] by proton/ion transport. After the water absorption, a proton may be transferred to a water molecule to form H_3O^+ and migrate by hopping from site to site across the glycerol moieties along the organohydrogel. Compared with traditional humidity sensing materials, gels feature additional characteristics such as the high stretchability and adaptability that are key for the design of next-generations of e-skins.^[64] To assess the robustness of the crosslinked samples to the exposure at different RHs, they have been exposed to multiple cycles of humidity changes. All samples revealed a complete reversibility in the range of RH from 20% to 80% (Figure S8, Supporting Information, empty dots).

2.4. MnAlgGel Organohydrogels as Photodetectors

A side-view scheme of MnAlgGel photodetector under white LED illumination is illustrated in the inset of Figure 3a. Throughout this study, the illuminated area on the hydrogel devices remains constant at 3.14 cm^2 , forming a circle with a radius of 1 cm. A polycarbonate substrate, which holds promise for wearable device applications (e.g., e-skins) due to its transparency and flexibility, was exploited to assess the photoresponsive characteristics of the MnAlgGel organohydrogel. The copper electrodes (Cu in the inset image of Figure 3a) were patterned onto the polycarbonate substrate as bottom contact electrodes. To optimize the contact electrodes, we tested three different metals (i.e., aluminum, gold, and copper), while employing MnAlgGel as the active channel. Interestingly, MnAlgGel with Cu electrodes exhibited light sensitivity under white LED illumination (Figure 3a), while the other devices with Al and Au electrodes hardly showed photoresponsive characteristics (Figure S9a–c, Supporting Information). Considering the ability of all three metals to facilitate ionic conduction in conventional electrolyte systems,^[69,70] the efficiency of electron injection at the MnAlgGel/Cu interface may promote enhanced ionic conduction within the hydrogel, thereby explaining the observed nontrivial photoresponse. To substantiate this interpretation, the secondary-electron cutoff was estimated using photoelectron yield spectroscopy in air (PYS), as shown in

Figure 3b. The varying work function values from depending on the employed metals result in the formation of a variable built-in electric field in the organohydrogel at the metal/hydrogel interface. The MnAlgGel/Cu contact exhibits the lowest electric field value, while the MnAlgGel/Al contact shows the highest value, thus hindering the injection of photoexcited electrons into MnAlgGel. See Figures S9d–f and S10 (Supporting Information) for more details.

To investigate the interface effect on photoresponse, we meticulously controlled the position of light irradiation, as illustrated in the inset of Figure 3c. We selected two different light exposure positions: i) Position A—placed at the center of hydrogel channel, not including a metal/hydrogel interface—and ii) Position B—located at the metal/hydrogel interface. Upon illumination at Position A, the current displayed a behavior similar to the one observed in the dark. On the other hand, when the LED was illuminating at Position B, a clear photocurrent (I_{PHOTO}) response was observed, demonstrating a 30% increase in ionic current. The importance of the built-in electric field generated at the interface between an ionic conductor and a metal in contributing to I_{PHOTO} has been reported in the literature.^[71,72] In particular, the photoresponse in our MnAlgGel device can be ascribed primarily to the trapped electrons at the metal/hydrogel interface and the resulting built-in electric field. Figure 3d illustrates the band diagram of the MnAlgGel/Cu interface, which is based on the Fermi energy levels of each component, and shows the trap-induced photoresponse. Figure 3a,e demonstrate a distinct difference in I_{PHOTO} between Mn^{2+} -crosslinked hydrogel and non-crosslinked hydrogel. The MnAlgGel device shows the best photoresponsivity compared to the others, as it has the highest polymer content (see Table 1) in the hydrogel, which suggests that MnAlgGel possesses a higher tendency to trap electrons within its polymer matrix.

While factors such as the type of metal, the light irradiation spot, and the active channel length (see Figure S11, Supporting Information) are expected to play an important role in the photoresponse of the materials, the presence of Mn^{2+} ions in gel matrix were found to be also essential to improve the durability/stability of the gel matrix, ensuring suitable ionic conduction. The excellent long-term stability of our hydrogel was confirmed by comparing I_{PHOTO} in its pristine state and after one week of storage under ambient conditions (see Figure S12, Supporting Information). For a channel length (L_{CH}) of 3 cm, MnAlgGel exhibited an I_{PHOTO} exceeding 3.5 nA, whereas AlgGel showed no photoresponse. Even with a channel length shortened from 3 to 1 cm, AlgGel's I_{PHOTO} reaches about 1.4 nA, as indicated by the black arrow in Figure 3e. However, MnAlgGel displayed a much greater photoresponse, with a 15-fold higher I_{PHOTO} compared to the uncrosslinked AlgGel. Additionally, the photoswitching rate of MnAlgGel was benchmarked with the MAlgGel variants containing different cations in Figure 3f. MnAlgGel displayed the fastest photoswitching response (rise time: 2.23 s and fall time: 3.13 s, respectively), while the other MAlgGels exhibited over 3 s of rise time and 3.5 s of fall time. To estimate photoswitching rate, 10% and 90% of normalized I_{PHOTO} were utilized, as represented by the black dashed line in Figure 3f. All estimated values are summarized in Table 2.

2.5. Mechanical Properties and Strain Sensitivity of the MAlgGel Organohydrogels

Figure 4b shows that the mechanical properties of the organohydrogels depend on the nature of the crosslinking cation. All the MAlgGel samples display lower stretchability with respect to the AlgGel sample due to the higher rigidity imparted by the crosslinking. Among the M^{2+} -crosslinked samples, CuAlgGel and MnAlgGel feature the highest stretchability ($\approx 140\%$), while FeAlgGel and ZrAlgGel samples are more rigid (maximum stretchability around 45% and 55% respectively). This phenomenon can be ascribed to the protonation of the alginate's polymer chains during the crosslinking, as a result of the acid pH of the Fe^{3+} and Zr^{4+} solutions. The higher rigidity contributes to increase the linearity of the stress versus strain curves with respect to AlgGel, the latter resembling stress versus strain curves reported in literature for gelatin.^[73] CuAlgGel shows the same behavior, while the interaction between alginate and Mn^{2+} ions is not strong enough to impart linearity. The Young's modulus (YM) of the crosslinked samples was extracted from the slopes of the stress versus strain curves in the 0–0.04 strain range (Figure S13, Supporting Information). The results shown in Table 2 indicate that the YM follows the order $\text{Mn}^{2+} < \text{Cu}^{2+} \approx \text{Zr}^{4+} < \text{Fe}^{3+}$, in analogy with the “long-distance” correlation lengths (ξ_l) extracted by SAXS analysis (see Section S3 and Table S2, Supporting Information). The ultimate tensile strength (UTS) of all the samples was assessed and the results are reported in Table 2. CuAlgGel shows the highest value of UTS (1.88 ± 0.04 MPa), while manganese the lowest (0.64 ± 0.02 MPa). This evidence, along with the YM and ξ_l values obtained, is in agreement with the M^{2+} -alginate affinity scale reported in literature.^[25,26,61] The changes in the ionic pathway induced by stretching the organohydrogels are responsible for significant variation in the conductivity, endowing our products with a huge potential for motion recognition application. We chose the 0–0.25 strain region to assess the electrical response (in terms of relative change of resistance, $\Delta R/R_0$) of the samples, to prove the high sensitivity of the device for low applied stresses. Figure 4c indicates that all the samples undergo a $\Delta R/R_0$ variation close to 50%, but it is important to keep in mind that the strain value does not contain information regarding the stress applied. The Gauge factor (GF) of the organohydrogels was determined using the following equation:^[74]

$$\text{GF} = (\Delta R/R_0) / \epsilon \quad (1)$$

in which $\Delta R/R_0$ is the relative change of resistance, while ϵ is the strain. GF was calculated in the strain ranges 0–0.04 (GF1) and 0–0.25 (GF2) in order to assess that this property is constant for all the examined strain values. The results, reported in Table 2, show that the response of AlgGel sample strongly fluctuates for very low strain values. This can be attributed to the lack of linearity of the stress versus strain curve (Figure S13, Supporting Information). Taking into account the error associated with the GF1 and GF2 (see Table 2), it is clear that CuAlgGel, FeAlgGel and ZrAlgGel are the most reliable among the crosslinked samples. Higher GFs were obtained for the Fe^{3+} and Zr^{4+} -crosslinked samples (2.15 ± 0.07 and 2.27 ± 0.18 ,

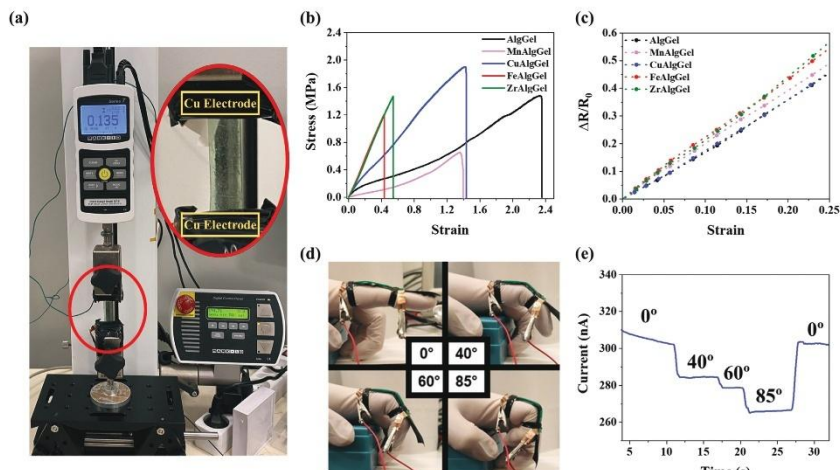


Figure 4. a) Photograph of the experimental setup for the samples connected using two copper electrodes. b) Stress versus strain curves and c) $\Delta R/R_0$ versus strain of AlGgel (black), MnAlGgel (pink), CuAlGgel (blue), FeAlGgel (red) and ZnAlGgel (green). Images of the finger bending steps for d) the strain sensing test and e) related electrical response.

respectively). The values of GF obtained for the MAlGgel (between 1.7 and 2.3) are comparable if not superior to most of the ionic conductive hydrogel strain sensors (typically showing GF falling in the range 0.5–1.7).^[52,54,75] However, considering the high rigidity of FeAlGgel and ZnAlGgel, CuAlGgel is preferable to detect movements that imply small stresses. CuAlGgel was tested to detect the bending of a finger, adopting the setup illustrated in Figure 4d. The organohydrogel proved to be particularly sensitive to the bending angle, as shown in Figure 4e. Furthermore, they demonstrated high durability, maintaining their sensitivity over 2500 stretching cycles (Figure S14, Supporting Information). This evidence, along with the low applied direct voltage required (i.e., 0.2 V), suggests promising perspectives for the use of our products for real time motion monitoring.

3. Conclusion

In summary, we successfully developed a novel class of transparent, stretchable, and multi-responsive organohydrogels, consisting of alginate crosslinked with various transition metal cations (Mn^{2+} , Cu^{2+} , Fe^{3+} , Zr^{4+}) and gelatin. These MAlGgel organohydrogels exhibit remarkable properties required for wearable electronics applications to enable environmental monitoring and human motion recognition. Through a systematic investigation of their mechanical, electrical, thermal, humidity/temperature sensing characteristics, we demonstrated the versatility and potential of these materials. Our results indicate that the addition of glycerol and crosslinking with

metal ions significantly enhance the stability, stretchability, and ionic conductivity of the hydrogels. The ability to modulate mechanical properties and ionic conductivity by varying the crosslinking ions offers flexibility in tailoring the performance of the organohydrogels for specific applications. Moreover, the temperature and humidity sensitivity of the MAlGgel samples (reaching 0.19 K^{-1} and $0.020\text{ RH}(\%)^{-1}$, respectively) make them promising candidates for real-time monitoring of physiological/environmental conditions. Our MAlGgel organohydrogels displayed a remarkable photoresponsivity ($9.2\text{ }\mu\text{A W}^{-1}$ upon exposure to visible light), which is a unique feature not commonly reported in the literature. This advancement opens up new opportunities for integrating wearable sensors with photodetection functionalities for diverse applications, including environmental monitoring and biometric authentication. Furthermore, our investigation into the electrical response of the MAlGgel samples under mechanical strain highlights their potential for motion recognition applications. The high sensitivity (gauge factor >1.6) and reliability of these sensors make them suitable for detecting subtle movements, such as finger bending, with low applied direct voltage (0.2 V) requirements. Overall, our findings contribute to the advancement of wearable electronics by introducing a new class of transparent, stretchable, and multiresponsive hydrogel-based sensors. The tunable properties of these MAlGgel organohydrogels and the biocompatible/biodegradable nature of their organic matrix offer promising avenues for the development of next-generation wearable devices with enhanced functionality and performance. Additional research endeavors in this direction are needed

to fully harness the potential of these materials in real-world applications.

4. Experimental Section

Materials: Alginate acid sodium salt was obtained from Sigma Aldrich (Product code 180947). Mannuronate/guluronate = 1.50 ± 0.04 , determined through FT-IR spectroscopy.^[24] Molecular weight ≈ 132 kDa, determined through viscosimetric analysis.^[24] Gelatin from porcine skin (Product code G2625, type A, gel strength ≈ 175 g Bloom) and glycerol (BioXtra, $\geq 99\%$) were also provided by Sigma Aldrich. Manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, ACS reagent $\geq 99.8\%$) and copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ACS reagent $\geq 99.0\%$) were purchased from Sigma Aldrich. Iron chloride hexahydrate was obtained by Thermoscientific ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99+%, for analysis), while zirconium chloride (ZrCl_4 , $\geq 99.5\%$ trace metals basis) was purchased from Aldrich. Deionized water was used to prepare all the solutions. All reagents were used without any further purification.

Preparation of MAlGel Organohydrogels: 1.36 g of gelatin were dissolved in 11.3 mL of water, gently stirring for 10 min at 50 °C. 3.80 g of an alginate 4% (w/v) water solution were then added, and the mixture was kept stirring at 50 °C for 10 min. The solution was poured into a petri dish (diameter = 9 cm) and let cool down for 20 min at room temperature. The petri dish was then kept in a fridge ($T = 4$ °C) for 10 min. Then, 20 mL of MCl_X (MnCl_2 , CuCl_2 , FeCl_3 and ZrCl_4) 0.5 M water solutions (pH 4.9, 3.1, ≈ 0 , ≈ 0 , respectively) were poured into the petri dish. After 1 h the gels were removed from the petri dish and dipped in 200 mL of deionized water for 1 h. The gels were then cut into squares ($l = 6$ cm) and dip into 30 mL of glycerol 25% (w/v) water solution for 3 h. At that point the gels were removed and kept drying overnight in the fume hood, before cutting 4.5 cm $\times$ 1.0 cm stripes. The obtained samples were named MAlGel (M = Mn, Cu, Fe and Zr). The non-crosslinked sample (i.e., AlGel) was prepared following the previously reported procedure, skipping the crosslinking-washing sections.

Characterization Glycerol Content Determination: The points below were followed, assuming that the amount of ions is not relevant:

- 1) The gels, in their pre-glycerol treatment stage, were dried under fume hood and then under vacuum. Their weight before and after the dehydration was recorded.
- 2) In this way, the ratio between the dry polymer content and the initial hydrogel mass was determined.
- 3) Wet pre-glycerol gels were weighed before undergoing the glycerol addition step. In their post-glycerol treatment stage, the gels were dried under fume hood and then under vacuum. Their weight after the dehydration was recorded.
- 4) The mass of dry polymer in the tested samples derives from point 2.
- 5) The glycerol amount is obtained by subtracting the dry polymer mass and the water content (determined by TGA) from the weight of the dried organohydrogels recorded at point 3.

UV-Vis Spectrophotometry: UV-Vis absorbance spectra of the gels were collected with a Cary UV-Vis multi-cell spectrometer (Agilent) in the 200–1000 nm range, simply sticking the gels to the wall of a quartz cuvette perpendicular to the light path.

Thermogravimetric Analysis (TGA): Discovery SDT650 (TA Instruments) was used to perform Thermogravimetric analysis. All the analyzed samples were previously equilibrated at RH = 33%. A heating ramp from room temperature (RT) to 1000 °C, with a rate of 10 °C min^{-1} , was applied to determine the degradation profile of the samples. Measurements were performed under air flux (100 mL min^{-1}), using aluminum pans. For the water content determination, a heating ramp from RT to 120 °C (rate of 10 °C min^{-1}), followed by a 10 min isotherm was applied. Measurements were performed under N_2 flux (100 mL min^{-1}), using aluminum pans. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Measurements were performed in duplicate.

Differential Scanning Calorimetry (DSC): DSC analysis was carried out by means of Discovery DSC 2500 (TA Instruments). Tzero aluminum hermetic pans (TA Instruments) were used for all the measurements. For the determination of the glass transition temperature (T_g), the samples were analyzed by applying a heating ramp from 5 °C to 80 °C, with a heating rate of 10 °C min^{-1} . In order to define the state of the water in the samples, the latter were subjected to a cooling ramp from 5 °C to -60 °C, followed by a heating ramp from -60 °C to 25 °C (in both cases with an heating rate of 1 °C min^{-1}). Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Measurements were performed in duplicate.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES): The content of crosslinking ions (Mn^{2+} , Cu^{2+} , Fe^{3+} , Zr^{4+}) in the MAlGel samples was determined using an Agilent 720-ES Inductively coupled plasma-atomic emission spectrometer (ICP-AES) equipped with a pneumatic nebulizer and a cyclonic spray chamber. Prior the analysis, approximately 10 mg of each sample was kept in 2 mL of a Na_2EDTA 0.05 M + NaOH 10% (w/v) water solution (2.00 mL and 0.100 mL respectively) for 1 h at 80 °C, under magnetic stirring. After dissolution, 1 mL of the solution was diluted 6 times with MilliQ water. The calibration lines were obtained by preparing the standard solutions starting from commercial standards certified at 1000 ppm. After each measurement, the system was washed with a 2% HNO_3 solution. Measurements were performed in triplicate.

Scanning Electron Microscopy (SEM): The morphology of the gels (prior to the glycerol addition) was assessed using a FEI Quanta FEG 650 scanning electron microscope. Samples were lyophilized at the end of the washing step of the preparation procedure. A 20 nm thick gold layer was sputtered on the samples. The micrographs were acquired with an accelerating voltage of 30 kV, sample-detector distance around 9.5 mm and using a detector for secondary electrons.

Small-Angle X-Ray Scattering (SAXS): Small-angle X-ray scattering analysis was carried out using Xeuss 3.0 (Xenocs). $\text{Cu K}\alpha$ radiation with a wavelength (λ) of 1.542 Å at a power of 30 W was obtained using an ultrabright point microfocus X-ray source (GENIX-Fox 3D, Xenocs, Grenoble). Two sample-to-detector distances of 450 and 1800 mm (calibrated using silver behenate) provided a measurable q -range between 0.006 and 0.6 Å $^{-1}$ (where q , the scattering vector, is given by $q = 4\pi/\lambda \sin \theta$, and 2θ is the scattering angle). Measurements were performed under vacuum using hermetic gel holders. Data were analyzed using Sasview software (<https://www.sasview.org/>).

Mechanical Properties: The mechanical properties of the organohydrogels were assessed using a Mark-10 M7-025E digital force gauge mounted on a Mark-10 ESM-303E motorized test stand. Samples were clamped at the edges: the length of the stretchable region was equal to 3 cm.

Temperature Sensitivity Test: The temperature sensitivity measurements were carried out using rectangular hydrogel stripes of 33 mm (length) $\times$ 10 mm (width) that were first connected with conductive copper tape on top of the Kapton/ Al_2O_3 cylinder. Subsequently, the samples were transferred to a home-made temperature test chamber, and the cylinder was filled with water at different temperatures. Finally, the samples were connected to the probe workstation (Keithley 2636B). The sensitivity of the samples was tested increasing the temperature from 10 °C to 50 °C. The related I versus t curves were recorded applying a direct voltage of 1 V. For the sensitivity evaluation, the conductivity versus temperature was plotted to obtain linear correlation. For each hydrogel sensor, three samples were tested and one of them was measured three times to assess the self-stability of the samples.

Humidity Sensitivity Test: The humidity sensitivity measurements were carried out using rectangular hydrogel stripes of 36 mm (length) $\times$ 2 mm (width), connected with iron crocodiles on a PCB board. A homemade humidity chamber was employed for the RH sensing test at room temperature. Finally, the samples were connected to the probe workstation (Keithley 2636B). During the testing, the RH was changed by adding either wet or dry air from a commercial humidifier. The humidity inside the chamber was monitored using a commercial humidity sensor (Sensirion SMART). The relative humidity of the test chamber was increased from 20% to 80% and the related I - t curves were recorded applying a direct voltage of 1 V. For the sensitivity evaluation, the resistivity versus relative humidity was plotted to obtain linear correlation. For each hydrogel sensor, three

samples were tested and one of them was measured three times to assess the self-stability of the samples.

Photoresponsivity: Photoelectrical measurements of all organohydrogel-based photodetectors were performed using a Keithley dual-channel 2636B sourcemeter at room temperature under dark and white LED, with an intensity of 3.47 mW cm^{-2} (ambient condition).

Photoelectron Yield Spectroscopy: The work function (WF) was measured by photoelectron yield spectroscopy in air (PYSA), using a AC-2 photoelectron spectrometer (Riken-Keiki Co.). The ambient photoelectron yield measurements were performed onto an Au/glass pattern substrate for the organohydrogels, which was prepared by photolithograph and thermal evaporation, and placing the gel directly on the metal electrodes. The ultraviolet (UV) incident light powers were of 300 nW for the metal electrodes, and 1000 nW for the organohydrogels with a counting time of 10 s per point.

Strain Sensitivity Tests: The sensitivity of the MAgGel samples to strain was assessed using a Mark-10 M7.025E digital force gauge mounted on a Mark-10 ESM-303E motorized test stand. Samples were clamped at the edges (the length of the stretchable region was equal to 3 cm) and then connected to the probe workstation (Keithley 2636B) to measure current variations. The related I - f curves were recorded applying a direct voltage of 1 V. For the sensitivity evaluation, the normalized change in resistance versus strain to obtain a linear correlation was plotted. The experimental setup is illustrated in Figure 4a.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P.T., A.T., and Y.J. contributed equally to this work. P.T., A.T., Y.J., M.B., and P.S. conceived the experiments and designed the study. P.T., A.T., and Y.J. performed all electrical characterization. All authors discussed the results and contributed to the interpretation of data. P.T., A.T., Y.J., M.B., and P.S. cowrote the paper.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

alginate, gelatin, multiresponsive sensors, organic electronics, wearable electronics

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Cation-Alginate Complexes and Their Hydrogels: A Powerful Toolkit for the Development of Next-Generation Sustainable Functional Materials

Pietro Tordi, Francesca Ridi, Paolo Samorì,* and Massimo Bonini*

The use of materials from renewable sources instead of fossil fuels is a crucial step forward in the industrial transition toward sustainability. Among polysaccharides, alginate stands out as a versatile and eco-friendly candidate due to its ability to form functional complexes with cations. This review provides an up-to-date and comprehensive description of alginate complexation with specific cations, focusing on how interaction forces can be harnessed to tailor the physicochemical properties of cation-alginate-based functional materials. Methodologies and approaches for the development and multiscale characterization of these materials are introduced and discussed. Alginate complexes with mono-, di-, tri-, and tetravalent cations (namely Ag^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , UO_2^{2+} , Cr^{3+} , Fe^{3+} , Al^{3+} , Ga^{3+} , Y^{3+} , La^{3+} , Ce^{3+} , Nd^{3+} , Eu^{3+} , Tb^{3+} , Gd^{3+} , Zr^{4+} , Th^{4+}) are reviewed. Each cation is discussed individually, highlighting how it can uniquely influence the material properties thereby unlocking new potentials for the design of advanced functional materials. Key challenges and opportunities in applying these complexes across diverse fields, such as biomedicine, environmental remediation, food additives and supplements, flame retardants, sensors, supercapacitors, catalysis, and mechanical isolators are assessed, providing evidence of the transformative potential of cation-alginate complexes for tackling global challenges and advancing cutting-edge technologies.

1. Introduction

Alginate is an anionic polysaccharide primarily sourced from brown algae of the Phaeophyceae family^[1] through alkaline extraction, which was first described by E.C.C. Stanford in 1881.^[2] However, its presence in certain bacteria has also been documented.^[3] Certified as a safe product by the Food and Drug Administration (FDA) and classified as a food additive, alginate finds extensive use in medical, food, and cosmetic applications. The polymer structure, which has been extensively elucidated by means of ^1H - and ^{13}C -NMR analyses,^[4–7] consists of (1,4) linked β -D-Mannuronate and α -L-Guluronate residues. The ratio of Mannuronate to Guluronate (M/G)^[8–10,4] and the sequence of the residues can vary depending on the extraction source, leading to the coexistence within the same polymeric chain of homogeneous (GG or MM) and heterogeneous blocks (GM or MG).^[4] Alginates are commercial products typically comprising a G-block content ranging from 14.0% to 31.0%, while their average molecular weight falls between 32 and 400

kDa,^[11] resulting in significant differences in the viscosity of aqueous solutions. Another crucial factor affecting the viscosity is the pH level. An increase in proton concentration significantly raises the viscosity, reaching its maximum at pH values close to 3.5. At this pH, carboxylate groups become protonated, promoting strong interchain interactions facilitated by hydrogen bonds.^[11] The carboxylate groups existing in the residues can strongly interact at the supramolecular level with cationic species, resulting in the formation of complexes with diverse geometries (see Figure 1). This chain reassembling, known as crosslinking, occurs with monovalent, divalent, trivalent, and tetravalent cations, and offers a straightforward method for producing hydrogels. The nature of the complex is heavily influenced by the ion's charge, size, as well as the sequence of the M and G residues, thereby impacting on the properties of the resulting hydrogel. Alginate's biocompatibility and biodegradability, combined with tunable cation interactions, offer a powerful approach to developing advanced materials. This can drive sustainable technologies, improve industrial processes, and reduce reliance on synthetic polymers, promoting eco-friendly

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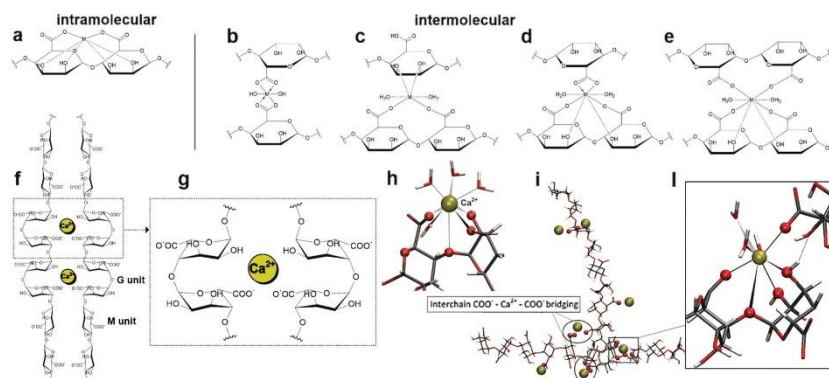


Figure 1. Cation-alginate coordination geometries: intramolecular a) and intermolecular coordination b–e) Adapted with permission.^[13] Copyright 1993, John Wiley and Sons. f) Alginate egg box coordination of Ca^{2+} ions, as proposed by Fu et al.,^[14] based on Grant's and Morris' evidences.^[15,16] Adapted with permission.^[17] Copyright 2019, Springer Nature. This panel highlights the role of G units in chelating the Ca^{2+} ions. g) Inset where the coordination geometry is magnified. h) The egg-box binding site for Ca^{2+} and i) two poly-G chains aggregating in a perpendicular motif via three bridging Ca^{2+} ions, as obtained from molecular dynamics simulations. Reproduced with permission.^[18] Copyright 2013, Elsevier. The inset highlights the details of the egg box component of this junction zone. Oxygen atoms that are directly interacting with a calcium ion are rendered as small red spheres. In (h) and (i) oxygen atoms on the poly-G chains are shown as red spheres, while coordinated water molecules are shown as stick models.

alternatives for a more sustainable future. Despite extensive research on alginate, to the best of our knowledge only one work has tried to summarize properties and applications of different cation-alginate complexes (limiting the focus to a reduced number of cations)^[12] in fact, the extensive literature on alginate poses a challenge in gaining a comprehensive knowledge, discouraging the adoption of a wide perspective and hindering a systematic research in the field.

This review fills a gap in the literature by providing a comprehensive overview of how combining alginate with various cations modulates the physicochemical properties of metal-alginate complexes. Recent studies often focus on individual ions, overlooking broader comparisons across systems. To guide researchers, we have organized the content into distinct sections, highlighting the significant potential of cation-alginate complexes in functional materials development. This structure is designed to engage both novice and expert readers, offering essential knowledge for beginners and a detailed, accessible resource for experienced researchers seeking the latest findings.

Section 2 provides a comprehensive overview of the strategies and characterization techniques crucial for developing cation-alginate complexes and understanding their physical and chemical properties. It covers crosslinking methods, nanocomposite formation, advanced processing, and essential validation techniques. Subsequently, Section 3 explores ion-specific interactions that shape the behavior of these complexes, organized by cation valency to highlight each cation's unique influence on material properties. This detailed analysis, at atomic, molecular, and supramolecular levels, is vital for understanding how cation-alginate complexes can be optimized for designing ad-

vanced functional materials. **Table 1** effectively summarizes key aspects of ion-alginate complexation discussed in Section 3, spanning from the molecular level to the properties of the hydrogel matrix.

Finally, in Section 4, the functional applications of these complexes are reviewed, organized by application type to highlight their current uses and future potential. The section emphasizes how interaction strength impacts application suitability (e.g., strong cation interactions enhance toughness and resistance for mechanically demanding uses, while weaker interactions enable cation exchange or release in more dynamic applications). Opportunities and challenges are discussed, proposing a roadmap for future research in this promising field. The information above is summarized in **Table 2**, which highlights the sectors that could benefit from the use of M^{2+} -alginate complexes: the physicochemical properties described in Table 1 impart specific functionalities and, as a consequence, determine the potential for applications.

2. Strategies and Characterization Techniques for the Development of Functional Materials Based on Cation-Alginate Complexes

Cation-alginate complexes are essential for creating functional materials with tunable mechanical properties, biocompatibility, and responsiveness. This section covers key strategies for developing these materials, including crosslinking, composite formation, advanced processing methods, and characterization techniques. We intentionally exclude discussion of chemical modifications to the alginate backbone, as these have been extensively

Table 1. Cation-specific complexation modalities and hydrogel matrix properties. References for each specific ion are also provided.

Cation	Complexation	Hydrogel properties	References
Ag ⁺	- Inter/Intramolecular - Involving carboxylate and hydroxyl groups	- Low-strength gel - Biocompatible - Antimicrobial	[77, 91–94]
Mg ²⁺	- Inter/Intramolecular - Involving carboxylate and hydroxyl groups	- Low-strength gel - Biocompatible	[102–104]
Ca ²⁺	- Inter/Intramolecular - Egg box buckled chain structure involving G blocks	- Medium-strength gel - Biocompatible	[15, 16, 24, 25, 83, 97–99, 101, 108–110, 129]
Sr ²⁺	- Inter/Intramolecular - Egg box buckled chain structure involving G blocks - More interaction sites than Ca ²⁺	- Medium/High-strength gel - Biocompatible - Osteogenic	[32, 97–99, 101, 132, 134–137, 141]
Ba ²⁺	- Inter/intramolecular - Egg box buckled chain structure involving G and M blocks - More stable than Ca ²⁺ and Sr ²⁺	- High-strength gel - Biocompatible	[34, 97–99, 101, 142, 143, 145–148]
Mn ²⁺	- Inter/Intramolecular - Involving carboxylate and hydroxyl groups from G and M blocks	- Low/Medium-strength gel - MRI active	[72, 97–99, 101, 153, 156]
Co ²⁺	- Inter/Intramolecular - Involving carboxylate and hydroxyl groups from G and M blocks - Stronger than Mn ²⁺	- Medium-strength gel - Toxic	[72, 97–99, 101, 162]
Ni ²⁺	- Inter/Intramolecular - Involving carboxylate and hydroxyl groups	- Medium-strength gel - Toxic	[97–99, 101, 167, 168, 170, 171]
Cu ²⁺	- Inter/Intramolecular - Egg box buckled chain structure for low Cu ²⁺ concentration - Lower binding selectivity than Ca ²⁺	- High-strength gel - Biocompatible - Antimicrobial	[15, 68, 72, 97–99, 101, 175–181]
Zn ²⁺	- Inter/Intramolecular - Involving carboxylate and hydroxyl groups - Not ascribable to egg box	- Medium-strength gel - Biocompatible - Antifouling	[15, 74, 97–99, 101, 189, 190, 196]
Cd ²⁺	- Inter/Intramolecular - Involving carboxylate and hydroxyl groups	- High-strength gel - Toxic	[97–99, 101, 197, 202]
Pb ²⁺	- Inter/Intramolecular - Involving carboxylate and hydroxyl groups	- High-strength gel - Toxic	[97–99, 101, 203–205]
UO ₂ ²⁺	- Inter/Intramolecular - Involving carboxylate and hydroxyl groups	- Gel strength not documented - Toxic	[208]
Cr ³⁺	- Inter-molecular (predominant) - Involving carboxylate and hydroxyl groups	- Gel strength not documented	[209, 211, 212]
Fe ³⁺	- Inter-molecular (predominant) - Involving carboxylate and hydroxyl groups - Concurrent alginate protonation	- High-strength gel - Biocompatible	[209, 222–226]
Al ³⁺	- Inter-molecular (predominant) - Involving carboxylate and hydroxyl groups - Concurrent alginate protonation	- High-strength gel - Biocompatibility not assessed	[209, 227, 231, 232]
Ga ³⁺	- Inter-molecular (predominant) - Involving carboxylate and hydroxyl groups	- Medium-strength gel - Biocompatible - Antimicrobial	[35, 209, 233–236]
Y ³⁺	- Inter-molecular (predominant) - Involving carboxylate and hydroxyl groups	- Gel strength not documented - Biocompatibility not assessed	[209, 237–240]
La ³⁺	- Inter-molecular (predominant) - Involving carboxylate and hydroxyl groups	- Gel strength not documented - Biocompatibility not assessed	[209, 241, 242, 246]
Ce ³⁺	- Inter-molecular (predominant) - Involving carboxylate and hydroxyl groups	- Medium/high-strength gel - Biocompatible - Antimicrobial	[209, 247–250]
Nd ³⁺	- Inter-molecular (predominant) - Involving carboxylate and hydroxyl groups	- High-strength gel - Biocompatible - Fluorescent	[75, 209, 251, 252]
Eu ³⁺	- Inter-molecular (predominant) - Involving carboxylate and hydroxyl groups	- Gel strength not documented - Fluorescent	[209, 254]

(Continued)

Table 1. (Continued)

Cation	Complexation	Hydrogel properties	References
Tb ³⁺	- Intermolecular (predominant) - Involving carboxylate and hydroxyl groups	- Gel strength not documented - Fluorescent	[209, 254]
Gd ³⁺	- Intermolecular (predominant) - Involving carboxylate and hydroxyl groups	- Gel strength not documented - Biocompatible - MRI active	[209, 255]
Zr ⁴⁺	- Intermolecular - Involving carboxylate and hydroxyl groups - Concurrent alginate protonation	- High-strength gel	[13, 256–260]
Th ⁴⁺	- Intermolecular - Involving carboxylate and hydroxyl groups	- Gel strength not documented - Toxic	[13, 261, 262]

covered in the literature. Modifications like grafting methacrylate, cyclodextrins, amine groups, oxidation, sulfation, or hydrophobic alterations are well-documented for alginate and other polysaccharides.^[19–22]

Readers are encouraged to consult these sources for comprehensive details on such modifications. Within this context, it is important to note that these chemical modifications can significantly enhance the mechanical properties, biocompatibility, and functionality of materials. Additionally, partial

chemical modifications can synergistically complement cation-alginate interactions, which are the primary focus of this review.

2.1. Crosslinking Strategies

Crosslinking is a powerful method to form cation-alginate complexes, by transforming the water-soluble polymer into a gel

Table 2. Function and sector of possible impact of the M^{K+}-alginate complexes described in this review. References for each specific cation are also provided.

Function	Sector of possible impact	Cation
Carrier (release and uptake)	– Water purification – Drug delivery – Wound healing – Agriculture	Ag(I) ^[77,91] ; Mg(II) ^[104] ; Ca(II) ^[24,25,27,108–110,113,115,116] ; Ba(II) ^[149–151] ; Mn(II) ^[140,161] ; Ni(II) ^[69,173,172,174] ; Zn(II) ^[193,196] ; Fe(III) ^[215–218,224–226] ; Al(III) ^[227–230] ; Y(III) ^[238–240] ; La(III) ^[242–244,246] ; Ce(III) ^[249] ; Zr(IV) ^[256–260]
Contrast agent	– Medical imaging	Mn(II) ^[156–158] ; Gd(III) ^[255]
Scaffold for cell growth	– Tissue engineering – Regenerative medicine	Ca(II) ^[26,117–120] ; Sr(II) ^[134–141] ; Ba(II) ^[33,145–147] ; Mn(II) ^[157] ; Co(II) ^[165] ; Cu(II) ^[24,179] ; Fe(II) ^[222,223] ; Ga(III) ^[25,236]
Antimicrobial	– Tissue engineering – Wound healing – Antifouling treatments	Cu(II) ^[177–181] ; Zn(II) ^[74,189,190] ; Ga(III) ^[233,235] ; Ce(III) ^[250]
Food additive and supplements	– Food packaging – Food storage – Dietary supplements – Nutraceuticals	Ca(II) ^[39,30,128–131] ; Zn(II) ^[131]
Flame retardant	– Automotive – Textiles – Building and construction – Wires and cables – Electronics	Ba(II) ^[144] ; Mn(II) ^[81] ; Co(II) ^[41,186] ; Ni(II) ^[169] ; Zn(II) ^[80,192] ; Fe(III) ^[79] ; Al(III) ^[79,231]
Catalyst	– Organic synthesis – Water purification	Cu(II) ^[182–184]
Supercapacitor ^[203]	– Automotive – Electronic devices – e-skins	Ca(II) ^[122] ; Zn(II) ^[194]
Sensor	– Environmental monitoring – Physiological monitoring – Robotics – e-skins	Ca(II) ^[125–127] ; Mn(II) ^[76] ; Cu(II) ^[176,185] ; Fe(II) ^[76] ; Eu(III) ^[254] ; Tb(III) ^[254] ; Zr(IV) ^[26]
Vibration isolator	– Automotive – Aerospace – Construction – Electronics	Al(III) ^[232]

or solid material with specific mechanical and structural properties. The choice of cation and crosslinking method dramatically affects the properties of the final material, as highlighted in the following section where cations are individually discussed. The most commonly employed method involves the ionic crosslinking of alginate with divalent cations like calcium (Ca^{2+}).^[23–27] This process leads to the formation of hydrogels through interactions between the cations and the G-blocks of alginate. Calcium-alginate gels are widely used due to their biocompatibility and ease of gelation, making them ideal materials for agriculture,^[28] food,^[29–31] and biomedical applications,^[32–35] such as soil conditioners, controlled-release fertilizers, gelling agents, edible films, wound dressings, and drug delivery systems.

Crosslinked alginate networks can be formed through either external or internal gelation. In external gelation, the crosslinker diffuses toward the interior of the polymer solution. In internal gelation, the crosslinker is embedded within the alginate in an insoluble form and is gradually released (typically by lowering the pH of the medium), often by adding a reactant. Controlling the crosslinking kinetics allows for the preparation of networks with different mechanical strengths and stabilities, as well as materials with anisotropic properties. Layered crosslinking is also possible, adopting an external gelation approach^[25]; this advanced technique often involves the sequential layering of different cations, which can create materials with gradient properties or hierarchical structures. Layered crosslinking can also be achieved using a single cation as a function of its concentration. The diffusion process creates uneven concentration gradients of the crosslinker, leading to discontinuities in the gel's physicochemical properties. This method is useful for developing materials with complex mechanical requirements, such as those required for the successful integration into multifunctional biomedical devices.

2.2. Composites

Cation-alginate complexes can function as matrices that allow for the incorporation of specific micro- and/or nanomaterials to enhance the properties of the composite. This can be done either by using cations as precursors for the in situ formation of nanostructures or by adding pre-formed nano- or microstructures to alginate dispersions, where they can act as active crosslinkers or fillers. This approach improves the material's functionality, introducing additional properties, such as conductivity, magnetism, or antimicrobial activity, depending on the specific materials utilized.^[36–39]

Embedding metallic nanoparticles (NPs) like silver or gold into cation-alginate matrices can impart antimicrobial^[40–42] and/or catalytic properties^[43,44] to the material. For example, silver nanoparticle-enhanced calcium-alginate hydrogels have demonstrated significant promise in wound healing applications by preventing bacterial infections and promoting tissue regeneration.^[45,46]

The combination of magnetic nanoparticles with cation-alginate complexes allows for the design of magnetically responsive materials, which are highly valuable in targeted drug delivery,^[47] where an external magnetic field can direct the mate-

rial to a specific location in the body, or in environmental cleanup efforts,^[48] where magnetic fields can be used to recover the material after it has adsorbed pollutants.

By incorporating conductive nanomaterials, such as graphene, carbon nanotubes, or 2D metal carbides (MXenes) into cation-alginate complexes, electrically active hydrogels or films can be fabricated.^[49–54] These materials are ideal for flexible electronics, electromagnetic shielding, biosensors, and electroactive tissue engineering, where electrical stimulation impacts cell behavior and tissue growth.

Graphene and MXenes have also been shown as effective fillers in nanocomposites including alginate for the preparation of ion-selective membranes for different applications, such as enhanced ion-sieving membranes for recovery of acids from iron-containing wastewater^[55] and for osmotic energy harvesting by reverse electrodialysis.^[56]

SiO_2 reinforced-alginate hybrid films have been shown to improve the poor Coulombic efficiency and unsatisfactory lifespan of aqueous rechargeable Zn metal batteries^[57]; in fact, the ability to modulate metal solid-liquid interaction energy and spatial distribution of all species in the electric double layer (EDL) near the Zn electrode stabilizes the Zn/electrolyte interface which often causes Zn dendrite growth and side reactions.

2.3. Advanced Processing Techniques

Processing techniques are crucial in shaping cation-alginate complexes into functional forms that meet specific application needs. The method of processing often dictates the material's morphology, mechanical properties, and overall performance. As mentioned earlier, the ability to control the kinetics of cation crosslinking allows for the creation of complex, gradient materials with customized mechanical and biological properties. This can be best achieved through a subtle control over the interplay of concentration (of both cation and alginate), viscosity, and processing technique, such as casting, extrusion, spraying, etc.^[38–60]

Cation-alginate complexes and hydrogels are highly compatible with 2D and 3D printing technologies, which allow for the high-throughput fabrication of intricate, custom-shaped structures. These methods are particularly beneficial in creating patient-specific implants or scaffolds for tissue engineering,^[58] where precise geometry, tunable porosity, and structural integrity are critical, as well as microparticles for the immobilization and culture of algal cells and single cell encapsulations.^[12]

Highly porous, low-density structures with controlled pore size and distribution can be prepared by freeze-drying cation-alginate gels.^[61] These materials are ideal for use in tissue engineering, where porosity is necessary for cell infiltration and nutrient diffusion, an in environmental applications, where high surface area is crucial for adsorption processes.

Another strategy toward the preparation of materials with high surface area and tunable porosity is electrospinning,^[62] which can be used to produce nanofibrous mats of cation-alginate complexes. These characteristics are advantageous for applications such as tissue scaffolds, where the high surface area promotes cell attachment and growth, or in filtration membranes, where porosity is key to performance.

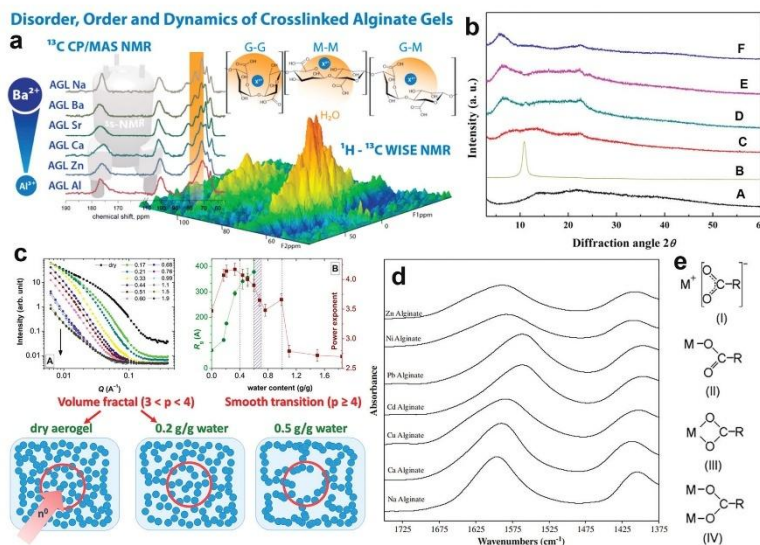


Figure 2. a) Sketch illustrating the potential of NMR in studying M^{x+} -crosslinked alginate samples. Adapted with permission.^[63] Copyright 2017, American Chemical Society. b) XRD patterns of (A) Na-alg, (B) GO (graphene oxide), (C) Na-alg/GO, (D) Ca-alg/GO, (E) Ba-alg/GO, and (F) Fe-alg/GO. Adapted with permission.^[65] Copyright 2016, John Wiley and Sons. c) Small-angle neutron scattering (SANS) measurements of Ca-alginate aerogel (CaAG) at various hydration levels (A). The scattering curves represent CaAG samples with different water contents, and have been vertically offset for clarity. The arrow indicates the direction of increasing water content in the samples, with the specific water contents provided in the legend in g/g units. Power exponent (p) values and gyration radius, estimated using the Beaucage model, plotted as a function of the water content in CaAG. The dotted vertical lines mark the approximate water content levels at which notable structural changes take place (B). Adapted with permission.^[66] Copyright 2021, American Chemical Society. d) FT-IR spectra of (from bottom to top) $Na^+/Ca^{2+}/Cu^{2+}/Cd^{2+}/Pb^{2+}/Ni^{2+}/Zn^{2+}$ -crosslinked alginate and e) coordination geometries for the M^{x+} -carboxylate coordination: ionic (I), monodentate (II), bidentate chelating (III), and bidentate bridging (IV). Adapted with permission.^[64] Copyright 2009, Elsevier.

2.4. Characterization Techniques for Validating Cation-Alginate Complexes

Developing functional materials based on cation-alginate complexes requires thorough, multiscale characterization to link structure and properties, ensuring they meet application-specific requirements. This section offers a guide to key characterization tools relevant for designing and optimizing these materials. Techniques are organized by the specific properties they assess, enabling a more efficient, targeted approach. By utilizing these comprehensive methods, researchers can rigorously validate the properties and functionalities of cation-alginate complexes, ensuring their suitability for various practical applications.

2.4.1. Structural and Compositional Analysis

To unravel the structural and compositional characteristics of these complexes, several techniques could be employed.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for unraveling the assembly of the alginate chains around the cationic species, reaching atomic-resolution (see Figure 2).^[63] Fourier transform infrared spectroscopy (FT-IR) is instrumental in confirming interactions between alginate and cations, as it identifies shifts in characteristic absorption bands.^[64] This method is particularly useful for revealing the extent of crosslinking and the presence of specific functional groups within the complex. X-ray diffraction (XRD)^[65] further complements this by providing insights into the crystalline structure, especially when filler materials are incorporated. Through XRD, the phase distribution and crystallinity, which are critical for assessing the material's mechanical properties and overall stability, can be assessed. Small angle scattering of neutrons and X-rays (SANS and SAXS)^[66–68] can significantly complement structural studies by providing detailed insights into the nanostructure of cation-alginate complexes, with the distinct advantage of allowing the investigation of hydrated samples, such as hydrogels, in their native state without the

need for drying, thereby preserving their inherent structural characteristics.

For compositional analysis, inductively coupled plasma atomic emission spectroscopy (ICP-AES) is used to precisely quantify the elements in the cation-alginate complexes. This technique is particularly valuable for determining the concentration and distribution of cations within the material, providing essential data for understanding how these ions influence the material's properties. When focusing on the surface elemental composition and chemical states, X-ray photoelectron spectroscopy (XPS) plays a crucial role, thereby confirming the presence of cations and understanding the nature of their binding with the alginate.^[69]

2.4.2. Morphological and Microstructural Analysis

Examining the morphology and microstructure of cation-alginate complexes requires the use of advanced imaging techniques, especially in composites where fillers are incorporated within alginate. Field emission scanning electron microscopy (FE-SEM)^[25] offers high-resolution images of the surface without the need for metallization, allowing for detailed observation of porosity, surface roughness, and, when present, the distribution of filler particles. For an even more detailed view of the internal nanostructure, transmission electron microscopy (TEM) could be employed. TEM provides essential information on the dispersion, size, and interaction of fillers within the alginate matrix, which is vital for understanding how composites will perform in various applications. Additionally, Cryo-transmission electron microscopy (cryo-TEM) can be utilized to examine thin sections of hydrogels at cryogenic temperatures, preserving their native hydrated state and providing further insights into their internal structure and interactions without the need for drying. Atomic force microscopy (AFM) and confocal laser scanning microscopy (CLSM) are effective in analyzing the interior morphology of cation-alginate hydrogels,^[70,71] where uniform crosslinking plays a critical role. This uniformity not only ensures the long-term stability of the microcapsules but also significantly influences their mechanical properties, such as elasticity and resistance to deformation.

2.4.3. Mechanical Properties

Understanding the mechanical properties of cation-alginate complexes is crucial, particularly for applications requiring robust materials. Rheometry is commonly exploited to assess the viscoelastic properties of hydrogels.^[14,23,72] By examining gelation kinetics and crosslinking density, rheometry offers detailed information on the mechanical stability of the materials under stress. Furthermore, the results from rheometry can be analyzed using various models to derive structural insight on the network, which helps in understanding the material's behavior under different conditions.

Tensile and compression testing are essential for evaluating the mechanical strength, elasticity, and durability of the complexes.^[73–75] These tests are particularly important for applications like load-bearing tissue scaffolds, where mechanical performance is critical. As the development of functional materials expands into areas, such as wound healing patches, sensors,

and artificial skins, adhesion tests are becoming increasingly relevant, especially to evaluate the ability of the materials to adhere to different surfaces, which is crucial for ensuring effective performance in practical applications.

2.4.4. Thermal Properties

The thermal behavior of cation-alginate complexes is another key area of focus. Differential scanning calorimetry (DSC) is utilized to investigate thermal transitions, such as the glass transition temperature (T_g), which can indicate changes in the self-assembly dictated by cation interactions.^[76,77] Additionally, low-temperature differential scanning calorimetry (LT-DSC) is particularly relevant for understanding the interaction between cation-alginate complexes and water.^[78] In fact, LT-DSC allows for the quantification of free and bound water within the material, offering valuable insights into how water influences the thermal properties and stability of the complexes. This technique provides essential information on the hydration state of the material, which is crucial for applications involving moisture-sensitive environments.

Thermogravimetric analysis (TGA) is also critical, as it monitors weight loss with temperature, providing important insights into the thermal degradation behavior of the material (which often depends on the presence of different cations) and the content of any incorporated solid material.^[79–81]

2.4.5. Swelling and Degradation Behavior

Swelling and degradation behaviors are important for applications like soil conditioning, edible films, drug delivery, and tissue engineering.^[82,83] Swelling ratio measurements provide information on the crosslinking density and the material's responsiveness to environmental conditions. These measurements are crucial for designing materials that can perform effectively in specific settings. Notably, in vitro degradation tests are conducted to monitor the rate of degradation under physiological conditions,^[83,84] helping to predict the material's lifespan and performance in biomedical contexts. These tests also offer insights into how different cations affect the stability and durability of the material. In particular, swelling and degradation tests serve as important prescreening tools to assess the suitability of samples before more complex and costly biological tests are carried out, ensuring that only the most promising candidates advance to the next stage of evaluation.

2.4.6. Biological Properties

Finally, the biological properties of cation-alginate complexes are of paramount importance, especially for biomedical applications. Ensuring biocompatibility is a critical step, and this is often achieved through cytotoxicity assays, such as MTT or Live/Dead staining.^[85–87] These assays evaluate the impact of the complexes on cell viability, which is essential for ensuring their safety and effectiveness in medical contexts. Additionally, cell adhesion and proliferation studies are conducted to assess how well cells adhere to and proliferate on cation-alginate scaffolds. The data are

crucial for applications in tissue engineering and regenerative medicine, where the interaction between the material and biological cells is a key factor in success.

3. Ion-Specific Interactions and Their Impact on Cation-Alginate Complexes

The previous section's strategies and validation techniques highlight the versatility of cation-alginate complexes in material design. Their tunability, biocompatibility, and sustainability make them a key platform for next-generation materials. This section delves into the interactions between alginate and various cations, grouped by valence. The cation's nature crucially impacts properties like gelation behavior, mechanical strength, and thermal stability. By examining monovalent, divalent, trivalent, and tetravalent cations, we offer a comprehensive overview of how these interactions shape functional materials, enabling customization for specific applications.

3.1. Monovalent Cations

Alginate is notorious for its strong affinity toward divalent cations, such as calcium and strontium, also because of the relevance of these cations in biomedical^[11] and food applications.^[88] However, this focus often overlooks instances where alginate also coordinates monovalent cations like sodium, potassium, and, more relevant toward functional materials, silver.

3.1.1. Silver

Despite the widespread use of alginate composite materials containing silver nanoparticles or silver flakes,^[42,89] there is a scarcity of literature offering a molecular level insight into the crosslinking of alginate with silver cations. This shortage can be attributed to the relatively weak nature of the Ag^+ -alginate interaction, often ascribed to the large ionic radius of Ag^+ (1.15 Å).^[90] which limits the number of accessible binding sites and the diversity of products that can be obtained. Nevertheless, the antimicrobial, electronic, and SERS (surface-enhanced Raman spectroscopy)-enhancing properties of Ag have garnered significant interest from researchers. Hassan and co-workers performed FT-IR spectroscopy studies on silver-alginate complexes, and concluded that in analogy to divalent cations, the Ag^+ -binding could occur either at the intermolecular or at the intramolecular level (see Figure 1a).^[91] At the intermolecular level alginate has the ability to interact with one Ag^+ ion by means of either two carboxylate groups or one carboxylate and one hydroxyl group from separate alginate chains, resulting in the formation of a planar complex perpendicular to the plane of the polymeric chains. At the intramolecular level, silver can coordinate the carboxylate groups belonging to two neighboring glycosidic units.^[91] Moreover, the conductivity of Ag^+ -alginate hydrogels suggests that the coordination of silver can induce the decarboxylation of alginate, eventually resulting in the reduction of Ag^+ ions.^[91,92] Hollow Ag^+ -alginate microcontainers, designed for precise drug release targeting and responsive to ultrasounds, were developed by Lengert

et al.^[93] The Ag^+ -alginate backbone is prepared initially, followed by treatment with ascorbic acid, resulting in a homogeneous distribution of AgNPs (silver nanoparticles) throughout the device. The presence of silver not only guarantees device biocompatibility but also enhances Raman signals, encouraging future application in theranostics.^[93] However, the weak interaction between alginate and Ag^+ makes it challenging to produce hydrogels with complex shapes, such as fibers, which significantly limits the potential applications of Ag^+ -alginate complexes.^[94,95] On this topic, we have recently demonstrated that Ag^+ -crosslinked alginate can be obtained through wet spinning; the optimization of multiple boundary conditions (such as the flow of extrusion and the concentrations of both the polymeric solution and the crosslinking bath) made it possible to obtain fibers with lengths up to several meters with consistent cross-sections.^[77] The Ag^+ ions can be easily reduced using mixtures of citric and ascorbic acid, to decorate the surface with homogeneously distributed AgNPs.^[77]

3.2. Divalent Cations

Divalent cations represent the largest subset of ions interacting with alginate to form crosslinked structures. The following M^{2+} ions are reportedly capable of crosslinking alginate: Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , UO_2^{2+} . The crosslinking of the polymeric chains can occur by forming inter or intramolecular complexes.^[13] Brus et al. demonstrated through NMR studies that these structures can vary to some extent depending on the type of ion, exhibiting decreased regularity with the decreasing ionic radius (see Figure 2).^[63] FT-IR spectroscopy was used by Papageorgiou et al. to determine the coordination geometries between cations and carboxylate groups on the alginate backbone (see Figure 2).^[64] Such an assessment relies on the consideration of the carboxylate groups asymmetric and symmetric stretching (ν) vibrations and derives from Nakamoto's work on cation-carboxylate complexes.^[96] The addition of divalent cations to sodium alginate solutions can determine change in pH, which affects the affinity between alginate and M^{2+} ions. The systematic work by Haug et al. and Seely et al., involving pH evaluation and complexometric titration, respectively, made it possible to order most of the divalent ions previously introduced in terms of their affinity toward alginate:^[97–99] $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Co}^{2+} \approx \text{Ni}^{2+} \approx \text{Zn}^{2+} > \text{Mn}^{2+}$. Schweiger et al. demonstrated by viscometric analysis that the stability of the M^{2+} -alginate complex, among alkaline-earth metals, decreases upon lowering the ion size.^[100] Increasing the amount of EDTA in solutions containing crosslinked polymeric chains produces an increase in the viscosity due to the sequestration of cations by EDTA and to the increase of the interaction between alginate chains and water. The cation is the main factor regulating this effect: a higher EDTA concentration is required in high-stability cation-alginate complexes to reach maximum viscosity when compared to low-stability ones.^[100] The Young modulus of M^{2+} -alginate hydrogels follows the following trend: $\text{Cd}^{2+} > \text{Ba}^{2+} > \text{Cu}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$.^[101] It is clear that the macroscopic properties of alginate gels not always align with the previously reported affinity scale. The latter, however, remains a

useful tool to rationalize multiple phenomena. All the aforementioned M^{2+} cations will be detailed in the following paragraphs.

3.2.1. Magnesium

Mg^{2+} is the least investigated among the divalent cations, most reasonably due to its small size, which lowers the stability of its complexes with alginate. The crosslinking phenomenon, however, could be relevant to many applications, such as in the case of water filtration systems, where it can induce polysaccharide fouling in membranes.^[102]

Topuz et al. conducted rheological studies on the gel formation process occurring between alginate and magnesium, emphasizing its slow kinetics, which is dependent on the concentration of both inorganic and organic components.^[103] Additionally they noticed that an increased number of G units enhances the strength of the resulting gels; however, the crosslinked structures exhibited low stability in water.^[103]

An intriguing and promising perspective is the use of Mg^{2+} -alginate formulations to treat gastroesophageal reflux in infants, suggested for the first time by Baldassarre et al.^[104] In this framework, the reduced stability of the complexes represents a potential advantage toward the exchange with more effective ions.

3.2.2. Calcium

Among the divalent cations interacting with alginate, calcium is undoubtedly the most extensively studied, owing to both the strength of its interactions and its significance in biomedical applications. Although it is capable of binding both the mannuronate and guluronate residues on alginate, Ca^{2+} is believed to form “egg box” junctions (ionically interacting with $-COO^-$ groups) only with poly-guluronate sequences (see Figure 1f,g).^[83] In this case, the binding strength is superior with respect to mannuronate complexes, resulting in the formation of gels that are kinetically stable against dissociation.^[83,105,106] The term “egg box” was used for the first time by Grant to describe the geometry of interaction between alginate chains and Ca^{2+} ions.^[15] Circular dichroism (CD) combined with computer modeling provided evidence for the formation of this buckled chain structure (see Figure 1h) which takes place through cooperative organization of the functional groups on the alginate backbone crosslinking Ca^{2+} ions.^[15,16]

Small angle X-ray scattering was found to be a powerful technique to shed light on Ca^{2+} -alginate interaction, suggesting that the homoguluronic acid sequences associate laterally during the complexation.^[67] Interestingly, authors concluded that alginate's mannuronic acid residues act as elasticity moderators (increasing the flexibility of the crosslinked chains), while guluronic acid units produce crosslinked regions with high rigidity,^[107] acting similarly to a block copolymer.

Farrés et al. highlighted, through rheological analysis, that high weight averaged molecular weight (M_w) alginates form Ca^{2+} -alginate gels faster compared to their lower M_w counterparts (with equivalent M/G).^[23] The measurements were performed while gradually releasing Ca^{2+} ions from $CaCO_3$ using GDL (glucono- δ -lactone) and maintaining a neutral pH. This approach allowed the authors to isolate the effect of the cation on

the polymer assembly, separating it from the effects of its concentration and pH.

Ca^{2+} -alginate gels are suitable for use as carriers in drug delivery and food supplement systems, owing to their easily modifiable properties and biocompatibility. To this purpose, alginate-based food supplements are often prepared in the form of beads, commonly dropping an alginate solution in a Ca^{2+} -containing crosslinking bath.^[108–110] Multiple preparation parameters (e.g., concentration of alginate and Ca^{2+} solutions and the crosslinking time) can be adjusted to obtain specific release kinetics.^[111] Alternatively, Poncelet et al. prepared Ca^{2+} -alginate beads via internal ionotropic gelation in emulsion, dispersing calcium carbonate (almost insoluble in water at neutral pH^[112]) in an alginate solution and inducing its gradual dissolution through acidification.^[113]

The diffusion of BSA (bovine serum albumin) in Ca^{2+} -alginate hydrogels was found to be susceptible to the guluronate content. In fact, it was shown that an increasing amount of G blocks lowers the diffusion kinetics, as a consequence of the higher rigidity of the crosslinked structure obtained.^[24] Voo et al. developed ultrahigh concentration (UHC) Ca^{2+} -alginate beads capable of prolonging methylene blue release 2.5 times longer than normal Ca^{2+} -alginate beads.^[25] The study also highlighted that a high Ca^{2+} ions concentration in the crosslinking bath induces a stratified structure in the obtained Ca^{2+} -alginate beads. The fast crosslinking and water expulsion processes were suggested to be responsible for the phenomenon, as schematically represented in Figure 3.

Interestingly, micrometer-sized Ca^{2+} -alginate beads can mimic the mechanical properties of human cells: in this case the required monodispersity can be easily reached through microfluidics.^[114]

The water purification sector can benefit from Ca^{2+} -alginate matrices, especially the removal of metal ions through ion exchange: Cu^{2+} , Cd^{2+} , and Pb^{2+} are reportedly absorbed by Ca^{2+} -alginate beads.^[115] In this context, Tao et al. developed nanostructured crosslinked Ca^{2+} -alginate hydrogels characterized by fast adsorption kinetics for Cu^{2+} and Cd^{2+} at room temperature,^[116] while Papageorgiou's Ca^{2+} -alginate beads proved to be selective toward Pb^{2+} ions.^[27]

In tissue engineering, the flexibility and biocompatibility of Ca^{2+} -crosslinked alginate matrices are advantageous. Tubular scaffolds with controlled diameter and good cell viability can be easily prepared through electrodeposition, serving as excellent candidates to realize cell-oriented scaffolds.^[26] Chondrocytes-loaded Ca^{2+} -alginate scaffolds with good cell viability were employed by Paige et al., to generate cartilaginous tissue de novo in mice.^[117] Weber et al. also demonstrated that Ca^{2+} -alginate hydrogels can be used to repair tympanic membrane perforations in Chinchilla.^[118] While injectable formulations of that type are suitable for endovascular embolization purposes.^[119]

It is worth mentioning that the strong interaction between alginate and Ca^{2+} ions allows for the preparation of alginate hydrogels with filiform structures, adopting a wet spinning approach.^[120,121] These products show high tensile strength and a low cytotoxicity, being suitable for wound healing applications.^[120]

Superstiff Ca^{2+} -alginate supercapacitors were developed by Ji et al.: the polymeric matrix was used as a sponge, loading

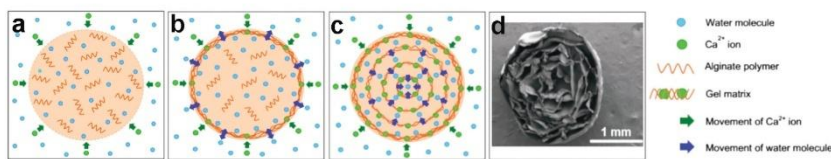


Figure 3. Hypothesized mechanism (a, b, and c are sequential) of Ca^{2+} -alginate gel formation in ultra-high concentration (UHC) alginate beads (from 10% w/v alginate solution).^[25] d) Cross-sectional scanning electron microscope image of a UHC alginate bead, highlighting its layered structure. Adapted with permission.^[25] Copyright 2016, Elsevier.

huge amounts of Li^+ and Fe^{3+} (the latter acting as additional crosslinker) to increase both the ionic conductivity and the capacitance.^[122] In this framework, it is useful to point out that dried Ca^{2+} -crosslinked alginate starts to degrade around 200 °C (decarboxylation), showing therefore lower thermal stability compared to sodium alginate.^[123,124]

Guo et al. developed Ca^{2+} -crosslinked/polyacrylamide alginate fibers, suitable as optical fibers: their flexibility, biocompatibility, and stretchability make these fibers promising building blocks for wearable sensors.^[125] Regarding this topic, calcium-alginate hydrogel structures were profitably used as strain sensors taking advantage of their good ionic conductivity and significant flexibility.^[126,127]

The food industry can take advantage of Ca^{2+} -alginate formulations in multiple fields. For instance, Ca^{2+} -alginate emulsion gels have been proposed as additives for the preparation of low-fat mayonnaise.^[128] Furthermore Ca^{2+} -alginate microbeads obtained by emulsification have been suggested for *Spirulina* (a health beneficial alga) encapsulation, to enhance the taste and nutritional content of yogurt.^[129] Ca^{2+} -alginate edible coatings loaded with essential oils have demonstrated the ability to improve the postharvest quality of raspberries,^[29] while the use of natamycin-loaded Ca^{2+} -alginate films was suggested for antimicrobial food packaging.^[130] Moreover, Vitamin B12 encapsulation and controlled release can be easily achieved using Ca^{2+} -alginate-PVA (polyvinyl acetate) scaffolds.^[30] Deng et al. reported the preparation of Ca^{2+} -alginate microbeads with immobilized polygalacturonase enzyme for apple juice clarification.^[131]

3.2.3. Strontium

Strontium is characterized by strong affinity toward alginate, which, along with its osteogenic properties, is the primary reason for its application potential. Zhang et al. demonstrated by means of mechanical and FT-IR investigations on alginate fibers that the Sr^{2+} -alginate interaction is stronger than the Ca^{2+} -alginate one, probably due to the presence of a higher number of interaction sites.^[32] This finding is supported by the Agulhon's DFT (Density Functional Theory) calculations performed on some alginate complexes with transition/alkaline earth divalent cations.^[132]

Crosslinking alginate with Sr^{2+} ions is a viable method to prepare functional hydrogels with huge application potential. Rheological analysis performed by Pastore et al. revealed that Sr^{2+} -alginate gels experience two regimes of stress relaxation.^[133] The first, on early/intermediate length scales, can be ascribed to local

relaxations (break of physical crosslinking junctions). The second, at a longer time, suggests the occurrence of a more collective rearrangement, such as syneresis and aging.^[133] It is interesting to note that hitherto no studies focusing on the thermal properties of Sr^{2+} -alginate gels have been reported.

The known osteogenic properties of strontium push the research activity on Sr^{2+} -alginate hydrogels. Scaffolds were prepared by adding a Sr^{2+} -containing aqueous solution to an alginate-containing one, possibly incorporating additional elements, such as collagen.^[134–136] Yuan et al. also investigated the use of Sr^{2+} -alginate coordination to prepare coatings for titanium surfaces: Sr^{2+} release proved to be long-lasting and capable of increasing osteoblast-like cell (MG63) proliferation.^[137]

Injectable Sr^{2+} -alginate hydrogel formulations, with or without hydroxyapatite (HAP) and tricalcium phosphate (TCP) as fillers, are reportedly osteogenic.^[138–140] Concerning this topic, Neves et al. developed an injectable Sr^{2+} -alginate soft hydrogel containing Sr^{2+} -crosslinked alginate beads to obtain a composite with tunable Sr^{2+} release kinetics.^[141]

3.2.4. Barium

Ba^{2+} -alginate complexes are the most stable among the alkaline-earth derivatives, due to Ba^{2+} capability of crosslinking both guluronate and mannuronate functionalities of the polymeric backbone.^[142,143] This high affinity toward alginate leads to a fast crosslinking that reduces the homogeneity of Ba^{2+} -alginate hydrogels with respect to the Ca^{2+} -crosslinked ones.^[142] Thermogravimetric analysis (TGA) showed that dry Ba^{2+} -alginate gels undergo decarboxylation around 205 °C, analogously to Ca^{2+} -alginate ones. Moreover, the high residue in the 300–500 °C interval (significantly superior to that of sodium alginate) clearly indicated that Ba^{2+} -crosslinked alginate can find application as flame retardant.^[144]

These networks were proven to be an excellent matrix for cell encapsulation: the low permeability toward antibodies reduces inflammatory reactions when used in allo- and xeno-graft transplantation,^[133,145,146] without introducing permselective layers, such as poly-L-lysine (PLL) or poly-ethylene-glycol onto the surface.^[147] Transplantation experiments conducted by Zekhorn et al., with Ba^{2+} -alginate encapsulated rat islets, revealed a significant prolongation of postprandial normoglycaemia in recipient mice for at least several weeks, while nonencapsulated islets induced normoglycemia for only a few days.^[148] Ba^{2+} -alginate beads also demonstrated a higher affinity for chromium (VI)

with respect to Ca^{2+} -alginate ones, resulting capable of physically adsorbing significant amounts of the aforementioned chemical species.^[149] Concerning chemicals removal, Xu et al. proposed Ba^{2+} -alginate beads as a novel adsorbent for sulfate removal in lithium refining.^[150] Zhang et al. realized a Ba^{2+} -alginate-PET(polyethylene terephthalate) composite membrane capable of performing molecule/ion separation.^[151] Methylene blue (MB) was found to be selectively separated from NaCl (99.5% rejection of MB and 8.3% rejection of NaCl) more efficiently than in analogous devices based on Ca^{2+} -crosslinked alginate.^[151]

The good stability of the Ba^{2+} -alginate hydrogel structure in the swollen state—reported in the aforementioned works—was shown to be particularly promising for water purification purposes.^[152]

3.2.5. Manganese

Although the interaction between Mn^{2+} and alginate is one of the weakest reported in the literature, Mn^{2+} -alginate complexes possess unique properties: the five unpaired electrons in Mn^{2+} valence shell (and the consequent paramagnetic character) make Mn^{2+} -alginate hydrogels particularly intriguing for applications related to magnetic resonance spectroscopy and imaging (MRI).

Paramagnetic-induced peak broadening allows the study of the interaction between alginate and manganese divalent cations through ^{13}C -NMR. In this way, Emmerichs et al. highlighted that poly-mannuronate alginate sections, due to their stretched ribbon-like structures, interact with C-6 and C-5 carbons. On the other hand, poly-guluronate moieties interact with Mn^{2+} ions through C-6, C-5, and C-1 carbons, forming structures with higher integration of the cation.^[153]

Agulhon et al. investigated the rheological properties of Mn^{2+} -alginate formulations revealing that storage and loss modulus (G' and G'' , respectively) always intersect, regardless of the guluronate content of the alginate^[72]; therefore, such system cannot be defined as gel according to the old IUPAC classification,^[154] although the term can be used according to the recent IUPAC terminology.^[155] TGA analysis showed that crosslinking sodium alginate with Mn^{2+} ions lowers the decarboxylation onset (around 200 °C) with respect to sodium alginate.^[81] However, the low amount of gaseous products released upon heating makes Mn^{2+} -alginate gels intriguing as flame retardants.^[81]

Mn^{2+} -alginate hydrogels were profitably used as a system for controlled release of Mn^{2+} ions for applications in manganese-enhanced MRI (MEMRI)^[156] and proved to be biocompatible and unable to generate immune response when implanted.^[157] Using a microfluidic approach, Su et al. also developed doxorubicin-loaded Mn^{2+} -crosslinked alginate nanoparticles for cancer therapy.^[158] In this system, doxorubicin acted as chemotherapeutics generating a large amount of H_2O_2 in the proximity of tumor cells, while Mn^{2+} enhanced MRI contrast and acted as chemodynamic therapeutic generating hydroxyl radicals through a Fenton-like reaction.^[158,159]

Interestingly, Mn^{2+} -crosslinked alginate/gelatin organohydrogels (MnAlgGel) demonstrated photoresponsivity under visible light (see Figure 4)^[76]; the MnAlgGel matrix, due to its higher tendency trap electrons, shows photocurrent ($9.2 \mu\text{A W}^{-1}$) and photoswitching speed (2.23/3.13 s) superior to that of Cu^{2+} - Fe^{3+} - and

Zr^{4+} -crosslinked analogues. This family of gels is also sensitive to temperature, humidity, and strain with excellent cyclability.^[76]

Finally, Mn^{2+} -crosslinked alginate is a good candidate for the removal of arsenite (III), arsenate (V), cadmium (II), and chromium (VI) ions in water.^[160,161]

3.2.6. Cobalt

Co^{2+} -alginate gels have garnered limited attention compared to those of other divalent cations, mostly due to the toxicity associated with this element.^[162] Nevertheless, its affinity for alginate and the appropriate dosage have demonstrated significant potential for specific applications.

Rheological studies revealed that for Co^{2+} -alginate gels with low guluronate content, the storage (G') and loss (G'') moduli intersected at higher angular frequency with respect to their Mn^{2+} equivalents.^[72] Additionally, high guluronate-content Co^{2+} -alginate gels did not exhibit a crossover point ($G' = G''$), unlike the Mn^{2+} -alginate equivalents. This suggests a stronger interaction between Co^{2+} ions and alginate chains, in agreement with the affinity scale previously reported.

Co^{2+} -alginate gels were used as green, low-cost precursors for the preparation of Co_3O_4 NPs,^[163] known antimicrobial and antioxidant agents,^[164] via calcination. $\text{Ca}^{2+}/\text{Co}^{2+}$ -alginate beads induced human adipose-derived mesenchymal stem cells (hAD-SCs) differentiation into cartilage producing chondrocytes.^[165]

Interestingly, TGA and FT-IR analysis indicate that incorporating Co^{2+} -alginate powder (produced by drying an hydrogel matrix) in epoxy resins increases the flame retardant properties of the latter.^[166] Liu et al. deeply investigated this aspect, proving that crosslinking alginate with Co^{2+} ions accelerates the thermal degradation of the polymer chains (decarboxylation onset around 185 °C).^[81] However, in the 180–340 °C range a lower amount of gaseous products was produced with respect to sodium alginate, confirming the previously mentioned flame retardancy.^[81]

3.2.7. Nickel

The well-known risks associated with the use of Ni^{2+} (e.g., allergy, lung fibrosis)^[167] significantly lowered the interest in Ni^{2+} -crosslinked hydrogels. Despite this, the distinctive properties imparted by this ion and the high stability of Ni^{2+} -alginate hydrogels still make them of interest to researchers.

Studies on the sol–gel transition of alginate induced by Ni^{2+} ions highlighted a second order kinetics for the process.^[168] The resulting networks exhibited lower stability toward decarboxylation (onset ≈ 180 °C) with respect to sodium alginate, but superior flame retardant properties due to the reduced amount of gas released during thermal degradation.^[169] XPS analysis of Ni^{2+} -alginate hydrogels performed by Zhang et al. showed that the Ni^{2+} binds to both carboxyl and oxydriol groups of the alginate backbone.^[69] DFT calculations also indicated that Ni^{2+} preferably coordinates 4 glycosidic units maintaining a distance of ≈ 1.9 Å from each oxygen/containing functional group (both in gas and water phase).^[170]

Recently, Xiong et al. developed a device for cancer immunotherapy consisting of a histidine-tagged Interleukin 2 (IL2)

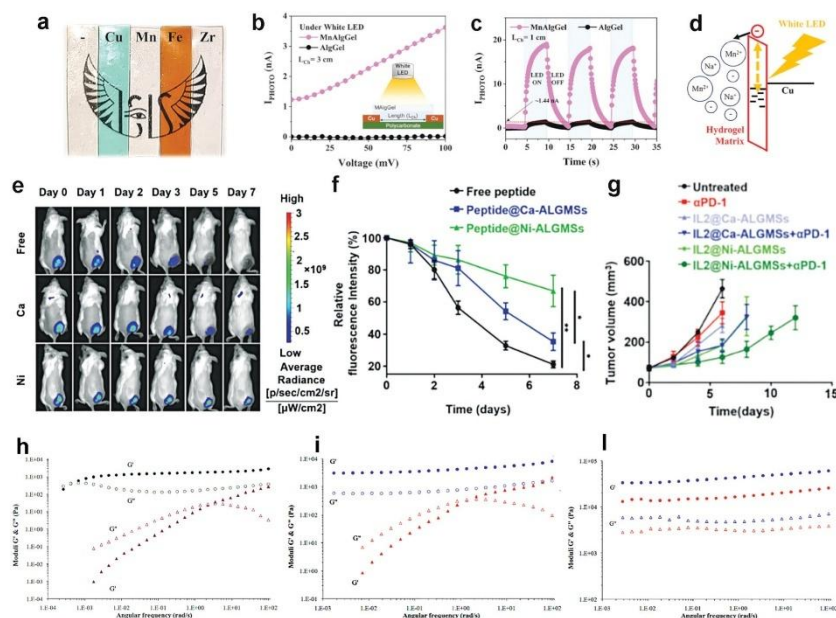


Figure 4. First row: photoresponsive ionic conductive M-alginate/gelatin (M = Cu, Mn, Fe, Zr) organohydrogels compared with their sodium alginate/gelatin (AlgGel) counterparts. Adapted with permission.^[76] Copyright 2024, John Wiley and Sons. a) Optical image of the prepared MAlGels samples placed on top of a printed logo. b) Photoresponse of MnAlGels and AlgGels upon exposure to white LED. c) Time-resolved photoresponse of the MnAlGels and AlgGels photodetector with a channel length of 1 cm. d) Band diagram of the MnAlGels/Cu electrode interface. Second row: Injectable Interleukin 2 (IL2) loaded into Ni²⁺-alginate microspheres for cancer therapy. Adapted with permission.^[171] Copyright 2022, John Wiley and Sons. e) In vivo fluorescence imaging of mice after injection of free Cy5.5 labeled his-tagged peptide (Cy5.5-his-peptide), Cy5.5-his-peptide@Ca-ALGMSs, and Cy5.5-his-peptide@Ni-ALGMSs. f) The relative fluorescence at tumor areas from day 0 to day 7 postinjection of the above Cy5.5 labeled agents. g) Average B16-F10 tumor volumes of different groups during the treatment. Third row: influence of transition metal cations and guluronate content on the frequency-dependent viscoelastic properties of: h) Mn-HG (●/○) and Mn-LG (▲/△) alginates. i) Co-HG (●/○) and Co-LG (▲/△) alginates. j) Cu-HG (●/○) and Cu-LG (▲/△) alginates. G' (filled symbols) and G'' (open symbols)—G' (filled symbols) and G'' (open symbols)—T = 25 °C; σ_0 = 20 Pa. Adapted with permission.^[172] Copyright 2014, Elsevier.

loaded into Ni²⁺-alginate microspheres (Figure 4 highlights the results) thanks to the coordination to the metallic center. The formulation could be injected directly in the tumor, enhancing the production of inflammatory cytokines and minimizing the adverse effects caused by intravenous administration of the drug alone.^[171]

The selectivity of Ni²⁺-alginate hydrogels toward polyhistidine tags was reported also by Dumitrascu et al.^[172] It is noteworthy that calcination at 500 °C of Ni²⁺-alginate beads resulted in the formation of single cubic phase nickel oxide (NiO) nanoparticles, thanks to the slow collapsing of the alginate network during the thermal treatment.^[173]

Previously mentioned Zhang's XPS studies were instrumental to determine the favored binding sites of ciprofloxacin on Ni²⁺-

crosslinked alginate gels, in order to prove their suitability for the removal of this antibiotic from water.^[69] Sami et al. reported that Ni²⁺-alginate hydrogels can act as selective absorbents for lead (II) ions in water.^[174] However, the ion exchange mechanism highlighted by the authors casts doubts on the utility of such products, as it can lead to the potential release of Ni²⁺ in the environment.

3.2.8. Copper

Rodrigues and Lagoa reported a lower selectivity of Cu²⁺ with respect to Ca²⁺ toward the alginate binding sites. Cu²⁺ absorption studies (Cu²⁺ concentration in the crosslinking solution, be-

fore and after gelation, was determined by molecular absorption spectroscopy) highlighted that the egg box coordination model^[15] is verified only at low Cu^{2+} concentrations, while the number of interacting binding sites reduces to one or two at high crosslinker concentrations.^[175] Viscometric and spectroscopic evaluations of Cu^{2+} -alginate diluted solutions support this binding modality.^[176] Rheological tests on Cu^{2+} -alginate gels (with both low and high guluronate content) showed no flow regions ($G'' > G'$): this behavior, in contrast with Mn^{2+} - and Co^{2+} -alginate gels, suggests an atypical binding modality that results in networks with high cohesion.^[72]

Small angle X-ray scattering (SAXS) analysis made it possible to monitor Cu^{2+} -induced alginate sol–gel transition, highlighting that copper prefers a less selective binding mode than the egg box.^[68] SAXS was also useful in correlating the assembly at the molecular scale with the macroscopic mechanical properties. In fact, while the system's correlation length (ξ) remains unaffected by the Cu^{2+} concentration, the resulting hydrogels proved to be rigid enough to be suitable for the encapsulation of actives. Camacho et al. developed Cu^{2+} -alginate beads for folic acid encapsulation, enabling pH-responsive release: the hydrogels shrunk in acidic pH (e.g., in the stomach), while started to swell and release folic acid when pH was higher than 5. This device therefore allowed the release of folic acid in the intestinal environment, protecting the active during the previous path of the digestive system.^[34]

Cu^{2+} -alginate complexes leverage copper's antimicrobial properties to prepare biocidal products. The treatment of wool and cotton cellulose fabrics with Cu^{2+} -alginate has been shown to impart antimicrobial properties durable after several washing cycles.^[177,178] Cu^{2+} -alginate hydrogels' antimicrobial and drug encapsulation properties can be used to prepare scaffolds for bone tissue regeneration: Qi et al. demonstrated that cannabidiol loaded Cu^{2+} -alginate hydrogels exhibit antibacterial, anti-inflammation, angiogenic, and osteogenic activities and are beneficial for bone defects healing.^[179] Additionally, Klinkajon et al. also highlighted that alginate hydrogels containing Cu^{2+} ions are suitable for antimicrobial wound dressing since they are capable of absorbing a high quantity of body fluids, enhancing prothrombotic coagulation and platelet activation.^[180] Wound dressing hydrogels of that kind can be prepared by electrodeposition (gradually dissolving $\text{Cu}_2(\text{OH})_2\text{CO}_3$ precursor), with excellent control over the structure and chemical composition (see Figure 5).^[181]

The strong affinity of alginate for Cu^{2+} can be also exploited in the design of hydrogels with complex shapes: for example, wet spinning has been recently demonstrated as a viable and promising strategy to produce fibers.^[78] Combined with its antimicrobial properties, the Cu^{2+} -alginate affinity could be extensively exploited for the preparation of inks for extrusion 3D printing, thereby expanding its application potential into additional technological fields.

Cu^{2+} -alginate hydrogels were employed as catalyst for the 1,3-dipolar cycloaddition of alkynes with azides and oxidative coupling of 2-naphthols and phenols in water.^[182] For example, Bahsis et al. developed a reusable superporous hydrogel with high catalytic activity and regioselectivity (confirmed through DFT calculations) for the synthesis of 1,4-disubstituted-1,2,3-triazoles in water.^[183] Souza et al. reported the preparation of a Cu^{2+} -alginate

gel catalyst for the synthesis of 4-organylselenyl-1H-pyrazoles: the crosslinking strength contributes to the recyclability of the product (5 cycles tested).^[184]

It is worth mentioning that CuAlg composites with polyacrylamide (PAM), obtained through radiation-induced polymerization of AM followed by alginate's ionic gelation, were found to effectively operate as highly stretchable ionic conductive strain sensors.^[185] Application of Cu^{2+} -alginate gels always needs to take into account that Cu^{2+} ions strongly catalyze alginate chains degradation.^[186]

3.2.9. Zinc

Zn^{2+} -alginate interaction, although being one of the weakest among the M^{2+} -alginate ones, has demonstrated significant potential for various applications, primarily due to the unique properties of this element. Viscometric characterization of Zn^{2+} - Ca^{2+} -alginate diluted formulations proved that Ca^{2+} and Zn^{2+} do not compete for the same binding sites, suggesting that the egg box coordination^[15] is inadequate to describe the Zn^{2+} -alginate complex.^[187] Dynamic light scattering (DLS) analysis performed on diluted mixtures of alginate and zinc highlighted that the complexation process leads to the formation of alginate nanoparticles.^[188]

Zn^{2+} -crosslinked alginate coatings can be used for diverse applications. For example, by leveraging the antifouling properties of zinc,^[189,190] Nassif et al. developed an electrophoretic method for the preparation of uniform Zn^{2+} -crosslinked alginate coatings for stainless steel.^[191] Additionally, due to the thermally induced conversion of Zn^{2+} ions to ZnO , Zn^{2+} -crosslinked alginate films proved to act as flame retardants.^[192]

Zn^{2+} -alginate pyrolysis behavior strongly differs from that of sodium alginate: Liu et al. pointed out (using TGA, TG-FTIR, and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)) that crosslinking with Zn^{2+} shifts the decarboxylation onset abundantly below 200 °C, while reducing the number of pyrolysis compounds (less flammable gaseous products).^[189]

Zn^{2+} -crosslinked alginate beads have been shown to perform slow release of nitrogen-based fertilizers, due to the strong Zn^{2+} -alginate interaction, resulting in hydrogels with small porosities.^[193]

Interestingly, Wen et al. developed zinc-ion hybrid supercapacitor (ZHS) based on a Zn^{2+} -alginate/PAAm hydrogel acting as electrolyte. This system is sensitive to applied pressures and allows easy modulation of energy density by adjusting Zn^{2+} concentration, suggesting its potential as a self-powered sensor for detecting human movement and breathing.^[194] Zn^{2+} -alginate has also been used to enhance the electrochemical performance of Zn ion batteries: coating Zn electrodes with thermoplastic polyurethane (TPU) infiltrated with ZnAlg minimizes corrosion and dendrite growth.^[195]

Zn^{2+} -alginate hydrogels with finely controlled morphologies can be prepared through internal gelation. D-(+)-gluconic acid δ -lactone (GDL) addition to $[\text{ZnCO}_3]_2[\text{Zn}(\text{OH})_2]_3$ -loaded alginate induces the progressive release of Zn^{2+} ions and produces a highly homogeneous network.^[74] Gray et al. showed that Zn^{2+} -alginate hydrogels are suitable for performing slow insulin release. This evidence was attributed to

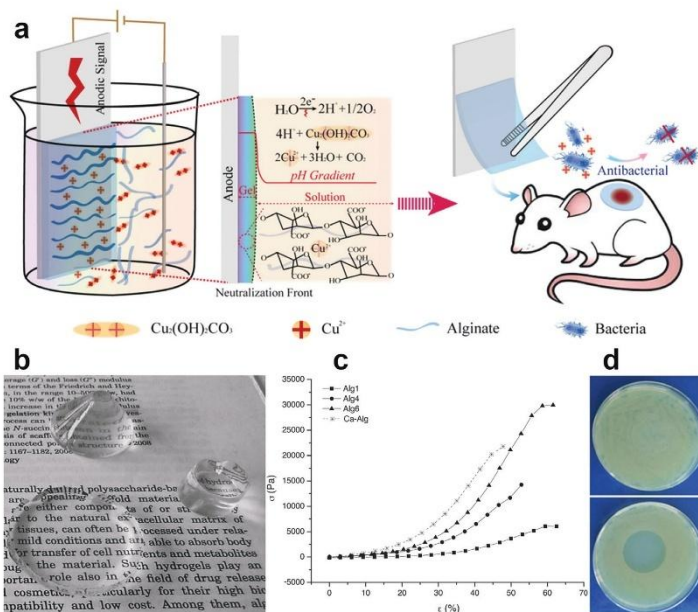


Figure 5. First row: a) Sketch of the preparation of antimicrobial Cu^{2+} -alginate dressing through electrodeposition. Adapted with permission.^[181] Copyright 2021, Springer Nature. Second row: b) Transparent Zn^{2+} -crosslinked alginate gels obtained by internal gelation. Adapted with permission.^[74] Copyright 2015, Elsevier. c) Stress versus strain curves of Zn^{2+} -alginate gels (Alg1, Alg4, Alg6) prepared under different pH conditions, compared to a Ca^{2+} -alginate reference. Adapted with permission.^[74] Copyright 2015, Elsevier. d) Bacteria inhibition zones of Ca^{2+} -alginate (top) and Zn^{2+} -alginate (bottom) gels. Adapted with permission.^[74] Copyright 2015, Elsevier.

the high density of the Zn^{2+} -crosslinked hydrogel structure with respect to Ca^{2+} and to a possible Zn^{2+} -insulin bridge formation.^[196]

Interestingly Zn^{2+} -alginate formulations have been demonstrated to improve the stability of color and chemical composition of natural pigments from anthocyanin-rich purple corn extract, proposing a viable and sustainable opportunity for innovation in the beverage sector.^[31]

3.2.10. Cadmium

Although Cd^{2+} -alginate interaction is one of the strongest among the M^{2+} -alginate complexes (leading to gels with high Young modulus^[10]), the interest in this cation is strongly limited by its toxic nature.^[197] The strong interaction is also why alginate is often exploited for the removal of Cd^{2+} contamination from water: alginate gel beads (sometimes in the form of organic/inorganic composite systems), either crosslinked or not, were profitably

used for this purpose due to the fast ion exchange involving Cd^{2+} ions.^[198–201]

Wang et al. developed Cd^{2+} -alginate nanobeads for triple tumor marker detection (Alpha fetoprotein, AFP; Carcinoembryonic antigen, CEA; Prostate specific antigen, PSA), using a double-water-in-oil-emulsion procedure.^[202] The beads were used to immobilize labeled anti-AFP, anti-CEA, and anti-PSA and then immobilized on a conductive substrate. The presence of Cd^{2+} ions is crucial since they generate the anodic peaks necessary for analyte detection via differential pulse voltammetry (DPV).^[202]

3.2.11. Lead

As previously introduced, the affinity between alginate and Pb^{2+} ions is the strongest among all divalent cationic species. Lamelas et al. studied the complexation between Pb^{2+} and alginate, mixing alginate and lead-containing solutions in various conditions

and using Pb^{2+} -selective electrodes,^[203] authors highlighted that, in the pH 4.0–8.0 range, the uptake of lead ions by the alginate matrix is a linear function of the Pb^{2+} concentration in the bath, regardless of pH variations. Furthermore, cation-alginate complexation experiments (performed with variable ionic strength) proved that coulombic interaction accounts for 15% of the formation of the complex.^[203]

As observed by Andresen and Smidsrød, the elasticity modulus (E) of Pb^{2+} -crosslinked alginate gels decreases as a function of the temperature (from 10 to 50 °C),^[204] suggesting their potential use as thermoresponsive functional materials. The negative temperature dependence of E testifies that the entropy of the system increases during compression, likely due to the rupture of linkages in the organized hydrogel matrix.^[204]

Due to the high toxicity of lead,^[205] the strong interaction between Pb^{2+} and alginate is often exploited to remove the ion from water or gastric juices.^[174,206] Ca^{2+} -alginate gels are suitable for this purpose, since the calcium can be easily replaced by lead in the polymeric network.^[207,115]

3.2.12. Uranyl

This subsection is titled “Uranyl” rather than “Uranium” and it belongs to the divalent cations section because of a well-defined reason. In fact, although uranium has an oxidation state of (VI) in the uranyl cation, this cation behaves similar to divalent elements. A unique study of Hassan demonstrated that the interaction between alginate and uranyl cations (UO_2^{2+}) results in the formation of hydrogels.^[208] Titrimetric analysis examined the competition between uranyl cations and protons for the carboxylate groups, revealing an equilibrium constant of ≈ 15.5 for the UO_2^{2+} -alginate complex. IR spectroscopy confirmed the coordination between UO_2^{2+} ions and the polymer backbone, evidenced by characteristic shifts of the $\nu(\text{COO}^-_{\text{asym}})$ and $\nu(\text{COO}^-_{\text{sym}})$ bands with respect to sodium alginate reference (to lower and higher energies, respectively).^[208] This coordination with the uranyl groups also led to the appearance of a band at 930 cm^{-1} , absent in the sodium alginate spectrum. XRD diffraction patterns proved the amorphous nature of the UO_2^{2+} -alginate complex.^[208] Two coordination geometries were proposed for the UO_2^{2+} -alginate complex. In the case of intrachain interaction, or “planar interaction,” both hydroxyl and carboxylate groups are involved in the coordination. On the other hand, interchain interactions (see Figure 1b–d) involve only carboxylate groups from different polysaccharide chains, forcing the uranyl cations to arrange in a plane that is perpendicular to that of the polysaccharide chains (nonplanar geometry).

3.3. Trivalent Cations

Cr^{3+} , Fe^{3+} , Al^{3+} , Ga^{3+} , La^{3+} , Ce^{3+} , Eu^{3+} , Tb^{3+} , and Gd^{3+} form hydrogels through interactions with alginate chains. Their complexes typically exhibit octahedral geometries, where the binding of M^{3+} ions is predominantly intermolecular due to the reduced strain on the cation-oxygen bonds in this configuration.^[209] The coordination involves two carboxyl groups from one alginate chain and one carboxyl group from another, resulting in asym-

metrical attraction forces. Consequently, the formation of M^{3+} -alginate hydrogels takes place anisotropically, with a preferential direction, especially when diluted alginate solutions are used.^[13]

Thermogravimetric studies by Zaafarani et al. on various alginate complexes have shown that the thermal stability of M^{3+} -alginate gels is cation-dependent, following the order (determined from the decarboxylation onsets): $\text{Al}^{3+} > \text{Cr}^{3+} > \text{Fe}^{3+}$.^[210] M^{3+} -alginate complexes were also characterized through FT-IR spectroscopy, unraveling that the coordination of M^{3+} ions leads to shifts of the symmetric and asymmetric $-\text{COO}^-$ stretching bands with respect to sodium alginate.^[209] The following sections will provide a detailed discussion for each of the trivalent cations mentioned above.

3.3.1. Chromium

The preparation of Cr^{3+} -alginate hydrogels was first reported and patented by Milin et al. in 2003,^[211] although the interaction between alginate and Cr^{3+} ions was already known.^[212] This material has been proposed for artificial chromium supplementation. Additionally, Cr^{3+} -alginate interaction can be exploited for Cr^{3+} removal from water. Araújo et al. demonstrated that Ca^{2+} -alginate gels are effective for this purpose, as they can load substantial quantities of Cr^{3+} , mainly through ion exchange.^[212]

3.3.2. Iron

Fe^{3+} is the most extensively studied among the M^{3+} ions capable of crosslinking alginate due to its strong ionic interactions, which create stable and versatile hydrogels with desirable mechanical properties, biocompatibility, and functionality for various biomedical and industrial applications. Notably, Fe^{3+} -alginate hydrogels can be formed either using Fe^{3+} or Fe^{2+} salts as precursors. The latter approach is less common and requires the oxidation of the ions after the crosslinking.

Sreeram et al. proved through pH-metric titration that the complexation with alginate increases the stability of Fe^{3+} ions, preventing precipitation of ferric hydroxides till pH 4.2.^[213] This aspect is particularly interesting since it suggests that Fe^{3+} -alginate could possibly replace chromium (III) ions in the leather industry, during the tanning process.^[214]

Fe^{3+} -alginate crosslinked structures and derivatives demonstrated high application potential in the removal of water contaminants, such as Cr(VI) and As(III) .^[215–217] Zhang et al. developed an Fe^{3+} -alginate photocatalyst capable to concomitantly reduce Cr(VI) to Cr(III) and oxidize As(III) to As(V) . The obtained products, beyond their lower toxicity with respect to their precursors, are easier to adsorb on the crosslinked polymeric structure.^[218]

Furthermore, Fe^{3+} -alginate films have been shown to catalyze the decolorization of methyl orange through Fenton-like processes, with good recyclability.^[219] The ease of reducing Fe^{3+} to Fe^{2+} via UV irradiation—with a consequent reorganization of the alginate chains—enables to obtain photoresponsive Fe^{3+} -alginate composites, suitable as soft actuators.^[220]

It is worth mentioning that, as described by Liu et al., replacing sodium with iron strongly improves the flame retardant properties of alginates, achieving an excellent V-0 rating

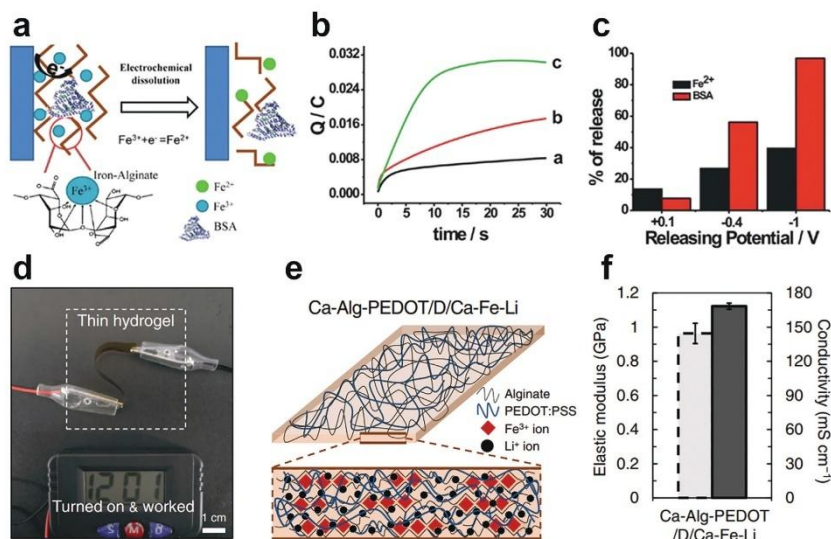


Figure 6. First row: a) Scheme of the electrochemically induced BSA release from Fe³⁺-alginate scaffold.^[226] b) Chronocoulometry curves obtained for the electrochemical dissolution of the BSAFeAlg films upon application of different reductive potentials: a) +0.1, b) -0.4, c) -1.0 V to the modified electrode. Adapted with permission.^[226] Copyright 2011, American Chemical Society. c) Percentage (from the total amount in the BSAFeAlg film) of the released iron cations and BSA upon application of different reductive potentials for 30 min. Adapted with permission.^[226] Copyright 2011, American Chemical Society. Second row: d) Demonstration of the stable working performance of Ca-Alg/D/Ca-Fe-Li hydrogels solid gel electrolytes. e) Schematic structure of the Ca-Alg-PEDOT/D/Ca-Fe-Li hydrogel matrices. f) Elastic modulus and conductivity of Ca-Alg-PEDOT/D/Ca-Fe-Li hydrogels. Adapted with permission.^[122] Copyright 2022, Springer Nature.

in the UL-94 test (i.e., the Standard for Safety of Flammability of Plastic Materials for Parts in Devices and Appliances testing), making iron alginate an inherent flame-retardant material.^[79]

Fe³⁺-alginate photodegradable gels were produced by Narayanan et al.,^[221] following this procedure in order to obtain a homogeneous distribution of cations in the network. These gels, when supplemented with sodium lactate, showed to be photodegradable if exposed to UV light ($\lambda = 365$ nm) and therefore suitable for biomedical applications.^[221]

Fe³⁺-alginate films have shown significant potential as tissue engineering scaffolds due to their superior protein adsorption properties (especially vitronectin) with respect to Ca²⁺-alginate films, supporting fibroblast adhesion, spreading, and proliferation.^[222] Machida-Sano et al., corroborated fibroblast adhesion, noting that the phenomenon becomes more favorable as the alginate's guluronate content increases.^[223] Fe³⁺-alginate gels have been also proposed as carriers for the release of DNA fragment^[224] or proteins (e.g., lysozyme and BSA).^[225,226] In this latter case, Jin et al. demonstrated that electrochemical reduction of the Fe³⁺ ions allows the modulation of the drug release profile,

due to the lower stability of the Fe²⁺-alginate crosslinked network (Figure 6).

3.3.3. Aluminum

Due to the high affinity between Al³⁺ and fluoride ions, Al³⁺-alginate gels were proposed for the removal of fluoride (F⁻) from water by the groups of Kaygusuz^[227] and Zhou.^[228] Both papers describe devices with intriguing properties, even though some details are still to be fully addressed, such as the effect of pH on the carboxylate stretching bands of alginate.

Al³⁺-alginate hydrogels have also been suggested as carriers for drug delivery,^[229,230] although their use in this field is limited compared to other cations (e.g., Ca²⁺).

In addition to Fe³⁺ ions, Liu et al. also investigated the effect of Al³⁺ ions on the thermal degradation mechanism of alginate, using TGA-FTIR-MS and Py-GC-MS: Al³⁺ ions proved to favor dehydration, decarboxylation, and decarbonylation of alginate.^[231] This study is particularly relevant in the view of the use of Al³⁺-alginate gels as flame retardants.

Yang et al. demonstrated that Al^{3+} -mediated crosslinking of alginate/polyacrylamide hydrogels significantly enhances the mechanical properties of the matrix making it suitable for use as a vibration isolator.^[1232]

3.3.4. Gallium

Ga^{3+} -alginate gels are well-known for their antimicrobial properties, as recently highlighted by Li et al.^[233] This antimicrobial efficacy can be attributed to the similarity between Ga^{3+} and Fe^{3+} ions, which allows Ga^{3+} to interact with iron-binding proteins, thereby disrupting iron-dependent metabolic pathways in bacteria.^[234,235] Rasting et al. demonstrated that gallium-mediated crosslinking imparts significant antimicrobial activity and compressive strength to alginate-containing inks for 3D bioprinting.^[235] The resulting scaffolds were capable of maintaining the viability of encapsulated fibroblasts over 90% for 7 days. It is worth mentioning that composites comprising Ga^{3+} -alginate and bioactive glass exhibited promising properties for bone tissue engineering application.^[35,236]

3.3.5. Yttrium

Y^{3+} ions are reportedly capable of interacting with alginate carboxylate groups^[237] leading to crosslinking phenomena. However, Y^{3+} -crosslinked alginate scaffolds have not garnered particular attention and their applications are limited to water purification. Electrostatic interaction and hydrogen bonding between pollutants and yttrium ions were found to be the main factors responsible for the efficiency of Y^{3+} -alginate beads in the removal of dyes^[238,239] and fluoride ions.^[240] As proved by He et al. through XPS characterization, F^{-} ions have the ability to replace the hydroxide groups bonded to the Y^{3+} .^[239]

3.3.6. Lanthanides

Despite the high cost of lanthanide salts, research on alginate complexations persists due to the unique properties these complexes offer, such as in bioimaging and sensing applications. This ongoing interest is summarized in the following subsections and it reflects the significant potential and value of these materials.

Lanthanum: The high cost of lanthanum-based salts limits the study of La^{3+} -alginate gels. However, due to the strong affinity between La^{3+} and phosphate (PO_4^{3-}) ions,^[241] several studies regarding La^{3+} -alginate matrix for PO_4^{3-} removal are reported. In most of them La^{3+} -alginate hydrogels were dehydrated^[242,243] or even calcined^[244] before use. Liu et al. proposed a composite La^{3+} -alginate-attapulgite (an aluminum silicate clay^[245]) hydrogel adsorbent for PO_4^{3-} ions removal from water.^[244] The system gained mechanical strength and stability from attapulgite, while the sorption properties primarily derived from the La^{3+} -crosslinked polymer matrix.^[244] Additionally, Li et al. proved that La^{3+} -alginate beads can efficiently remove azo-dyes from water, mainly due to electrostatic and hydrogen bonding interactions.^[246] The coordination between La^{3+} and alginate carboxylic groups was confirmed through FT-IR spectroscopy, as evidenced by the shift of the asymmetric $-\text{COO}^{-}$ stretching band to higher energies.^[246]

Cerium: Ce^{3+} complexes with alginate have been relatively underrepresented in literature, primarily due to the high cost of cerium salts. Nonetheless, investigations have revealed robust interactions between Ce^{3+} ions and alginate chains, resulting in densely packed structures with high thermal stability (i.e., main degradation in 700–850 °C range).^[247] Interestingly, DFT calculations highlighted the Ce^{3+} -alginate interaction is more favorable than the Cu^{2+} -alginate one.^[247] Ce^{3+} -alginate complexes have been proposed for corrosion protection applications, leveraging the facile substitution of Ce^{3+} ions by the common ions produced during corrosion processes (e.g., Fe^{2+} , Fe^{3+} , and Cu^{2+}) while exhibiting low toxicity profiles.^[248] Moreover, the affinity between Ce^{3+} and fluoride (F^{-}) ions can be exploited for the design of crosslinked scaffolds for water purification purposes.^[249] In the biomedical sector, Ce^{3+} -alginate beads have demonstrated wound healing capacities owing to their antimicrobial character (evaluated against *Staphylococcus aureus* and *Escherichia coli*).^[250]

Neodymium: Nd^{3+} ions attracted significant interest for in vivo applications, due to their low toxicity^[251] and high fluorescent emission intensity when complexed with alginate.^[25] Additionally, Nd^{3+} -alginate scaffolds showed impressive mechanical properties, surpassing those of their Ca^{2+} -based counterparts.^[75] Huang et al. exploited the affinity of Nd^{3+} toward alginate carboxylate groups to develop crosslinked alginate-(carboxyl-functionalized graphene) composites with high tensile strength and solvent resistance.^[252] Konishi et al. described in detail the ion exchange process that leads to the sorption of Nd^{3+} on alginate acid particles, highlighting its reversible nature.^[253] Their findings indicated that the sorption process is predominantly governed by the rate of ion exchange between H^{+} and Nd^{3+} , with external mass transfer and intraparticle diffusion playing negligible roles.^[253]

Europium and Terbium: Ma et al. developed Eu^{3+} - and Tb^{3+} -alginate hydrogels capable of emitting red and green light, respectively (see Figure 7), when exposed to UV radiation.^[254] FT-IR spectroscopy revealed shifts to higher energies in both the asymmetric and the symmetric $-\text{COO}^{-}$ stretching bands as a consequence of the coordination between alginate and the M^{3+} center. The fluorescent emission of these hydrogels proved to be sensitive to the presence of the anthrax biomarker sodium dipicolinate (NaDPA), with low detection limits (8.3×10^{-8} M for Eu^{3+} -alginate and 9.0×10^{-8} M for Tb^{3+} -alginate).^[254]

Gadolinium: Podgórná et al. developed Gd^{3+} -alginate nanogels through a reverse oil in water emulsion method, highly stable in suspension.^[255] The formulation is a promising contrast agent since it demonstrated to be nontoxic for human neuroblastoma cells line SH-SY5Y and capable of shortening the T1 relaxation time in magnetic resonance imaging (MRI).^[255]

3.4. Tetravalent Cations

The group of tetravalent cations did not attract particular interest and therefore solely two M^{4+} -alginate are described in the following paragraphs. It is worth mentioning that, as suggested by Hassan, tetravalent ions are restricted to crosslinking via intermolecular association: M^{4+} ions chelate two adjacent carboxylate groups from one chain and two from another.^[13] This complexation mechanism results in identical attraction forces be-

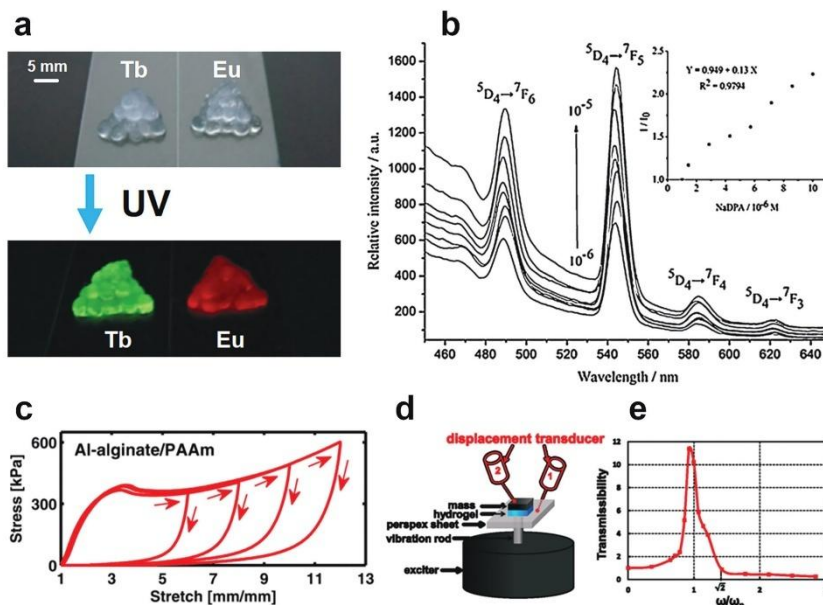


Figure 7. First row: a) UV light-sensitive Eu^{3+} - and Tb^{3+} -alginate hydrogels. b) Emission spectra ($\lambda_{\text{ex}} = 275 \text{ nm}$) of the Tb^{3+} -alginate beads in the presence of different concentrations of NaDPA, from 10^{-6} M to 10^{-5} M . Adapted with permission.^[254] Copyright 2015, Elsevier. Second row: c) Hysteresis curves of various kinds of alginate/PAAm hydrogels under stress. d) Scheme of the vibration isolation experiment set-up and e) transmissibility versus frequency ratio ω/ω_n . Adapted with permission.^[132] Copyright 2013, American Chemical Society.

tween the ion and the carboxylate groups in all direction, potentially explaining the spherical symmetry and favorable mechanical properties of M^{4+} -alginate gel droplets, regardless of the alginate concentration.^[13]

3.4.1. Zirconium

The high positive charge of Zr^{4+} facilitates the formation of strong interactions with the alginate chains, resulting in the formation of hydrogel networks. This charge was also reported to be responsible for an easy hydrolysis of the metal center and formation of a solvation sphere, beneficial for the coordination of polluting species.^[256] Li et al. developed magnetic Zr^{4+} -alginate hydrogels with high efficiency and reusability for the removal of Pb^{2+} ions.^[256] Due to their high electron density, phosphate (PO_4^{3-}), fluoride (F^-), and nitrate (NO_3^-) ions interact with Zr^{4+} active sites and therefore can be easily adsorbed onto Zr^{4+} -crosslinked alginate beads.^[257–259] To enhance the adsorption capabilities, fillers (e.g., graphene oxide and kaolin^[258,259])

are commonly added. Interestingly, Zr^{4+} ions can be used for the preparation of crosslinked alginate fibers, adopting a wet spinning approach.^[260] Zr^{4+} -alginate fibers developed by Chen et al. are capable of performing methylene blue removal from water, showing good recyclability. Due to the acid character of the Zr^{4+} crosslinking bath, the polymer network is partially protonated (highlighted through FT-IR spectroscopy).^[260] This aspect is often neglected or misinterpreted (i.e., wrong FT-IR spectra assignment), although it plays a crucial role in the swelling properties (and on the water purification performances, as a consequence) of Zr^{4+} -alginate hydrogels.

3.4.2. Thorium

Zaafarani et al. demonstrated that Th^{4+} ions can effectively serve as crosslinkers for the formation of alginate hydrogels.^[261] Titrimetric studies highlighted that the coordination of Th^{4+} ions is thermodynamically favorable, while IR spectroscopy revealed that Th^{4+} -alginate interactions determine a shift to higher en-

ergies of both the asymmetric and symmetric —COO^- stretching bands ($\nu(\text{COO}^-_{\text{asym}})$ and $\nu(\text{COO}^-_{\text{sym}})$, respectively).^[261] Furthermore, the chelation of Th^{4+} by the alginate backbone was evidenced by the emergence of a band at 890 cm^{-1} . An inter-chain association mechanism—the only one enabling an octahedral coordination between (tri/tetra)valent cations and alginate—was proposed for the coordination of Th^{4+} ions.^[261] As extensively known, thorium is a radioactive element and therefore the interaction with alginate can be used only for its removal (e.g., from water). Ding et al. developed alginate-immobilized *Aspergillus niger* microspheres (AAM) to perform thorium (IV) removal from water.^[262] Like in the aforementioned Zaafarani's study, alginate $\nu(\text{COO}^-_{\text{asym}})$ IR absorption band shifted to higher energies in the presence of Th^{4+} , testifying the coordination: the ionic exchange mechanism contributes to increase the amount of loaded contaminant.^[262]

3.5. Key Insights into Complexation and Hydrogel Properties

The information in this section is summarized in Tables 1 and 2, which provide valuable guidance for less experienced readers in shaping future research strategies on advanced alginate-based functional materials. Table 1 details the specific features of M^{X+} -alginate complexation and the intrinsic properties of the resulting hydrogel matrix, while Table 2 outlines the sectors that could benefit from the use of these complexes. For instance, Ca^{2+} -alginate is commonly applied in drug delivery and the food industry due to its nontoxic nature (even at high crosslinker concentrations), while Cu^{2+} -alginate is preferred for antimicrobial and catalytic applications because of its high reactivity. Lanthanides, with their intrinsic fluorescence, present promising opportunities for applications in sensing technologies and medical imaging. The precise description of the M^{X+} -alginate interactions reported in Table 1 is crucial to understanding why certain ions are selected for the specific applications shown in Table 2. It is also important to recognize that the complexation process and the hydrogel matrix properties are strongly affected by environmental conditions. Increased ionic strength can introduce competition during complexation, while temperature changes can influence the viscosity of alginate solutions and the diffusion rate of the crosslinker within the polymer network, both of which can lead to significant alterations in the crosslinked matrix properties. Furthermore, low pH levels can greatly affect the characteristics of alginate-based materials by inducing protonation of the alginate chains, thereby increasing rigidity and hydrophobicity of the network. This phenomenon commonly occurs while using Fe^{3+} , Al^{3+} , or Zr^{4+} as crosslinkers, as clearly mentioned in Table 1.

4. Functional Applications of Cation-Alginate Complexes: Current Technologies and Future Directions

Cation-alginate complexes serve as unique building blocks for advanced functional materials. Their strength derives not only from the inherent properties of the cation and alginate but also from the distinctive structures that form when alginate assembles around the cation. This dynamic interplay greatly enhances

their versatility, making them highly effective in applications ranging from drug delivery and environmental remediation to sensing and energy storage.

Overall, while cation-alginate complexes hold great promise across various applications, significant challenges related to stability, performance, and scalability must be addressed to unlock the full potential of cation-alginate complexes, driving technological advancements in diverse fields.

This section examines these challenges in depth and in a broader context, proposing strategies to overcome them by building on advanced processing techniques and focusing on technological innovations. The content is organized to guide the reader through both well-established and less conventional application fields, emphasizing the potential of cation-alginate complexes in each area while highlighting the challenges that must be addressed for real-world application. Table 2 summarizes the functions, sectors of impact, and involved cations, along with relevant examples from the literature. It serves as a roadmap for researchers who may not yet be fully aware of the potential applications of cation-alginate complexes. While consulting Table 2, readers are encouraged to refer to Table 1 to gain a complete understanding of the physicochemical properties that determine the suitability of different ions (and related crosslinked alginate networks) for specific applications.

4.1. Food Additive and Supplements

Cation-alginate complexes are utilized in food products and supplements to enhance texture, stability, and nutritional value (e.g., preventing oxidation).^[29–31,128–131,264,265] However, their effectiveness can be inconsistent due to sensitivity to processing conditions like temperature, pH, and moisture. This variability can affect the performance and stability of these complexes throughout a product's shelf life. Achieving desirable sensory qualities without compromising taste or texture is also a significant challenge.

In food supplements, managing the controlled release of encapsulated nutrients is essential to ensure bioavailability. Environmental factors can disrupt this control, leading to variable outcomes, and protecting sensitive nutrients during processing and storage remains crucial.

Innovative processing techniques can address these issues. Spray-drying produces more uniform alginate particles, enhancing consistency and stability. Advanced encapsulation methods, including freeze-drying and supercritical fluid processing, offer additional protection for nutrients and optimize release profiles, making cation-alginate complexes more reliable in food applications.

4.2. Biomedical Applications

Due to their well-known biocompatibility, mechanical stability, and capacity to retain large amounts of fluids, cation-alginate complexes hold significant promise in various biomedical applications, including their use as contrast agents in imaging, scaffolds for tissue engineering, drug delivery systems, and wound healing.^[266–286] However, the successful implementation of these applications faces several challenges, such as ensuring

biocompatibility, minimizing toxicity, achieving precise mechanical properties, and controlling the release and stability of therapeutic agents.

In imaging, the careful selection and combination of cations can optimize contrast, enhancing image clarity while minimizing potential side effects. The biocompatibility of these complexes is crucial, as any toxicity could limit their use in clinical settings. Developing formulations that maintain high contrast while reducing adverse effects remains a key area of research.

In tissue engineering, advanced fabrication techniques like electrospinning improve scaffold integrity, supporting cell growth and tissue regeneration. However, achieving the necessary mechanical properties is challenging, as the scaffold must be strong enough to provide structural support while being porous enough to allow cell infiltration and nutrient exchange. Advanced fabrication techniques, such as electrospinning, can improve the integrity of these scaffolds, enhancing their ability to support cell proliferation and tissue integration.

In drug delivery, controlling the release and stability of encapsulated drugs is essential to ensure therapeutic efficacy. The modification of alginate structures, combined with innovative encapsulation methods like spray-drying, can enhance the stability of the complexes and provide more predictable release profiles. This approach can be particularly effective in delivering and releasing pharmaceuticals products over extended periods, improving patient outcomes.

Wound healing is another promising application of cation-alginate complexes. These materials can be used to create dressings that promote healing by maintaining a moist environment, absorbing exudates, and delivering antimicrobial agents directly to the wound site. However, challenges such as ensuring the optimal release of therapeutic agents or maintaining the structural integrity of the dressing over time are still to be addressed. The incorporation of bioactive cations and the use of advanced processing techniques can enhance the healing properties of these dressings, offering better control over drug release and improving the overall effectiveness of the treatment.

By addressing these challenges through innovative strategies, cation-alginate complexes could become vital tools in the development of next-generation biomedical materials. These materials have the potential to provide new solutions for imaging, tissue regeneration, targeted drug delivery, and wound healing, significantly advancing patient care and treatment outcomes.

4.3. Artificial Skins and e-Skins

Cation-alginate complexes offer promising potential for artificial skin applications due to their biocompatibility and flexibility.^[76,127,287–289] However, several challenges need to be addressed to optimize their performance. Achieving a balance between flexibility and mechanical strength represents a major challenge. Cation-alginate materials can sometimes be too rigid or excessively soft, affecting their effectiveness as artificial skin. Additionally, maintaining consistent performance over time is crucial, as degradation due to moisture, UV exposure, or mechanical stress can compromise the material.

Another critical factor is the adhesion properties of these materials. For artificial skin to function effectively, it must adhere

securely to underlying tissues without causing irritation or detachment over time. Poor adhesion can lead to slippage, discomfort, or compromised healing, particularly in dynamic or high-movement areas of the body.

In the context of electronic skins (e-skins), cation-alginate complexes can be further enhanced to exhibit sensor and super-capacitive properties, making them suitable for advanced biomedical and wearable technologies. These e-skins require materials that not only mimic the flexibility and durability of natural skin but also integrate functionalities, such as pressure sensitivity, temperature responsiveness, and energy storage. By incorporating conductive nanomaterials and optimizing the crosslinking processes, cation-alginate complexes can achieve the necessary electrical conductivity and mechanical resilience, enabling the development of multifunctional e-skins that can monitor physiological signals or power small devices.

To overcome these issues, enhancing the mechanical properties of cation-alginate materials through chemical modifications and the incorporation of reinforcing agents, such as elastic polymers or fibers, can improve both flexibility and strength. Advanced fabrication techniques like additive manufacturing enable precise layering and customization, allowing for a closer mimicry of natural skin. By employing these strategies, cation-alginate complexes can be developed into highly effective artificial skins suitable for various applications.

4.4. Antimicrobials

Cation-alginate complexes have potential as antimicrobial agents due to their ability to bind and, in certain conditions, release antimicrobial cations like silver or copper.^[74,177,178,233,250] However, bottlenecks such as inconsistent ion release and resistance development need to be overcome. Controlling the release of these cations is crucial to avoid inadequate antimicrobial activity or excessive release leading to cytotoxicity. The potential for resistance development also limits the long-term effectiveness of single-ion antimicrobial agents.

Future research should focus on multication complexes that combine various antimicrobial mechanisms to reduce resistance likelihood. Balancing the release rates of multiple cations while maintaining biocompatibility is essential. Innovative processing techniques, such as spray-drying and electrospinning, could be utilized to produce antimicrobial devices with controlled morphology, composition and release, enhancing their performance and reducing resistance development.

4.5. Remediation by Complexation/Filtration

Owing to their biodegradability, recyclability, and high charge density, cation-alginate complexes are highly effective in environmental remediation, particularly for capturing heavy metals and other contaminants.^[69,115,150,238,290–294] However, their broader application is challenged by limited selectivity, the capacity to handle multiple contaminants, and difficulties in regeneration and reuse.

To solve these problems, implementing ion-specific protocols during the remediation process (such as the use of competitive

complexing agents) could significantly enhance the efficiency of cation-alginate complexes. By tailoring the remediation strategy to target specific ions under certain environmental conditions, it is possible to optimize the uptake of particular contaminants while minimizing interference from others. This approach can improve the selectivity and overall performance of the complexes in diverse and complex environmental matrices.

Enhancing the physical stability of cation-alginate complexes is also critical. Techniques such as crosslinking alginate with other polymers or applying advanced surface coatings can increase the resistance of these complexes to leaching and degradation, ensuring they maintain functionality over extended periods. This enhancement would make them more viable for long-term remediation applications. Additionally, innovative processing methods like spray-drying or electro-spinning can produce structures with improved stability and increased surface area. This not only improves contaminant capture efficiency but also facilitates the handling and reuse of the complexes, addressing a significant obstacle to the widespread adoption of cation-alginate complexes in environmental remediation. By focusing on these solutions, cation-alginate complexes could become more effective and sustainable tools for environmental cleanup, offering improved performance and more immediate practical applicability in real-world scenarios.

4.6. Sensors

Cation-alginate complexes show promise in sensor applications (due to their sensitivity to the surrounding environment)^[76,125,295,296] but their widespread use is still hampered by their limited sensitivity and selectivity, particularly in detecting low concentrations of analytes in complex environments. The weak and nonspecific interactions between alginate complexes and target molecules often result in false positives or reduced detection limits, undermining the reliability of these sensors. Another significant challenge is the slow response time of cation-alginate-based sensors, which restricts their effectiveness in real-time monitoring applications.

To overcome these limitations, enhancing the specificity of cation-alginate sensors is crucial. One promising approach involves the incorporation of selective recognition elements, such as molecularly imprinted polymers (MIPs) or aptamers, into the alginate matrix. These elements can provide higher binding affinities for specific target molecules, reducing the likelihood of false positives and improving the overall sensitivity of the sensor.

Innovative fabrication techniques also offer potential solutions. Additive manufacturing, for example, could enable the creation of sensor platforms with complex geometries and integrated microfluidics. These advanced designs could optimize the interaction between the sensor surface and the analyte, leading to faster response times and improved detection capabilities. By incorporating microfluidic channels, sensors could be designed to rapidly transport analytes to the detection site, thereby reducing the time required for a response.

Spray-drying and electro-spinning are other techniques that could be utilized to produce sensor particles with controlled size, shape, and surface properties. This level of control can enhance

the interaction between the sensor and the analyte, improving both sensitivity and response time.

4.7. Supercapacitors

Cation-alginate complexes hold significant potential for energy storage applications, especially in supercapacitors,^[122,269,297,298] where they function as dielectrics with high ionic content. However, challenges such as low energy density, poor cycle stability, and the inherently low conductivity of alginate have limited their performance in high-energy applications.

To overcome these limitations, several promising solutions are being explored. Integrating conductive additives, such as carbon black, metal nanoparticles, or conductive polymers, into cation-alginate complexes can significantly enhance their electrical conductivity. This approach can help to bridge the gap between the insulating nature of alginate and the high conductivity required for effective supercapacitor electrodes.

Combining alginate complexes with advanced materials like graphene or carbon nanotubes offers another powerful strategy. These materials are known for their exceptional electrical properties and mechanical strength, making them ideal components for improving both the conductivity and structural integrity of alginate-based supercapacitor electrodes. By creating hybrid materials that leverage the strengths of both alginate and these high-performance additives, researchers can achieve better energy density and cycle stability, extending the lifespan and efficiency of the supercapacitors.

Innovative processing techniques also play a crucial role in enhancing supercapacitor performance. Additive manufacturing, for instance, can be used to create complex, layered architectures that optimize ion transport within the electrode structure. By precisely controlling the arrangement and composition of the layers, it is possible to maximize the surface area available for charge storage while ensuring efficient ion movement, which is key to improving the overall performance of the supercapacitor.

By focusing on these solutions, cation-alginate complexes could become more viable and effective materials for next-generation supercapacitors, offering enhanced energy density, better cycle stability, and greater overall efficiency in energy storage applications.

4.8. Catalysts

Cation-alginate complexes are emerging as promising candidates for catalytic applications (leveraging their recyclability and biodegradability) in green chemistry,^[182–184,299–301] but their effectiveness is often constrained by several key challenges. One significant issue is their stability and activity under harsh conditions: in fact, the structural integrity of alginate complexes can degrade over time, particularly when exposed to high temperatures or extreme pH levels.

Several strategic improvements should be adopted to overcome these limitations. Enhancing the robustness of cation-alginate complexes is crucial. By selecting cations known for their stability and catalytic efficiency, the longevity and performance of the complexes can be significantly improved. Additionally, chemically modifying the alginate matrix—for example by making use

of crosslinking or grafting with more resistant polymers—can enhance its resistance to degradation and improve overall stability.

Innovative fabrication techniques offer additional solutions to enhance catalytic performance. Additive manufacturing allows for the creation of catalytic structures with precise geometries, which can enhance the exposure of active sites and optimize mass transfer. Spray-drying is another valuable technique for improving the performance of cation-alginate catalysts. By producing finely divided particles with controlled morphology, spray-drying enhances the dispersion of the catalytic material and increases its surface area, leading to improved catalytic activity. This method can also contribute to more uniform particle sizes, which further optimizes the performance of the catalysts. Electrospinning provides a promising approach for producing high-surface-area devices. This technique generates fibrous materials with a large surface area relative to their volume, potentially increasing the overall efficiency of the catalytic process.

4.9. Flame Retardants

Cation-alginate complexes show promise as sustainable flame retardants,^[80,144,166,169,302–306] due to the significant amount of residue produced during combustion. However, their practical application is hindered by several challenges. One major issue is that incorporating these complexes often compromises the mechanical properties of the materials they protect. The addition of cation-alginate complexes can lead to increased brittleness or reduced strength, which can significantly affect the durability and usability of the materials.

Achieving uniform distribution of cation-alginate complexes within the host material also represents a difficult target. Poor dispersion can result in uneven flame retardancy, where some areas may not receive adequate protection. This inconsistency can undermine the effectiveness of the flame retardant and limit its practical applications.

Addressing these challenges requires targeted strategies. Improving the compatibility of cation-alginate complexes with various matrices is essential. Surface modifications to the alginate or the use of synergistic additives can enhance both flame retardancy and mechanical properties. For instance, incorporating additives that strengthen the material while preserving its flame retardant capabilities can help balance these conflicting requirements. Innovative fabrication techniques offer additional solutions. Additive manufacturing enables the precise incorporation of cation-alginate complexes into materials, which can improve uniformity and integration.

4.10. Mechanical Isolators

Cation-alginate complexes hold potential as mechanical isolators due to their flexibility, tunable mechanical properties, and lightweight nature.^[232] However, optimizing their performance requires addressing several challenges.

Above all, achieving effective mechanical isolation is particularly complicated. Cation-alginate materials must become capable of absorbing and dissipating vibrations and shocks without

compromising their structure. Current formulations may not always provide adequate isolation or can suffer from degradation when placed under stress.

Uniformity in performance is also critical. Heterogeneous distribution of the complexes can lead to areas featuring inadequate isolation. Additionally, the material must maintain its performance across various temperatures and environmental conditions.

Adhesion properties are equally important for the efficacy of cation-alginate isolators. Ensuring strong adhesion between the cation-alginate complexes and the substrates they are applied to is crucial for maintaining mechanical stability. Moreover, reversible adhesion, where the materials can be adhered and detached multiple times without significant loss of performance, can enhance the sustainability of these isolators. This capability allows for easier maintenance, reusability, and reduced material waste.

To overcome all these challenges, several strategies can be employed. Enhancing the mechanical properties of cation-alginate complexes through chemical modifications and the addition of reinforcing agents, such as fibers or fillers, can offer a major step forward in the improvement of isolation capabilities. Advanced techniques like additive manufacturing can allow the crafting of complex structures that optimize isolation by better distributing mechanical forces. Additionally, developing formulations that balance strong yet reversible adhesion can significantly contribute to the overall durability and sustainability of these materials.

5. Conclusion

The complexation of alginate with various cations represents an extremely powerful strategy for modulating the physicochemical properties of alginate-based hydrogels. Alginate, thanks to its sustainability, its ability to interact with various cations, and the resulting diverse properties, represents a unique building block for the development of hybrid materials when combined with cationic species. By fully controlling the interplay of thermodynamics and kinetics ruling the complexation process, and gaining an in-depth understanding of the supramolecular interactions between alginate and various metal cations forming functional complexes, we have explored the novel architectures and related properties that are imparted to the hybrids for each cation.

This review addresses a key gap in the literature by providing a comprehensive overview of how alginate-cation combinations influence the properties of metal-alginate complexes. We structured the content to guide research, starting with fundamental strategies and characterization techniques, particularly for less-experienced readers. We then explored ion-specific interactions at various levels, offering detailed insights into the mechanisms behind these complexes. Finally, we examined functional applications across fields like sensing and energy storage, highlighting current uses and future research directions. Each section stands alone, allowing readers to focus on areas of interest.

Opportunities and challenges toward the realization of unprecedented cation-alginate functional materials have been discussed, proposing a roadmap for future research in this dynamic field of high potential for sustainable technological breakthroughs. Their high ion-loading capacity within the polymeric matrix promotes them as active key components for advance-

ments in chemical sensors, water purification, and energy storage applications. Alginate-cation complexes also exhibit high ionic conductivity, opening the door to their application in the burgeoning field of flexible electronics, when combined with nonconductive polymers as scaffolds, to ultimately avoid the use of carbon-based fillers that can impair transparency. Tailoring matrix properties, such as thermal stability and mechanical response through careful cation selection, enhances the versatility of alginate in these applications. In the biomedical field, the ability to modify alginate's properties for specific cations enables the development of advanced drug delivery systems and tissue engineering scaffolds. By adjusting the mechanical and degradation characteristics, these formulations can be optimized for biocompatibility and functionality. The ability to finely tune these properties allows alginate to be a competitive alternative to other materials for both biomedical (tissue engineering, healing patches, artificial skins, etc.) and mechanical (mechanical isolators, reversible adhesives, etc.) applications.

Cation-alginate complexes face several overarching challenges across various applications. The high sensitivity to environmental conditions such as temperature, pH, and moisture represents a critical limitation of these materials, jeopardizing their performance and stability. This variability often impacts their effectiveness and longevity, making it crucial to address their degradation under extreme conditions, especially when used in water purification or energy storage applications. Additionally, achieving a balance between flexibility and strength remains a persistent challenge, especially when these materials are used in high mechanical stress demanding applications like artificial skin or mechanical isolators. Controlled release and specificity are other critical areas of concern. For applications like drug delivery and food supplements, the variable release rates of encapsulated cations can affect performance. This inconsistency is compounded by the challenge of ensuring selectivity in environmental and sensor applications, where precise targeting of ions or molecules is essential to ensure effectiveness. Ensuring biocompatibility and minimizing toxicity is crucial, especially for biomedical uses. The safety of cation-alginate complexes must be guaranteed to avoid adverse effects, which can be a significant barrier to their clinical implementation. Uniformity in structural and functional integrity is another key challenge. Inconsistent integration of cation-alginate complexes within materials can lead to uneven performance, which is particularly problematic in applications where reliability is crucial.

To address all these challenges, we have identified several promising future directions. Advanced processing techniques such as spray-drying, electrospinning, and additive manufacturing offer potential solutions for enhancing the consistency and performance of these complexes. By developing multication complexes, researchers aim to improve efficacy and reduce issues like resistance development. Chemical modifications and reinforcements can also play a crucial role. Enhancing the mechanical properties of alginate through chemical tweaks or incorporating reinforcing agents can significantly improve stability and performance. These modifications help ensure that the materials maintain their integrity and functionality under various conditions. Enhanced specificity and controlled release are key to improving performance in applications like sensors and drug delivery systems. Integrating selective recognition elements, such

as molecularly imprinted polymers or aptamers, can increase the specificity of sensors, while advanced encapsulation methods can better control the release profiles of therapeutic agents. The integration of high-performance materials, such as graphene or carbon nanotubes, with cation-alginate complexes offers a powerful strategy to boost conductivity and performance, especially in supercapacitors and mechanical isolators. Finally, adopting eco-friendly approaches and focusing on sustainable technologies will be important for developing greener solutions in catalysis and environmental remediation. By overcoming these limitations and exploring these future directions, cation-alginate complexes would become more versatile and effective for a wide range of applications.

All in all, alginate-metal complexes have proven to be sustainable, versatile functional hybrids with on-demand properties and high potential to drive innovations in sensing, catalysis, energy storage, environmental remediation, and filtration technologies, shaping sustainable solutions for diverse disruptive applications.

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Conflict of Interest

The authors declare no conflict of interest.

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Ionically Tunable Gel Electrolytes Based on Gelatin-Alginate Biopolymers for High-Performance Supercapacitors

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The development of sustainable, high-performance gel polymer electrolytes (GPEs) is crucial for next-generation energy storage; however, existing materials often exhibit limited mechanical stability, suboptimal ionic transport, or environmental drawbacks. Here, for the first time gelatin-alginate organohydrogels crosslinked with Cu^{2+} and Mn^{2+} are used as GPEs for supercapacitors, in combination with Li^+ incorporation to enhance ionic conductivity and transport. Small-Angle X-ray Scattering (SAXS) reveals that the choice of the crosslinking cation governs the nanoscale organization of the polymer network—reflected in distinct correlation lengths—which in turn critically influences ionic transport, mechanical stability, and electrochemical performance. Cu^{2+} -crosslinked gels achieve the highest areal capacitance (591.8 mF cm^{-2}), energy density (82.2 μWh cm^{-2}), and power density ($1957.8 \text{ μW cm}^{-2}$), whereas Mn^{2+} -crosslinked gels exhibit superior cycling stability (88.3% retention over 5000 cycles). Li^+ incorporation increases the mechanical flexibility of Mn-based gels—reducing the compressive modulus by over 60%—enhancing ion mobility and charge storage. Conversely, Cu-based gels maintain structural integrity while exhibiting improved conductivity. These findings demonstrate how biopolymer-based GPEs, designed through nanoscale engineering and ion doping, achieve an optimal balance of mechanical robustness and electrochemical performance. By combining scalability and exceptional energy storage capabilities, these materials establish a new paradigm for flexible supercapacitors and sustainable energy technologies.

1. Introduction

As global energy demand escalates, the development of efficient and sustainable energy storage systems has become increasingly critical.^[1,2] By closing the gap between batteries and traditional capacitors, supercapacitors have emerged as disruptive technology, offering power densities up to 10 kW/kg and lifespans extending to millions of charge-discharge cycles. Their ability to deliver rapid and intense energy bursts makes them well-suited for applications in electric vehicles, renewable energy systems, and backup power supplies. Unlike batteries, supercapacitors store energy electrostatically, minimizing degradation and ensuring long-term stability, making them a compelling alternative in power-intensive scenarios.^[3,4]

Electrolytes are key components of supercapacitors as they play a pivotal role in determining their energy storage efficiency and device stability.^[5] Aqueous electrolytes, such as sulfuric acid and potassium hydroxide, display high ionic conductivities and cost-effectiveness but suffer from corrosion and a restricted voltage window, limiting their energy density. Organic electrolytes, including acetonitrile-based solutions, allow for higher voltage operation (up to 3 V) yet they pose safety concerns due to flammability and cost. Ionic liquids offer an even wider electrochemical stability range ($\approx 4 \text{ V}$) and excellent thermal stability but their operation is hindered by the material's high cost and viscosity, with the latter determining a power density reduction. Gel polymer electrolytes (GPEs), which combine the advantages of liquid and solid-state electrolytes, offer enhanced safety and mechanical stability, positioning them as a promising alternative to conventional liquid and solid electrolytes.^[6,7] Upon immobilizing liquid electrolytes within a polymer matrix, GPEs mitigate issues like electrolyte leakage and ensure mechanical compliance required for modern energy storage technologies.^[6,7]

Among GPEs, biopolymer-based gel polymer electrolytes (BGPEs) offer a unique synergy of sustainability and electrochemical functionality.^[8] Conventional hydrogels have been explored as potential BGPEs; however, their susceptibility to water loss under ambient conditions, coupled with suboptimal mechanical

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properties, call for thoughtful modifications through blending, doping, or network reinforcement.^[8] Water evaporation not only compromises their mechanical integrity but also impairs ionic transport, limiting their viability for long-term energy storage applications. Organohydrogels, which combine the hydrophilic nature of hydrogels with enhanced environmental and mechanical stability, effectively overcome these limitations.^[9] However, their relatively low water content can impede ionic mobility, presenting a fundamental challenge in achieving an optimal balance in electrochemical performance.

Among the employed materials for organohydrogel fabrication, poly(vinyl alcohol) (PVA) is by far the most explored option due to its excellent mechanical properties and stability.^[10–12] Despite its widespread exploitation, PVA's limited biodegradability in natural environments raises concerns regarding its long-term sustainability.^[13–17] This underscores the need for alternative materials that offer both performance and environmental benefits. In this context, gelatin and alginate – both derived from renewable resources – have recently emerged as promising candidates. Gelatin, a polypeptide derived from collagen, forms highly elastic and versatile gel networks,^[18,19] whereas alginate, a polysaccharide extracted from brown algae, is distinguished by its ability to crosslink with divalent cations.^[20] This crosslinking behavior follows a well-defined affinity trend^[20–23]— $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Co}^{2+} \approx \text{Ni}^{2+} \approx \text{Zn}^{2+} > \text{Mn}^{2+}$, enabling precise modulation over gel properties, including mechanical strength and ionic conductivity.^[20]

Building on these principles, in this work we report the first application of a gelatin–alginate organohydrogel as a gel polymer electrolyte for supercapacitors, offering a fully biopolymeric alternative to conventional PVA-based systems. What distinguishes this system is not only its green composition, but the ionically tunable network, where Cu^{2+} or Mn^{2+} crosslinking, modulated by Li^+ incorporation, allows precise control over both mechanical stiffness and ionic transport.

Our approach integrates material sustainability, nanoscale structural tuning, and device-level optimization within a single platform. This results in exceptional electrochemical performance, with Cu^{2+} -crosslinked gels reaching areal capacitance of 591.8 mF/cm^2 , and Mn^{2+} -based gels achieving 88.3% retention over 5,000 cycles.

A direct comparison with state-of-the-art systems demonstrates that our materials offer competitive performance in terms of capacitance and energy density. This supports the potential of gelatin–alginate organohydrogels as a promising platform for sustainable, high-performance gel polymer electrolytes.

2. Results and Discussion

Figure 1a displays the synthetic pathway to form alginate–gelatin (AlgGel)-based organohydrogels. The procedure involves the dissolution of gelatin in water at 50 °C, followed by the incorporation of a 4% (w/v) alginate solution under continuous stirring (see experimental section for more details). The resulting mixture is cast into molds, cooled, and subsequently crosslinked in MCl_2 ($\text{M} = \text{Mn}$ or Cu) and LiCl solutions. After equilibration in a glycerol–water solution, the materials are dried at room temperature to yield MXAlgGel samples, where X denotes the molar concentration of MCl_2 , specifically 100 (1.00 M), 075 (0.75 M), 050 (0.50

M), or 025 (0.25 M). The LiCl concentration is adjusted to always maintain a total salt concentration of 1 M across all the formulations, ensuring a systematic modulation of the $[\text{Li}^+]/[\text{M}^{2+}]$ ratio within the crosslinking solution. This controlled ionic environment enables a precise investigation of the effects of ion composition on the physicochemical and electrochemical properties of the hydrogels (Table S1, Supporting Information). Additionally, LiAlgGel (1.00 M Li) and AlgGel samples serve as reference systems to evaluate the specific influence of metal ions on the organohydrogels. The comparable thickness of all formulations, confirmed in Figure S1 and Table S3 (Supporting Information), ensures a robust framework for performance comparisons.

The incorporation of Mn^{2+} and Cu^{2+} into alginate significantly alters the polymer matrix, restricting chain mobility and inducing water-insolubility. Qualitatively, Mn^{2+} -crosslinked hydrogels exhibit a softer texture compared to their Cu^{2+} -crosslinked counterparts, consistent with the stronger affinity of Cu^{2+} for alginate.^[20] On the other hand, MnXAlgGel and LiAlgGel organohydrogels share a similar mechanical consistency. The gels also exhibit distinct optical properties: Mn^{2+} -crosslinked samples appear transparent, whereas Cu^{2+} -crosslinked samples adopt a green hue (Figure 1a; Figure S1d, Supporting Information).

As detailed in Table S3 (Supporting Information), the organohydrogels predominantly consist of glycerol (≈ 60 wt%), while gelatin and alginate collectively contribute ≈ 20 wt%. The remaining mass (≈ 20 wt%) is attributed to water (Figure 1b), as confirmed by Thermogravimetric analysis (TGA) (Figure S2 and Table S3, Supporting Information), along with homogeneously dispersed ions. The absence of phase separation, combined with glycerol's plasticizing effect, preserves the structural integrity of the gels over several months (Figure S1d–f, Table S2, Supporting Information). Moreover, Differential Scanning Calorimetry (DSC) analysis (Figure 1c) reveals no detectable phase transition during the heating and cooling cycles, indicating that the water within the matrix is predominantly non-freezable.^[24] This suggests that the materials retain flexibility and ionic mobility even at subzero temperatures.

The composition of the crosslinking solution, which varies in Li^+ and Mn^{2+} (or Cu^{2+}) molar ratios (Table S1, Supporting Information), dictates the ion incorporation profile of the resulting organohydrogels (Table S4, Supporting Information). As illustrated in Figure 1d, the Li^+ uptake increases proportionally with its concentration in the crosslinking medium, although its incorporation efficiency differs significantly between Mn^{2+} - and Cu^{2+} -crosslinked systems. In particular, the experimental molar ratio of Li^+ to M^{2+} ($n_{\text{Li}^+}/n_{\text{M}^{2+}}$) in the hydrogel matrix reaches a maximum of 2.08 for Mn025AlgGel and 1.28 for Cu025AlgGel , underscoring the higher permeability of Mn^{2+} -crosslinked networks to Li^+ ions. This trend aligns with the structural characteristics observed through SAXS analysis, as discussed later.

Importantly, this controlled variation of ionic composition provides a straightforward and reproducible strategy to modulate the internal structure and functional behavior of the gels. Such systematic tuning of ion uptake within a fully biopolymer-based system offers a degree of design precision that is still underexplored in the field of sustainable gel polymer electrolytes.

Figure 1e,f displays the compressive behavior of the gels. They reveal that AlgGel , which is characterized by the lowest water content due to the lack of hygroscopic ions, exhibits

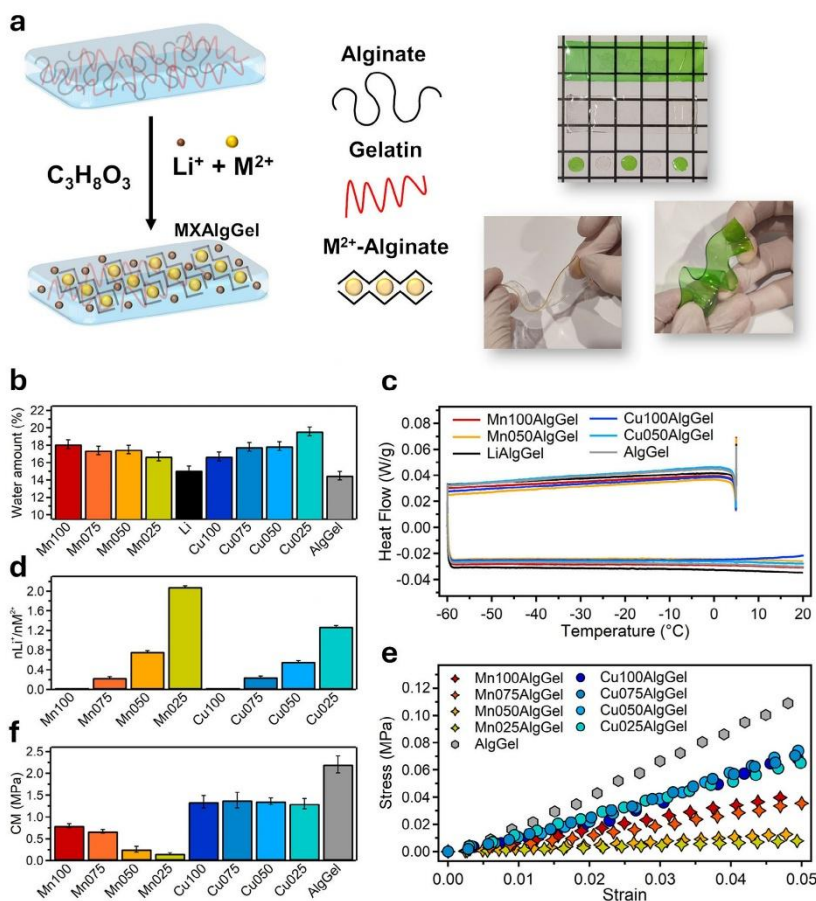


Figure 1. a) Schematic representation of the preparation process for AlgGel-based organohydrogels and their visual appearance. b) Water content, and c) freezable water evaluation through DSC analysis (Exo up). d) Experimental Li^+ over M^{2+} molar ratio (nLi^+/nM^{2+}) for the AlgGel-based organohydrogels. e) Stress-strain curves, and f) compressive modulus (CM) values of Cu100AlgGel, Cu075AlgGel, Cu050AlgGel, Cu025AlgGel, Mn100AlgGel, Mn075AlgGel, Mn050AlgGel, Mn025AlgGel and AlgGel.

the highest compressive modulus (CM, ≈ 2.20 MPa). Among Mn^{2+} -crosslinked gels, Mn100AlgGel attains a CM of ≈ 0.80 MPa, whereas Mn025AlgGel undergoes a pronounced decline to ≈ 0.15 MPa, reflecting progressive network disorganization with increasing Li^+ content. In contrast, Cu^{2+} -crosslinked gels display

consistently high CMs (≈ 1.36 MPa), irrespectively of Li^+ incorporation. This mechanical robustness is attributed to the strong Cu^{2+} -alginate interactions, which preserve network integrity even in the presence of Li^+ ions. These findings reveal that, while Li^+ ions addition destabilizes Mn^{2+} -crosslinked networks,

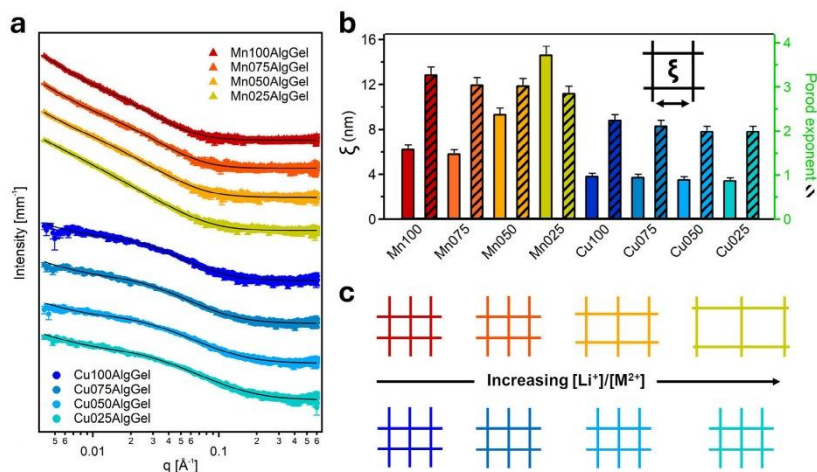


Figure 2. a) SAXS curves (in log scale and offset for clarity) and b) extracted correlation lengths (ξ) and Porod exponents (dashed bars) for MnXAlgGel and CuXAlgGel. c) Schematic representation of the structural differences between Mn²⁺- and Cu²⁺-crosslinked networks as a function of $[Li^+]/[Mn^{2+}]$ ratio in the crosslinking solution. MnXAlgGels show increasing ξ with higher Li⁺ content, indicating a progressively looser network. In contrast, CuXAlgGels maintain a consistently compact network structure.

Cu²⁺-crosslinked systems retain their mechanical strength, making them superior candidates for applications requiring both stability and adaptability.

The structural characteristics of alginate-gelatin gels crosslinked with Cu²⁺ or Mn²⁺ ions, in combination with Li⁺, offer valuable insights into their potential as GPEs for energy storage applications. SAXS analysis is employed to elucidate how these crosslinking ions govern the nanoscale organization of the gels, thereby establishing a direct correlation between their internal structure, mechanical and functional properties. To quantify the correlation lengths between the polymer chains, SAXS curves (Figure 2a) are fitted using the following equation:^[23–28]

$$I(q) = \frac{A}{q^n} + \frac{B}{1 + (q\xi)^m} + bkg \quad (1)$$

in which A is the Porod scaling factor, n is the Porod exponent, B is the Lorentzian scale factor, m is the Lorentzian exponent, ξ is the correlation length and bkg is the background. The results of the fittings are reported in Table S5 (Supporting Information), while correlation lengths and Porod exponents are presented in Figure 2b.

Cu²⁺ and Mn²⁺ ions facilitate alginate crosslinking primarily through interactions with carboxylate groups, though their binding strengths differ significantly. Cu²⁺ establishes stronger and more localized interactions compared to Mn²⁺, resulting in a denser and more rigid hydrogel network.^[24,29] This difference

is apparent in the SAXS analysis, where the correlation lengths (ξ) in Cu²⁺-crosslinked gels are consistently small (3.5–3.9 nm) regardless of the nLi^+/nCu^{2+} ratio, indicating a structurally resilient network. In contrast, the Mn²⁺-crosslinked gels exhibit a pronounced increase in ξ from 6.3 nm to 14.7 nm when increasing nLi^+/nMn^{2+} ratios, reflecting the progressive disruption of Mn²⁺ crosslinking by Li⁺ incorporation. This effect can be attributed to competitive ion exchange,^[20] which leads to a progressively more open network (Figure 2c). In contrast, Cu²⁺-crosslinked gels maintain their structural integrity, effectively resisting such perturbations.

The Porod exponent (n) further provides evidence of these structural differences. In Mn²⁺-crosslinked gels, n decreases from 3.29 to 2.87 as the nLi^+/nMn^{2+} ratio increases, indicating a transition from a compact, mass-fractal-like network to a more open structure.^[25–28] In contrast, Cu²⁺-crosslinked gels exhibit lower and less dissimilar n values (2.26 to 2.01), indicative of a surface-fractal-like morphology. This subtle yet important distinction emphasizes the rigidity imparted by Cu²⁺ ions, which creates a network resistant to deformation despite appearing less compact at the nanoscale.

This interplay between rigidity and flexibility presents distinct advantages for energy storage applications. The highly crosslinked, structurally robust Cu²⁺-gel network displays exceptional mechanical stability. Their highly organized nanoscale structure, as observed through SAXS, suggests efficient ion transport pathways, making them strong candidates for applications requiring robust and stable electrolyte frameworks,

such as solid-state batteries. Conversely, Mn^{2+} -crosslinked gels feature looser and more flexible networks with the increase of Li^+ ions concentration, providing enhanced ionic mobility due to their porous architecture. While this increased mobility, later confirmed by electrochemical characterization, may offer advantages in facilitating ion movement, the weaker crosslinking interactions could compromise long-term mechanical resilience. By modulating Cu^{2+} , Mn^{2+} , and Li^+ ratios, these gels can be engineered to achieve an optimal balance between mechanical robustness and ionic conductivity. Notably, this dual-ion crosslinking approach – combined with SAXS as a structural diagnostic – offers a rare opportunity to deliberately tune nanoscale gel architecture in fully biopolymer-based systems. This approach enables precise control over internal organization, directly linking nanoscale structure to electrochemical performance, a crucial but often overlooked factor in the design of next-generation sustainable gel polymer electrolytes.

This versatility underscores their potential as next-generation GPEs, with SAXS providing a critical foundation for understanding and optimizing their performance.

To evaluate the thermal stability of AlgGel-based gel electrolytes for energy storage applications, TGA was conducted. Figure S2 and Table S3 (Supporting Information) reveal that all samples undergo thermal degradation onset at approximately 190 °C, except for those with high Cu^{2+} content (Cu075–Cu100), which degrade at slightly lower temperatures (≈ 180 °C) due to the catalytic effect of Cu^{2+} on decomposition.^[20,30] These results confirm that, despite their biopolymeric nature, gelatin-alginate gels maintain the thermal tolerance required for practical energy storage applications, where organohydrogel electrolytes are generally expected to operate at temperatures up to approximately 80 °C.^[8,31,32]

Building on their distinct physicochemical properties, we assess the electrochemical performance of AlgGel-based organohydrogels as gel electrolytes in symmetric supercapacitors, establishing correlations with their nanoscale structures as unveiled by SAXS. To this end, coin-cells were assembled using activated carbon as both the cathode and anode materials, while the different organohydrogel formulations served as electrolytes (see experimental section for more details). Their electrochemical properties were systematically analyzed to determine their viability for energy storage applications.

Electrochemical impedance spectroscopy (EIS) was conducted to analyze the ionic transport characteristics (Figures 3a and S3, Supporting Information). A key parameter extracted from EIS is the bulk resistance (R_b), which accounts for intrinsic electrolyte resistance, including ion migration within the gel matrix. In Nyquist plots, R_b is identified as the high-frequency intercept on the real axis (Z'), reflecting the ease with which ions move within the electrolyte. For gel electrolytes, low bulk resistance is crucial, as it indicates efficient ionic conductivity and minimal energy loss during charge transport. It is important to note that the gels are electronically insulating; therefore, the conductivity values extracted from EIS (see Table S6, Supporting Information) refer exclusively to ionic transport. Elevated R_b may indicate hindered ion mobility due to factors such as poor ion dissociation, increased viscosity, or excessive crosslinking density within the gel network. Another critical parameter, the charge transfer resistance (R_{ct}), quantifies the efficiency

of ion exchange at the electrode-electrolyte interface, where lower R_{ct} values indicate faster electrochemical kinetics, enabling rapid charge/discharge cycles, which is essential for high-power applications.

Among gels crosslinked exclusively with single divalent metal ions, Cu100AlgGel exhibits the highest R_b (119.0 Ω , Table S6, Supporting Information), consistent with its tightly packed and localized Cu^{2+} -alginate network as revealed by SAXS ($\xi = 3.9$ nm). In contrast, Mn100AlgGel shows a lower R_b (73.3 Ω) due to its looser and more open structure ($\xi = 6.3$ nm), which facilitates faster ion diffusion through the bulk. However, the charge transfer resistance (R_{ct}) displays the opposite trend: Cu100AlgGel has a lower R_{ct} (239.9 Ω) compared to Mn100AlgGel (296.4 Ω). This suggests that the stronger coordination of Cu^{2+} with the alginate matrix forms a more cohesive and stable electrode–electrolyte interface, promoting efficient ion–electron exchange. Conversely, the weaker and more dynamic Mn^{2+} –polymer interactions, while favorable for bulk transport, may lead to a less well-defined interfacial structure and hinder charge transfer. These results demonstrate that R_b and R_{ct} capture different aspects of the electrochemical behavior – bulk conductivity and interfacial kinetics, respectively – and must be interpreted independently when evaluating gel electrolyte performance. LiAlgGel, with its highly disordered and porous matrix, exhibits the lowest R_b (32.7 Ω), indicating superior bulk ion mobility. Notably, as shown in Figure S3b, c (Supporting Information), even small additions of Li^+ in Mn^{2+} - and Cu^{2+} -crosslinked gels (Mn075AlgGel and Cu075AlgGel) significantly reduce R_b , making their impedance profiles increasingly similar to that of LiAlgGel.

Cyclic voltammetry (CV) measurements (Figure 3b) provide further insights into the electrochemical performance of the gel electrolytes. The area enclosed by the CV loop is directly proportional to the material's capacitance and overall electrochemical performance, with larger areas indicating greater charge storage capacity and improved ionic mobility. Among the samples, LiAlgGel displays the largest CV loop, demonstrating its high capacitance, which arises from its open structure and excellent ionic transport properties. In contrast, Cu100AlgGel and Mn100AlgGel display smaller loop areas due to the strong M^{2+} -polymer interactions that reinforce the polymer matrix. While these interactions enhance structural stability, they also restrict ionic mobility, leading to lower capacitances. As expected, AlgGel, lacking crosslinked metal ions, exhibits negligible electrochemical activity.

Figure 3c,d further illustrate the impact of Li^+ incorporation on electrochemical performance. Increasing the $n\text{Li}^+/n\text{Cu}^{2+}$ ratio progressively expands the CV loop area, as Li^+ ions disrupt the Mn^{2+} -dominated network, enhancing ionic mobility and increasing capacitance, while simultaneously reducing structural rigidity. In the Cu^{2+} -crosslinked gels, higher $n\text{Li}^+/n\text{Cu}^{2+}$ ratio yields a synergistic effect, where Li^+ ions improve ion transport while Cu^{2+} ions preserve structural integrity. This combination results in progressively larger CV loops, with Cu050AlgGel surpassing even LiAlgGel, demonstrating its high potential for energy storage applications.

The galvanostatic charge-discharge (GCD) profiles (Figure 4a,b) provide further insights into the electrochemical performance of Mn^{2+} - and Cu^{2+} -crosslinked organohydrogel electrolytes, revealing their charge storage capabilities and

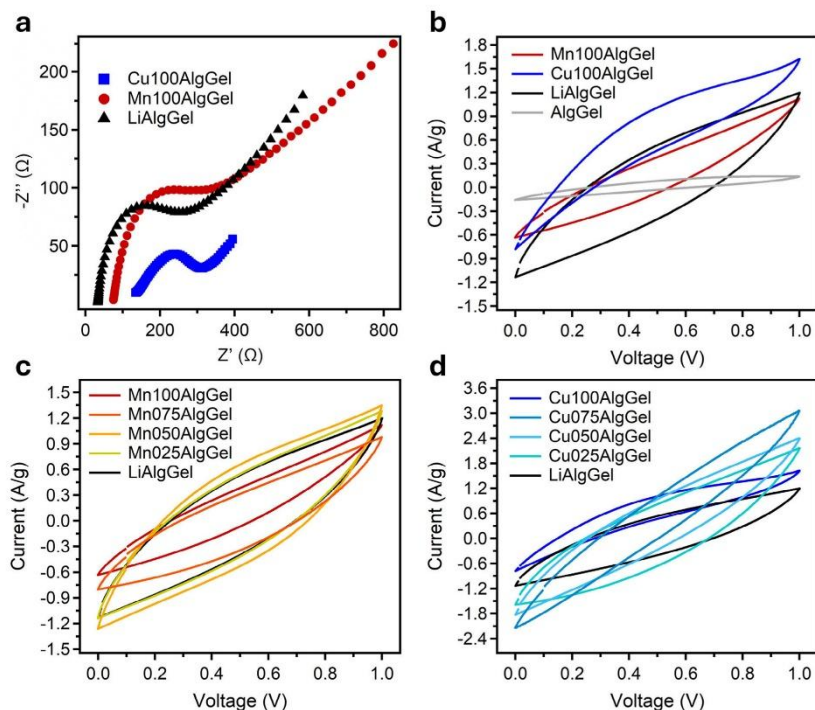


Figure 3. a) Nyquist plot showing the impedance behavior for Cu100AlgGel, Mn100AlgGel, and LiAlgGel in supercapacitors. A comparison with AlgGel is provided in Figure S3a (Supporting Information). b) CV curves of gels with single cationic species at 10 mV s^{-1} in supercapacitors. CV curves at 10 mV s^{-1} of c) MnXAlgGels and d) CuXAlgGels in supercapacitors. The CV curves for other scan rates are reported in Figures S4–S6 (Supporting Information).

stability. The shape and duration of the charge-discharge profiles reveal key differences in ionic transport and capacitance retention across the different formulations. The GCD curves of MnXAlgGels show a progressive improvement in charge storage when increasing the $n\text{Li}^+/n\text{Mn}^{2+}$ ratio. Mn050AlgGel exhibits the longest discharge time, confirming its optimal balance between structural stability and enhanced ionic mobility. This behavior aligns with the CV results, where Mn050AlgGel demonstrated a larger electrochemical response. In contrast, Mn100AlgGel shows a significantly shorter discharge time, indicating higher internal resistance, and limited ionic transport due to its more rigid Mn^{2+} -dominated network, in agreement with EIS and SAXS characterization, respectively. The gradual transition from Mn100AlgGel to Mn025AlgGel reveals how Li^+ incorporation progressively disrupts the Mn^{2+} network,

improving charge storage efficiency in full agreement with the previous characterizations.

The GCD curves for CuXAlgGels display notable differences in performance, reflecting the impact of Cu^{2+} crosslinking on ion mobility and capacitance. Cu050AlgGel outperforms the other Cu-based gels, exhibiting the longest discharge time, consistent with its superior capacitance observed in CV measurements (see Figure 3d). The synergy between Cu^{2+} and Li^+ optimizes both structural integrity and ionic transport, making Cu050AlgGel a promising candidate for energy storage applications. However, Cu100AlgGel and Cu075AlgGel struggle to reach 1 V, which suggests high internal resistance due to excessively strong Cu^{2+} -polymer interactions restricting ion mobility. This observation is further supported by the EIS data, where Cu100AlgGel exhibits the highest R_b . LiAlgGel, despite its high ionic mobility,

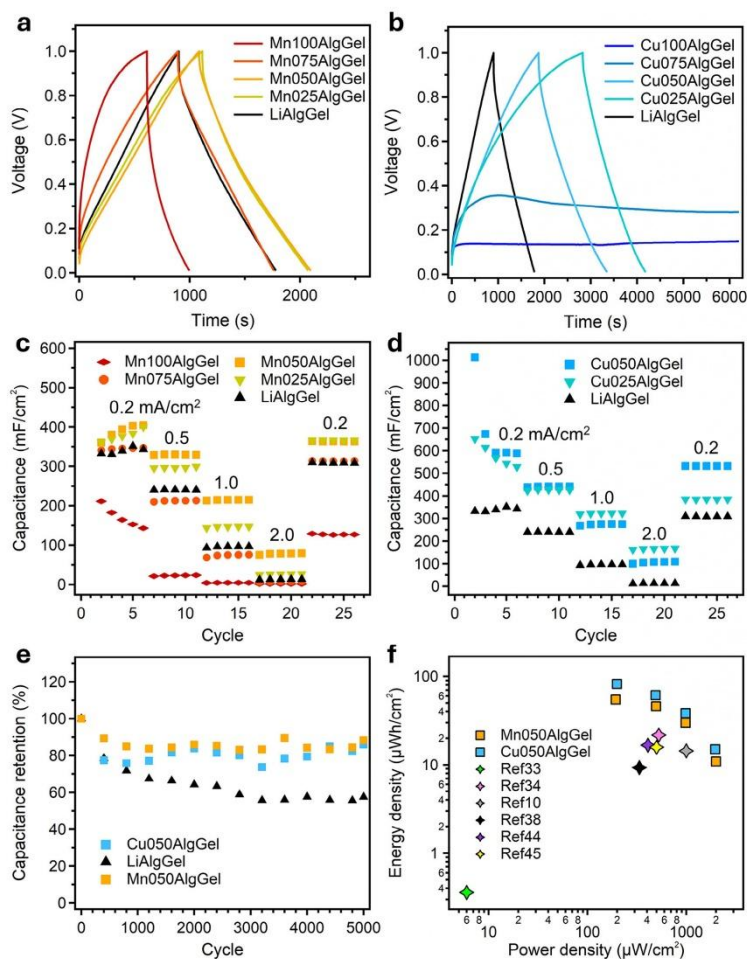


Figure 4. GCD curves of a) MnXAlgGels and b) CuXAlgGels along with LiAlgGel. (current density = 0.2 mA/cm², other current densities can be seen in Figures S7, S8, Supporting Information). Figure S9 (Supporting Information) compares the GCD curves of AlgGel, Mn100AlgGel, Cu100AlgGel and LiAlgGel. In panel c) and d) the areal capacitances of MnXAlgGels and CuXAlgGels (respectively) along with LiAlgGel, at different current densities (i.e., 0.2 mA cm⁻², 0.5 mA cm⁻², 1.0 mA cm⁻², 2.0 mA cm⁻²). Both Mn- and Cu-based systems exhibit excellent rate capability, as the capacitance measured at 0.2 mA cm⁻² is fully recovered and remains stable after cycling at a high current density of 2.0 mA cm⁻², indicating robust structural and electrochemical reversibility. e) Capacitance retention over cycling of Mn050AlgGel, Cu050AlgGel and LiAlgGel over 5000 charge/discharge cycles. f) Ragone plot comparing the energy and power densities of Mn050AlgGel and Cu050AlgGel with state-of-the-art references from Table S9 (Supporting Information).

shows a shorter discharge duration compared to Mn050AlgGel and Cu050AlgGel, reinforcing the idea that, while Li^+ enhances ion transport, the absence of divalent metal crosslinking reduces structural stability and long-term performance.

Figure 4c,d and Table S7 (Supporting Information) display the areal capacitance of AlgGel-based organohydrogels, highlighting the impact of crosslinking composition on ionic transport and charge storage. In Mn^{2+} -crosslinked gels (Figure 4c), capacitance improves with increasing the $n\text{Li}^+/n\text{Mn}^{2+}$ ratio, peaking at Mn050AlgGel (394.2 mF cm^{-2} at 0.2 mA cm^{-2}). This balance optimizes ionic mobility while maintaining structural integrity. In Cu^{2+} -crosslinked gels (Figure 4d), Cu050AlgGel achieves the highest capacitance (591.8 mF cm^{-2} at 0.2 mA cm^{-2}), surpassing both Mn-based gels and LiAlgGel. This outstanding performance arises from the synergistic effect of Cu^{2+} maintaining network stability while Li^+ enhances ion transport. SAXS and mechanical data confirm that the compact and stable Cu^{2+} network supports efficient ionic transport even with increasing Li^+ content.

The capacitance retention of Mn050AlgGel, Cu050AlgGel, and LiAlgGel over 5000 charge-discharge cycles (Figure 4e) provides further insights into their long-term electrochemical performance. Among the samples, Mn050AlgGel exhibits the highest capacitance retention (Figure 4e), maintaining 88.3% of its initial value (from 404.68 to $357.27 \text{ mF cm}^{-2}$) over 5000 charge/discharge cycles, highlighting its robust structural integrity and sustained ionic mobility over extended cycling. Cu050AlgGel follows closely, with 85.9% capacitance retention (from 588.6 to $505.56 \text{ mF cm}^{-2}$), reinforcing the mechanical resilience of Cu^{2+} crosslinking in preventing degradation while maintaining efficient charge storage. In contrast, LiAlgGel exhibits the lowest capacitance retention ($\approx 57.6\%$, from 342.76 to $197.38 \text{ mF cm}^{-2}$), which we attribute to minor interfacial rearrangements during extended cycling. This behavior is expected in non-crosslinked systems and does not reflect any change in composition or chemical stability, as confirmed by XPS analysis.

The ionic composition of Mn050AlgGel and Cu050AlgGel remains stable after prolonged cycling, as confirmed by XPS survey spectra (Figures S10a,S11a, Supporting Information) and the corresponding elemental analysis (Table S8, Supporting Information), which reveal no significant changes in atomic ratios. High-resolution Mn 2p and Cu 2p spectra (Figures S10c,d and S11c,d, Supporting Information) confirm the retention of the Cu^{2+} oxidation state and indicate the presence of partially oxidized Mn^{3+} , likely arising from surface oxidation of Mn^{2+} during sample handling or XPS measurement. Notably, these oxidation features remain unchanged after 5000 charge/discharge cycles, demonstrating redox stability. The gels also retain their macroscopic appearance (Figure S10b,S11b, Supporting Information), indicating structural integrity. These results demonstrate that the excellent electrochemical performance is primarily governed by the intrinsic chemical and physical stability of the ionically crosslinked biopolymer network.

Table S9 (Supporting Information) and Figure 4f demonstrate that Cu050AlgGel and Mn050AlgGel outperform most state-of-the-art organohydrogel electrolytes in capacitance, energy density, and power density, establishing them as highly promising materials for sustainable energy storage. Cu050AlgGel achieves the highest capacitance (591.8 mF cm^{-2} , 59.2 F g^{-1}) and en-

ergy density ($82.2 \text{ } \mu\text{Wh cm}^{-2}$, 8.2 Wh kg^{-1}), surpassing conventional hydrogel-based electrolytes, while Mn050AlgGel follows closely (capacitance: 394.2 mF cm^{-2} , 39.4 F g^{-1} ; energy density: $54.8 \text{ } \mu\text{Wh cm}^{-2}$, 5.5 Wh kg^{-1}). Their exceptional power densities ($1957.8 \text{ } \mu\text{W cm}^{-2}$, 196.5 W kg^{-1} for Cu050AlgGel and $1994.9 \text{ } \mu\text{W cm}^{-2}$, 192.7 W kg^{-1} for Mn050AlgGel) highlight their potential for high-power applications requiring rapid charge/discharge cycles. Additionally, Mn050AlgGel exhibits the best long-term stability (88.3% retention over 5000 cycles), while Cu050AlgGel retains 85.9%, reinforcing their durability. These results reflect the effectiveness of our ionically tunable design strategy, where compositional control and nanoscale structural optimization translate directly into device-level performance. Compared to existing materials, the gelatin-alginate gels developed in this work present an optimal balance between ionic conductivity, mechanical stability, and electrochemical performance, positioning them as strong candidates for next-generation, sustainable energy storage solutions. [33–35,10–12,36–45]

3. Conclusion

This study demonstrates the successful development of gelatin-alginate organohydrogels as gel polymer electrolytes for supercapacitors, leveraging divalent metal crosslinking and Li^+ doping to modulate their mechanical and electrochemical properties. Small-angle X-ray scattering provided fundamental insights into how nanoscale structural organization governs ionic transport and mechanical stability, shedding light on the electrochemical behavior of these materials.

The incorporation of Li^+ significantly influences both mechanical properties and ionic transport in Mn^{2+} - and Cu^{2+} -crosslinked gels. In Mn^{2+} -crosslinked gels, Li^+ disrupts the rigid network, reducing the compressive modulus (Mn050AlgGel: $\approx 0.26 \text{ MPa}$) while enhancing ion mobility, leading to improved charge storage (394.2 mF cm^{-2}), an energy density of $54.8 \text{ } \mu\text{Wh cm}^{-2}$, a power density of $1994.9 \text{ } \mu\text{W cm}^{-2}$, and excellent capacitance retention of 88.3% over 5000 cycles. In contrast, Cu^{2+} -crosslinked gels maintain structural integrity ($\approx 1.36 \text{ MPa}$) while benefiting from Li^+ -induced conductivity improvements, resulting in the highest capacitance (591.8 mF cm^{-2}), along with an energy density of $82.2 \text{ } \mu\text{Wh cm}^{-2}$, a power density of $1957.8 \text{ } \mu\text{W cm}^{-2}$, and capacitance retention of 85.9% over 5000 cycles. While Mn-based gels become more flexible with Li^+ , Cu-based gels balance mechanical stability and ionic transport, making Li^+ a crucial factor in optimizing gel polymer electrolytes for high-performance and durable supercapacitors.

These findings establish gelatin-alginate gels as promising sustainable candidates for energy storage applications, particularly in flexible electronics, wearable devices, and renewable energy systems. The scalability and environmental sustainability of gelatin and alginate position them as viable alternatives to conventional synthetic electrolytes, supporting industrial adoption. More broadly, this work introduces a rational design strategy for biopolymer-based electrolytes, where multivalent ionic crosslinking and nanoscale structural tuning are used to control functional performance. This platform may be extended to other soft electrochemical systems, bridging the gap between sustainable materials and application-specific engineering.

4. Experimental Section

Materials: Sodium alginate (alginic acid sodium salt) was obtained from Sigma-Aldrich (Product code: 180947, Mannuronate/Guluronate ratio = 1.50 ± 0.04 , determined via FT-IR spectroscopy^[46] molecular weight ≈ 132 kDa, determined via viscosimetric analysis^[46]). Gelatin derived from porcine skin (Product code: G2625, type A, gel strength ≈ 175 g Bloom) and glycerol (BioXtra, $\geq 99\%$) were also sourced from Sigma-Aldrich. Manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, ACS reagent $\geq 99.8\%$), lithium chloride (LiCl, ACS reagent $\geq 99.0\%$), and copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ACS reagent $\geq 99.0\%$) were purchased from Sigma-Aldrich. Polyvinylidene fluoride (PVDF) binder, and N-Methyl-2-pyrrolidone (NMP) were purchased in Sigma Aldrich, high-surface active carbon (AC) for super-capacitor electrode and Super P Conductive Carbon Black were purchased in MTI corporation. Deionized water was used for all solution preparations. All reagents were used without further purification.

Gel Polymer Electrolytes Preparation: To prepare the gel polymer electrolytes, 1.36 g of gelatin was dissolved in 11.3 mL of water under gentle stirring at 50°C for 10 minutes. A 4% (w/v) alginate solution (3.80 g) was then added, and the mixture was stirred at 50°C for an additional 10 minutes.

Next, 6 mL of the solution was poured into polystyrene molds (2×6 cm) and allowed to cool at room temperature for 10 minutes. The molds were subsequently refrigerated at 4°C for 10 minutes and immersed in 50 mL of an aqueous solution containing MCl_2 ($\text{M} = \text{Mn}$ or Cu) and LiCl for 1 hour. The specific concentrations of MCl_2 and LiCl used in the crosslinking solutions were detailed in Table S1 (Supporting Information).

The molds were then transferred to a glycerol:water solution (1:4 by volume) containing the same salt concentrations as detailed in Table S1 (Supporting Information) and incubated for 1.5 hours. To remove excess salts, the molds were immersed in a fresh glycerol:water solution (1:4 by volume) for an additional 1.5 hours. The samples, dried overnight under a fume hood and equilibrated at 40% relative humidity (RH), were named MXAlGel, where M refers to the metal ion (Mn, or Cu) and X refers to their molar concentration 100 (1.00 M), 075 (0.75 M), 050 (0.50 M), or 025 (0.25 M). Note that the LiCl concentration was adjusted accordingly to always maintain a total salt concentration of 1 M (see Table S1, Supporting Information). LiAlGel was also studied to understand the effect of the metal ion in the physicochemical properties and electrochemical performance of the resulting organohydrogels. AlGel was used as a blank for comparative purposes. All samples were stored in hermetically sealed Petri dishes under dark conditions until their use. The results labeled as 6-month-old samples were obtained from samples stored according to this protocol. Before characterization, samples were cut into disk shapes or stripes (1 cm diameter and width, respectively).

Coin-Cell Assembly: Working electrodes were prepared by mixing AC (80 wt%, 16 mg), Super P (10 wt%, 2 mg), and PVDF (10 wt%, 2 mg) in an agate mortar with several drops of NMP to form a homogeneous paste. The paste was coated onto carbon paper electrodes (0.8 cm diameter) and dried overnight under vacuum at 80°C . The mass loading of active carbon on each electrode was ≈ 2 mg cm^{-2} . Two electrodes were assembled in CR2032 stainless steel coin cells with the AlGel-based organohydrogels (1.0 cm diameter) serving as the electrolyte.

Characterization Techniques: **Small Angle X-ray Scattering (SAXS):** Small angle scattering measurements were performed using a Xeuss 3HR system with a scatterless collimation camera and a hybrid detector (Eiger 1M, Dectris). $\text{Cu K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) was produced by an ultra-brilliant point microfocus X-ray source (GENIX-Fox 3D, Xenocs, Grenoble) operating at 30 W. Measurements were taken at two sample-to-detector distances (375 mm and 1750 mm) to cover a q-range of $0.004 \text{ \AA}^{-1}$ to $0.6 \text{ \AA}^{-1}$. Data analysis was conducted using SasView software. (<http://www.sasview.org/>).

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES): The Li^+ , Na^+ , Mn^{2+} , and Cu^{2+} content in the AlGel-based samples was quantified using an Agilent 720-ES ICP-AES instrument equipped with a pneumatic nebulizer. Approximately 10 mg of each sample was dissolved in 2 mL of 0.05 M Na_2EDTA and 10% (w/v) NaOH solution at 80°C for 1

hour with magnetic stirring. After dilution, measurements were performed in triplicate using calibration lines from certified standards.

Thermogravimetric Analysis (TGA): A Discovery SDT650 (TA Instruments) was used. Samples were analyzed under air flow (100 mL min^{-1}) with a heating rate of $10^\circ\text{C min}^{-1}$ from room temperature to 950°C and using aluminum pans. For the water content determination, a heating ramp from RT to 120°C (rate of $10^\circ\text{C min}^{-1}$), followed by a 10 minutes isotherm. Measurements were performed under N_2 flux (100 mL min^{-1}), using aluminum pans. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Samples were all equilibrated at RH = 40% prior the measurement.

Differential Scanning Calorimetry (DSC): DSC measurements were performed using a Discovery DSC 2500 instrument. Samples equilibrated at 40% RH were hermetically sealed within Tzero Aluminum Hermetic pans (TA Instruments) and then investigated by cooling from 5°C to -60°C , then heated from -60°C to 25°C , in both cases using a heating rate of 1°C min^{-1} under nitrogen (N_2) flow. Data were processed with Trios v5.1.1.46572 software (TA Instruments).

Mechanical Properties: Compressive properties AlGel-based electrolyte disks (1 cm of diameter) were measured using a Discovery DHR-3 rheometer, using a head plate with 2 cm of diameter. The compression speed was $2 \mu\text{m s}^{-1}$. The compressive modulus (CM) of the samples was determined from the slope of the linear fit to the stress – strain curves shown in Figure 1e, within the 0.00 – 0.05 strain range. Traction tests on Mn050AlGel and Cu050AlGel samples, before and after storage, were performed using a Mark-10 M7-025E digital force gauge mounted on a Mark-10 ESM-303E motorized test stand. Samples were cut into stripes (1 cm width), clamped at the edges and stretched at a constant rate of 30 mm/min. The Young's modulus (YM) was determined by linear fitting of the stress vs. strain curves shown in Figure S1f (Supporting Information), within the 0.0 – 0.2 strain range.

Electrochemical Characterization: The electrochemical performance of the AlGel-based organohydrogels was studied using cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) on Autolab PG-STAT128N Potentiostat / Galvanostat instruments with a Metrohm Autolab DuoCoin Cell Holder (Metrohm AG) at room temperature. CV was performed at scan rates of $2\text{--}10 \text{ mV s}^{-1}$ in the voltage range between 0 and 1.8 V or 0 and 1.0 V. EIS measurement was recorded with a frequency range of 0.01 Hz to 1 MHz, with data fitted to an equivalent circuit model (Figure S12, Supporting Information) to extract key electrochemical parameters. The galvanostatic charge-discharge (GCD) tests were carried out on Neware Battery Tester (BTS-4008T-5V/10mA, Neware Technology Company, Guangdong, China). GCD curves were tested at current densities ranging from 0.2 to 2 mA cm^{-2} .

• Calculation of ionic conductivity (σ)

$$\sigma = \frac{l}{R_b \cdot A} \quad (2)$$

Being l the gel thickness (Table S3, Supporting Information), A the gel area (0.50 cm^2) and R_b the bulk resistance

X-ray Photoelectron Spectroscopy: X-ray Photoelectron Spectroscopy (XPS) (Thermo Scientific K-Alpha X-ray photoelectron spectrometer) equipped with an aluminum X-ray source (energy 1.4866 keV) at a vacuum level of 10^{-8} – 10^{-9} mbar in the main chamber. The spot size of the X-ray beam was fixed at 400 μm .

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P.T., V.M.G., M.B., P.S., and A.C. conceived the experiments and designed the study. P.T. performed the physicochemical characterization. P.T. and V.M.G. performed the electrochemical characterization. A.T. measured the electrical conductivity of the gels. P.T., V.M.G., A.T., M.B., P.S., and A.C. discussed the results and contributed to the interpretation of data. P.T., V.M.G., M.B., P.S., and A.C. cowrote the paper with input from all coauthors.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

alginate, crosslinking, energy storage, gelatin, gel electrolytes, organohydrogels, supercapacitors

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Fully Bio-Based Gelatin Organohydrogels via Enzymatic Crosslinking for Sustainable Soft Strain and Temperature Sensing

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Developing soft materials that integrate mechanical compliance, functional responsiveness, and environmental sustainability is key for next-generation wearable and implantable electronics. Here, a sustainable, fully bio-based organohydrogel sensor made entirely from food-grade and biodegradable components, including gelatin, microbial transglutaminase (TG), and glycerol, prepared via a simple one-pot process under mild thermal conditions, is reported. In this system, TG enzymatically crosslinks gelatin chains into a robust covalent network, while glycerol enhances flexibility, stabilizes hydration, and facilitates proton conduction. The multicomponent system reveals a tunable network morphology governed by enzymatic crosslinking density. The resulting gels exhibit remarkable stretchability (up to 450%), linear strain sensitivity up to 300%, and a high gauge factor of 2.86—placing them among the top-performing hydrogel-based strain sensors to date. In addition to strain sensing, the material shows strong thermal responsivity ($0.26\text{ }^{\circ}\text{C}^{-1}$ in the $20\text{--}45\text{ }^{\circ}\text{C}$ range) without being affected by variations in environmental humidity. Long-term electromechanical stability is demonstrated over 5000 cycles. Unlike conventional soft sensors that rely on synthetic polymers, fillers, or dopants, this platform entirely uses food-safe components and a simple one-pot process—offering a scalable and sustainable route to soft electronics. These findings establish enzyme-guided polymer engineering as a powerful tool for functional material design.

ambient conditions.^[1–9] Conventional conductors and synthetic composites often fall short in delivering the necessary stretchability, skin compatibility, and environmental resilience needed for real-world use. This challenge has fueled growing interest in developing materials that inherently combine mechanical compliance, ionic conductivity, and sustainability—particularly for applications in health monitoring, motion recognition, and transient systems.^[10–14] In this context, hydrogels have emerged as a promising class of soft conductors,^[15–21] owing to their hydrated networks that support efficient ion transport.^[22–24] However, standard hydrogels are prone to dehydration, mechanical fatigue, and instability under fluctuating humidity and/or temperature, limiting their suitability for long-term, on-skin sensing platforms.

To overcome these drawbacks, organohydrogels—hydrated polymer networks partially replaced with hygroscopic organic molecules such as glycerol—have been proposed as more robust alternatives.^[25,26] These materials exhibit improved dehydration resistance, enhanced elasticity, and increased resilience to mechanical stress, making them suitable for wearable sensors operating in real-world environments. However, most organohydrogels reported in literature rely on synthetic polymers or conductive fillers (e.g., reduced graphene oxide (rGO), carbon nanotubes (CNTs), polyaniline (PANI)), and

1. Introduction

The advancement of wearable and implantable electronics requires soft materials that can withstand mechanical deformation while maintaining stable electrical performance under

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poly(3,4-ethylenedioxythiophene) (PEDOT), which render the processing complicated, limit sustainability, and reduce key functional properties such as transparency.^[27–30] As a result, there is growing interest in developing biopolymer-based organohydrogels capable of delivering multifunctional performance without compromising sustainability, safety, or fabrication simplicity.

Among available biopolymers, gelatin is particularly attractive due to its biocompatibility, biodegradability, low cost, and temperature responsiveness.^[31–33] Derived from the hydrolysis of collagen, gelatin exhibits excellent film-forming properties and contains functional groups amenable to chemical or enzymatic crosslinking. However, unmodified gelatin gels suffer from poor thermal and mechanical stability, especially under hydrated conditions. To overcome these limitations, microbial transglutaminase (TG), a food-grade enzyme produced by microbial fermentation, provides an effective and environmentally benign route to covalently stabilize gelatin networks. TG catalyzes the formation of ϵ -(γ -glutamyl)lysine isopeptide bonds between adjacent polypeptide chains, generating robust and permanent crosslinks without toxic reagents or harsh conditions.^[34–37] Despite its commercial availability, low cost, mild reactivity, and widespread use in the food industry, TG remains surprisingly underexplored in the context of soft electronics and responsive organohydrogels, where sustainable and biofriendly crosslinking strategies are in high demand.

Herein, we report a fully bio-based and transparent organohydrogel based on gelatin, glycerol, and TG, fabricated through a simple one-pot process at 60 °C. Unlike previously reported hydrogel sensors that rely on synthetic matrices or conductive additives, our system uniquely combines enzymatic covalent crosslinking and glycerol-mediated stabilization to achieve multifunctional sensing entirely from bio-derived components. Glycerol, a cheap and widely available food-grade byproduct, serves as a biocompatible plasticizer and humectant, ensuring flexibility and water retention for real-world applications. The resulting organohydrogels (GELTG) exhibit high stretchability (up to 450%), excellent strain sensitivity over a wide deformation range (0–300%) with a gauge factor of 2.86, and robust temperature sensitivity (0.26 °C^{−1}) within the physiological range. Importantly, these properties are achieved without conductive fillers, salt dopants, or synthetic monomers, and the materials display stable and robust responses under humidity fluctuations (20–80% RH). To our knowledge, this represents the most accessible strategy reported to date for fabricating multiresponsive, stretchable polymer-based sensors using only bio-based, sustainable products. Thanks to the enzyme-assisted network structure and the absence of inorganic ions, the gels maintain stable conductivity and mechanical resilience over thousands of stretching cycles. This work demonstrates how enzymatic polymer engineering can enable the preparation of green, low-cost, and high-performance soft sensors for next-generation wearable interfaces, implantable diagnostics, and transient electronics.

2. Results and Discussion

To develop a robust, fully bio-based soft material, we fabricated organohydrogels by combining gelatin, glycerol, and microbial transglutaminase (TG) under mild thermal conditions. As il-

lustrated in Figure 1a, TG catalyzes the formation of covalent ϵ -(γ -glutamyl)lysine isopeptide bonds between the side chains of glutamine and lysine residues on gelatin, establishing a permanent, enzyme-crosslinked network. Glycerol serves both as a humectant and a plasticizer, promoting water retention and enhancing elasticity. The fabrication process consists of a single step at 60 °C, using only edible, water-dispersible components—providing a sustainable and scalable route to soft functional materials (see the Experimental Section and Figure S1, Supporting Information for further details).

To systematically assess the effect of crosslinking, samples were coded based on the concentration of TG solution used during preparation, as detailed in the Experimental Section. Specifically, GELTG000 denotes the uncrosslinked control, while GELTG025, GELTG125, and GELTG250 correspond to gels prepared by mixing 5 mL of a 20% (w/v) gelatin solution formulated in a 1:2 (v/v) glycerol:water mixture with 1 mL of 0.025, 0.125, and 0.250 g mL^{−1} (respectively) TG solution. FTIR and XPS analyses (see Figures S2 and S3, Supporting Information, respectively) were performed to probe potential chemical changes upon enzymatic crosslinking. The spectra of the gels revealed no discernible or systematic shifts in the main bands or core-level peaks, indicating that TG incorporation does not significantly alter the chemical environment of gelatin functional groups. All samples exhibit comparable thickness ($\approx$ 630 μ m, measured on self-standing gel matrices after removal from their casting molds; see Table S1, Supporting Information) and show high optical transparency in the visible region, as evidenced by the UV–vis spectra in Figure 1b. Below 400 nm, a progressive increase in absorbance is observed, indicating enhanced UV-blocking ability. This attenuation may provide partial protection from ultraviolet radiation, a desirable characteristic for wearable or dermal applications. Inset photographs in Figure 1b further demonstrate the transparency of the gels: each sample appears colorless and homogeneous when overlaid on a black-white grid, confirming their optical uniformity and supporting their suitability for transparent bioelectronics and optically interactive devices.

Differential scanning calorimetry (DSC) thermograms in Figure 1c reveal no detectable exothermic/endothermic transitions associated with water freezing/ice melting, indicating that all water present in the system is in a nonfreezable state.^[38] This behavior stems from strong molecular interactions among gelatin, glycerol, and water, which suppress ice crystallization even at subzero temperatures. Such complete inhibition of water freezing is a defining feature of organohydrogels, crucial for maintaining mechanical flexibility and ionic mobility under cold conditions, thus enabling reliable operation across varying environments. Notably, the water content determined by thermogravimetric analysis (TGA) remains constant at $\approx$ 14 wt% across all formulations (Figure S4a and Table S1, Supporting Information), reinforcing the conclusion that observed differences in sensing behavior and material properties arise from the architecture dictated by the structural reorganization of the polymeric network rather than by changes in the hydration level. The single-step preparation process ensures precise control of the gel composition, enabling reproducibility and systematic tuning of material properties. Remarkably, the pronounced differences in physicochemical behavior discussed in the following sections stem from subtle changes in TG content (ranging

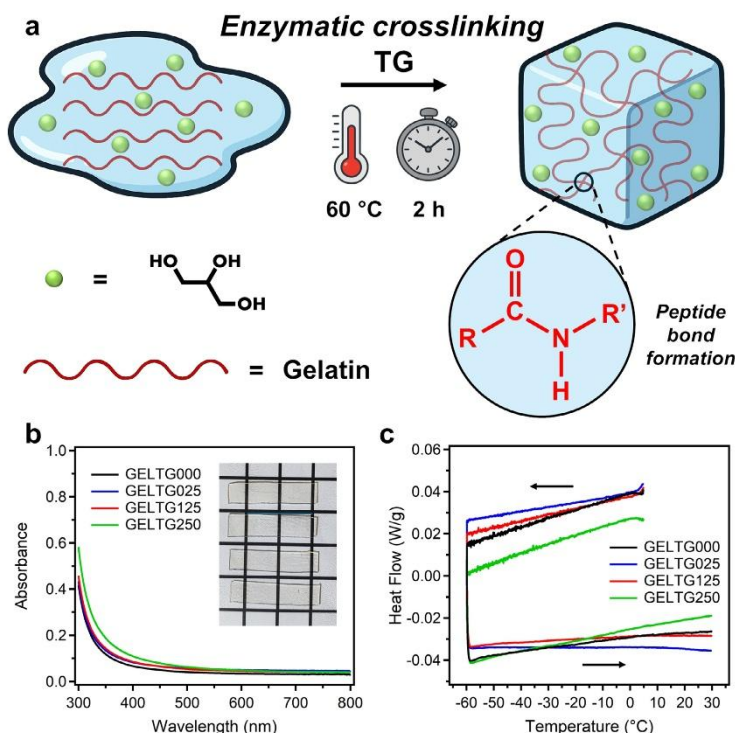


Figure 1. Fabrication and basic characterization of TG-crosslinked gelatin organohydrogels. a) Schematic of the enzymatic crosslinking process using microbial transglutaminase (TG). b) UV-vis spectra of GELTG samples (GELTG000–GELTG250) showing high transparency across the visible range. Inset: photographs of gels over a black-and-white grid. c) Differential scanning calorimetry (DSC) curves, indicating the absence of water freezing/ice melting transitions and confirming that all water in the organohydrogels is nonfreezable due to strong gelatin-glycerol interactions (Exo-up).

from 0 to 7.2 wt/wt%) - underscoring the pivotal role of enzymatic crosslinking in dictating the performance of protein-based stretchable sensors.

Furthermore, TGA analysis confirms that TG-mediated crosslinking does not affect the onset of thermal degradation ($\approx 180^\circ\text{C}$), which remains dictated by the decomposition of glycerol (Figure S4b and Table S1, Supporting Information). Similarly, the electrical conductivity (σ in Table S1, Supporting Information) is not significantly influenced by TG concentration, as it primarily originates from the intrinsic protic character of type A gelatin (see Figure S5, Supporting Information) - derived from the acid hydrolysis of collagen.

GELTGXXX organohydrogels exhibit remarkable electrical robustness under varying humidity conditions. Although the poly-

meric matrix is hydrophilic and capable of interacting with moisture, humidity-dependent electrical measurements (Figure S6, Supporting Information) show that the change in resistance remains nearly constant from 20% to 60% relative humidity (RH). Only a slight decrease in resistivity is observed above 70% RH, likely due to the formation of a superficial water layer that introduces a limited extrinsic conduction pathway without affecting the bulk structure.

This behavior represents a major advantage over conventional ionic hydrogels incorporating metal salts, such as NaCl, LiCl, and FeCl_3 . In such systems, absorbed water promotes ion dissociation and enables proton conduction through Grotthuss-type hopping mechanisms between hydronium ions and water clusters, leading to pronounced humidity-dependent conductivity

shifts.^[39–41] In our gels, by contrast, the absence of mobile metal ions eliminates the driving force for osmotic water uptake and prevents the generation of highly mobile ionic species upon hydration.

Here, conductivity arises from the protic character of type A gelatin, where protons are tightly confined within the polymer–glycerol hydrogen-bond network, ensuring stable charge transport with minimal dependence on ambient humidity. This structural and electrostatic confinement ensures a stable electrical response across a broad range of relative humidity. Such insensitivity to humidity further underscores the suitability of GELTG materials for wearable applications, where consistent signal transduction under fluctuating environmental conditions is essential.

To assess the thermal stability of GELTG organohydrogels, we examined their thermal transitions via DSC. As shown in Figure 2a, all samples exhibit a subtle endothermic inflection $\approx 42^\circ\text{C}$ (Table S1, Supporting Information), corresponding to the glass transition temperature (T_g) of the gelatin-based polymer network (Table S1, Supporting Information). The near-constant T_g across all formulations suggests that enzymatic crosslinking does not significantly affect the intrinsic segmental mobility of the gelatin chains. This observation is further supported by small-angle X-ray scattering (SAXS) analysis (Figure S7, Supporting Information), which reveals nearly identical scattering profiles for all samples across the 1.3–63 nm range. These results indicate that the nanoscale architecture of the polymer network is preserved, regardless of crosslinking density.

In contrast, the macroscopic thermal stability of the gels, defined as the temperature at which structural integrity is lost, shows a strong dependence on TG concentration. As shown in Figure 2b, penetration tests reveal a marked increase in the phase transition temperature with increasing crosslinking density. GELTG000 and GELTG025 lose cohesion at $\approx 50^\circ\text{C}$, while GELTG125 remains stable up to $\approx 68^\circ\text{C}$. Remarkably, GELTG250 exhibits no visible collapse even above 120°C , confirming that dense enzymatic crosslinking significantly enhances thermal robustness. Taken together with the DSC and SAXS analyses, these findings suggest that the macroscopic collapse observed in lightly crosslinked samples originates from intrinsic structural rearrangements of gelatin chains. Such reorganization likely contributes to the abrupt loss of cohesion and performance degradation observed beyond the transition threshold. This hypothesis is further corroborated by SEM characterization (Figure 2e–h), discussed in detail below.

The organohydrogels also exhibit thermally induced changes in proton conductivity, underscoring their potential for applications in environmental monitoring and electronic skins. As shown in Figure 2c, the relative variation in conductivity ($\Delta\sigma/\sigma_0$) was evaluated across the 293–318 K (20 – 45°C) range, i.e., a relevant temperature window for bioelectronic systems.^[42–44] Despite the mechanical robustness of highly crosslinked samples, all of the formulations display a temperature-dependent increase in conductivity, attributed to thermally activated proton transport within the gelatin–glycerol–water matrix. Notably, GELTG000 and GELTG025 show an abrupt conductivity spike $\approx 40^\circ\text{C}$, aligning with the structural collapse previously mentioned. This discontinuity likely results from gel liquefaction, leading to fluid redistribution and transient ionic enhancement. In contrast, GELTG125 and GELTG250 exhibit smooth, linear increases in

conductivity, consistent with stable, intact networks. At low temperatures, proton mobility is restricted by strong hydrogen bonding with carboxylate and hydroxyl groups, whereas increasing temperature progressively weakens these interactions, enabling proton delocalization and more efficient charge transport. As temperature increases, these interactions progressively weaken, promoting proton delocalization and charge transport. The softening of the polymeric scaffold and enhanced molecular motions within the glycerol-rich phase further enhance conductivity. Importantly, this thermally responsive behavior is decoupled from ambient humidity, as the gels are fabricated without mobile salts or hygroscopic agents.

The extracted thermal sensitivity, defined as the slope of $\Delta\sigma/\sigma_0$ versus temperature in the widest linear range, is shown in Figure 2d. Among the formulations, GELTG125 exhibits the highest sensitivity (0.26°C^{-1}), outperforming both the uncrosslinked control and GELTG250. This superior sensitivity, competitive with state-of-the-art hydrogel-based temperature sensors,^[45–48] does not stem from differences in glass transition temperature, (identical across all samples as highlighted by DSC), but it can instead be ascribed to morphological variations.

To substantiate this conclusion, we conducted an SEM analysis. Since glycerol interferes with imaging, samples were washed with water prior to lyophilization. Although this step induces some swelling, the resulting micrographs reliably capture qualitative differences in network architecture. As illustrated in Figure 2e–h, increasing TG concentration progressively refines the pore morphology, size, and uniformity: GELTG000 and GELTG025 exhibit open, loosely connected networks, whereas GELTG250 forms a dense, tightly packed structure. GELTG125 displays an intermediate architecture, combining the porosity needed for water and glycerol mobility with the mechanical robustness required for stable operation.

To complement the SEM analysis, we investigated the swelling behavior of the hydrogels. As shown in Figure S8 (Supporting Information), GELTG000 and GELTG025 rapidly reach a swelling ratio (SR) of ≈ 1.2 within 5 min, consistent with their loose structures and eventually resulting in poor structural integrity. In contrast, GELTG125 and GELTG250 exhibit more controlled swelling behavior, stabilizing without collapsing, at SR values of ≈ 1.76 and ≈ 1.39 , respectively. The higher SR_{max} of GELTG125 reflects its greater structural flexibility compared to the more rigid GELTG250 network. These findings confirm that the microscopic architecture dictates macroscopic performance.^[49]

This balance underlies the observed thermoresponsive behavior. Lightly or noncrosslinked gels undergo structural collapse $\approx 313\text{ K}$ ($\approx 40^\circ\text{C}$), as evidenced by abrupt conductivity spikes and visible failure; their porous networks enable uneven fluid migration, resulting in erratic signals. In contrast, GELTG250 remains mechanically stable but shows limited conductivity variation, likely due to restricted ionic mobility in its compact matrix. Among the tested formulations, GELTG125 stands out as the optimal composition, combining mechanical robustness with efficient ionic transport for reliable strain and temperature sensing. Its moderate crosslink density enables a smooth, linear, and reproducible conductivity response to temperature, consistent across multiple fabrication batches. Overall, these results highlight that porosity and network organization, rather than

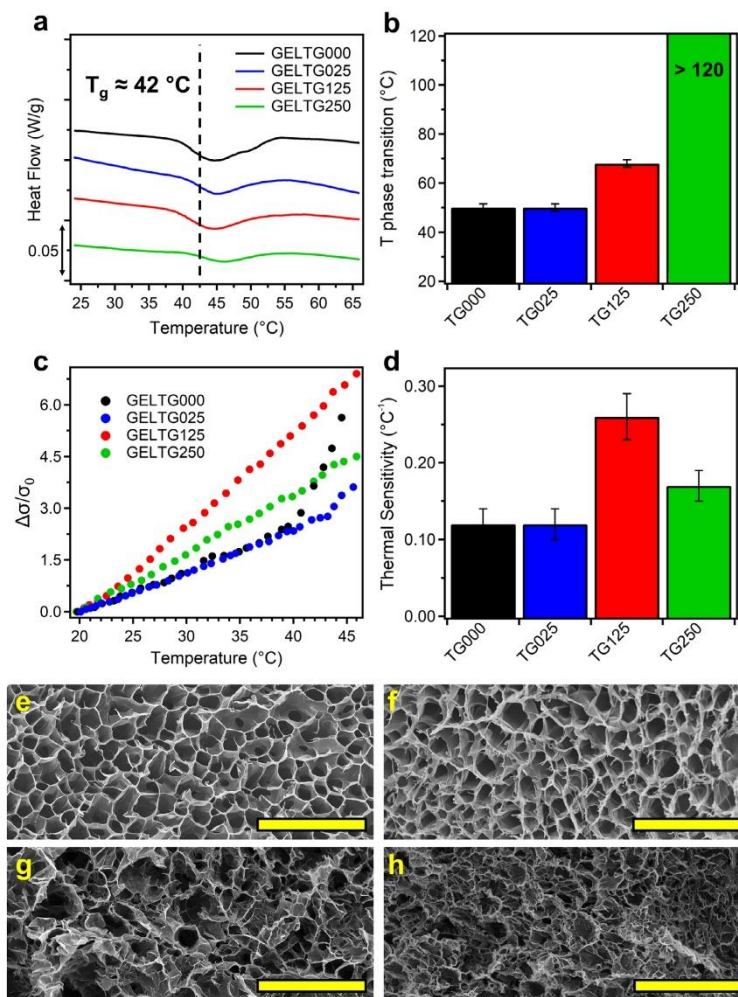


Figure 2. a) DSC thermograms showing a consistent glass transition temperature ($T_g \approx 42^\circ\text{C}$) across all samples. b) GELTGXXX phase transition temperature assessed via probe penetration tests, indicating improved thermal stability with increasing TG content. Inset: representative image of GELTG025 morphology above the phase transition. c) GELTGXXX relative conductivity change ($\Delta\sigma/\sigma_0$) as a function of temperature (20–45 °C). d) Thermal sensitivity values extracted from the $\Delta\sigma/\sigma_0$ curves; GELTG125 shows the highest sensitivity (0.26 °C⁻¹). SEM micrographs of freeze-dried e) GELTG000, f) GELTG025, g) GELTG125, and h) GELTG250 samples, showing a gradual transition from highly porous to more compact structures with increasing TG content. Scale bars: 30 μm.

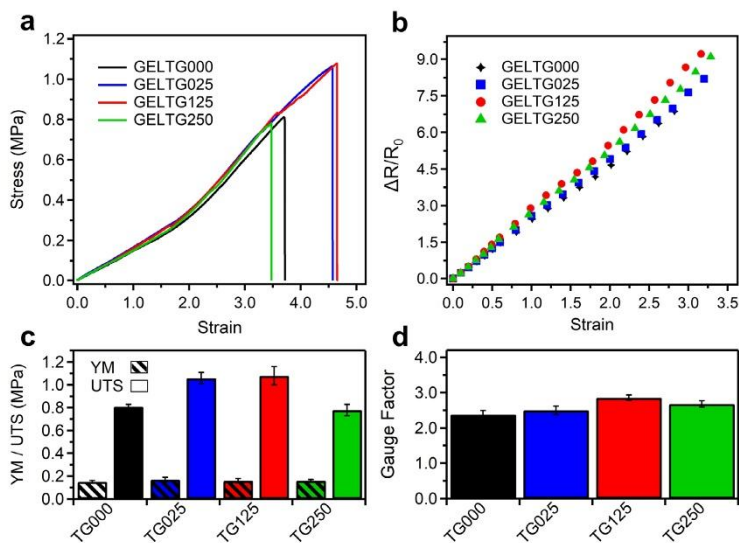


Figure 3. a) Stress–strain tensile curves showing enhanced stretchability and strength upon TG-mediated crosslinking. b) Relative resistance variation ($\Delta R/R_0$) as a function of strain, showing linear electromechanical response across all formulations. c) Young's modulus (YM) and ultimate tensile strength (UTS) values extracted from tensile tests. d) Gauge factor values derived from the linear strain range (0–300 %), with GELTG125 achieving the highest value (2.86).

local chain mobility, dictate thermal responsiveness in these biopolymer-based organohydrogels.

We also evaluated the mechanical and electromechanical properties of GELTGXXX. As shown in Figure 3a, all samples exhibit elastomer-like behavior characterized by an initial linear elastic region, followed by strain hardening and eventual rupture. Crosslinking markedly improves both stretchability and fracture resistance compared to the uncrosslinked control (GELTG000). In particular, GELTG025 and GELTG125 display higher elongation at break and tensile strength, indicating that an optimal degree of enzymatic crosslinking yields cohesive networks capable of effectively dissipating mechanical stress. In contrast, GELTG250 fractures at a lower strain, indicating that an excessive degree of crosslinking induces brittleness and reduces deformability. The extracted mechanical parameters are summarized in Figure 3c. The Young's modulus (YM) is nearly constant across all samples at ≈ 0.16 MPa, confirming that TG-mediated crosslinking does not significantly affect the gel's initial stiffness. In contrast, the ultimate tensile strength (UTS) noticeably varies with crosslinking density. Both GELTG025 and GELTG125 show a pronounced increase in UTS, suggesting that moderate crosslinking improves stress transfer and mechanical resilience. Conversely, GELTG250 exhibits a drop in UTS despite higher crosslink-

ing, consistent with brittle failure modes in over-crosslinked networks.

Electromechanical behavior was assessed by monitoring the relative resistance change ($\Delta R/R_0$) during uniaxial tensile deformation (Figure 3b). All formulations show a linear response up to 300% strain, validating their potential for stretchable sensing applications. The corresponding gauge factors (GF), reported in Figure 3d, range from 2.38 to 2.86. Among the tested formulations, GELTG125 displays the highest average GF, although the difference relative to GELTG250 lies within experimental uncertainty. Notably, the performance divergence among samples becomes more pronounced at higher strains: formulations with greater crosslinking exhibit enhanced linearity and signal stability under large deformations, due to more resilient conductive pathways and network cohesion. In contrast, GELTG000 and GELTG025 show reduced sensitivity and increasing deviation from linearity at high strain, likely due to limited structural integrity and poor modulation of conductive channels.

These differences can be directly correlated with the network morphologies observed by SEM (Figure 2c–h), where GELTG125 displays a moderately crosslinked architecture that preserves porosity for reversible deformation while maintaining structural continuity-ideal for stable electromechanical performance. In

contrast, GELTG250, with its over-crosslinked and brittle matrix, restricts dynamic rearrangement, leading to diminished sensing performance despite high cohesion.

These findings demonstrate that intermediate crosslinking yields the most favorable combination of mechanical robustness, thermal stability, and electromechanical responsiveness. Among all formulations, GELTG125 consistently emerges as the optimal composition—combining high extensibility and toughness with a reproducible, strain-dependent signal response and the highest thermal sensitivity observed across the series. This balanced performance profile renders GELTG125 particularly suitable for multifunctional, skin-compatible sensing platforms requiring reliable detection of both mechanical and thermal stimuli under dynamic conditions.

To position our material within the broader landscape of hydrogel-based strain sensors, we benchmarked the performance of GELTG125 against state-of-the-art systems reported in the literature (Figure 4a; Table S2, Supporting Information).^[50–73] Notably, our formulation combines a high gauge factor ($GF = 2.86$) with a wide linear-response working strain range (up to 300%)—a rare convergence in fully biopolymeric matrices. Most reported hydrogel sensors either operate at low strains or suffer from poor sensitivity under large deformation. For instance, gelatin- and cellulose-based systems typically exhibit GF values below 2 at strains beyond 150%, underscoring the uniqueness of our design. GELTG125 successfully bridges this trade-off, validating our strategy based on enzymatic crosslinking and glycerol-driven plasticization.

Notably, only a limited number of literature reports, highlighted by triangle symbols in Figure 4a, employ exclusively biopolymeric scaffolds, highlighting the distinctiveness of our approach. All other entries exploit the mechanical advantages of synthetic polymers such as PVA, which, while effective, compromise the material's sustainability. This comparison highlights the distinctiveness of our approach, which achieves competitive performance without resorting to synthetic or hybrid frameworks. Recent studies have elegantly shown that composite architectures and geometrical design strategies can be employed to further amplify strain sensitivity.^[74,75] Such inspiring directions will be explored in future developments to expand the performance landscape of this fully bio-based platform.

We then assessed the hydrogel's responsiveness to different strain amplitudes. As shown in Figure 4b, GELTG125 exhibits sharp, proportional, and fully reversible resistance changes ($\Delta R/R_0$) under incremental strains of 5 %, 10 %, 15 %, and 20 %. Signals show negligible hysteresis or drift, indicating stable conductive pathways and excellent structural reversibility across repeated cycles.

Long-term durability was confirmed through cyclic loading tests. Under 10 % strain, GELTG125 maintained a highly stable response over 1000 consecutive cycles (Figure 4c), with no signal degradation. A zoomed-in region highlights the excellent reproducibility of resistance modulation, suggesting minimal mechanical or electrical fatigue. This robustness was further validated over 5000 cycles (Figure 4d), with constant amplitude, confirming preservation of the conductive network and mechanical integrity under extended use (i.e., 98 % of performance retention).

To demonstrate practical functionality, we implemented a proof-of-concept Morse code transmission system. As shown in Figure 4e, programmable strain pulses encoded the sequences "HARE" (yellow trace) and "TORTOISE" (purple trace). Each character is distinctly resolved based on pulse width and spacing, with response and recovery time of ≈ 0.3 s, allowing accurate signal interpretation. The high contrast and temporal resolution confirm the material's potential for interactive soft electronics requiring clear digital output and rapid responsiveness.

To further validate durability and functional stability, additional tests were performed. Cyclic tensile and compressive experiments (Figure S9, Supporting Information) showed highly reproducible profiles over 100 cycles, confirming excellent elasticity and mechanical resilience. Thermogravimetric analysis after 16 months of storage (Figure S10, Supporting Information) revealed unchanged mass loss compared to fresh samples, indicating superior water retention. Moreover, mechanical, conductive, and sensing performances remained stable after long-term storage and under low-temperature (0°C) and high-humidity (84 %RH) conditions (Figures S11, S12 and Table S3, Supporting Information), with minimal variation in electromechanical sensitivity. These results confirm the outstanding environmental and long-term stability of the gelatin-TG organohydrogel. Real-time motion sensing was further demonstrated through finger-bending (angle-tracking) test (Figure S13, Supporting Information), both showing rapid and reproducible responses under dynamic conditions. MTT assays on 1929 fibroblasts (Figure S14, Supporting Information) confirmed the biocompatibility of the crosslinked hydrogels, with cell viability above 70% in accordance with ISO 10993. These results establish the gelatin-TG organohydrogel as a sustainable and biocompatible material for wearable soft electronics.

Altogether, these results underscore the exceptional combination of mechanical resilience, electromechanical sensitivity, signal fidelity, and operational stability offered by GELTG125. Coupled with its high thermal responsiveness and humidity resistance, this formulation delivers a rare synergy of performance parameters in a fully bio-based and biocompatible matrix. These attributes position GELTG125 as a promising material for next-generation wearable, implantable, and on-skin devices aimed at motion tracking, human-machine interfacing, and health monitoring in dynamic, real-world environments.

3. Conclusion

We have developed a fully bio-based organohydrogel composed of gelatin, glycerol, and food-grade transglutaminase (TG), combining mechanical stretchability, thermoresponsive conductivity, electromechanical sensitivity, and environmental resilience. The fabrication process is a simple one-pot, low-temperature protocol that employs only commercially available, food-safe ingredients—placing this platform among the most accessible and sustainable soft sensor materials reported thus far.

The optimized GELTG125 formulation exhibits a gauge factor of 2.86 with a linear response up to 300 % strain and a thermal sensitivity of 0.26°C^{-1} in the physiological range ($20\text{--}45^\circ\text{C}$). These properties are accompanied by excellent signal stability over thousands of deformation cycles and minimal sensitivity to

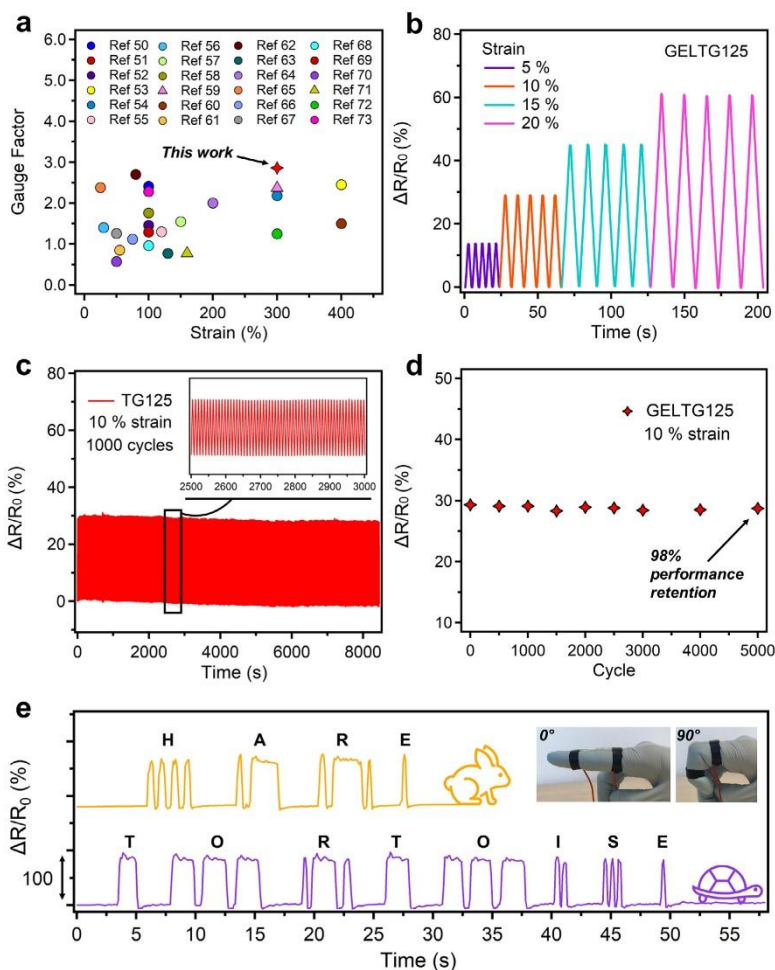


Figure 4. a) Comparison of gauge factor versus linear-response working strain range across reported hydrogel-based strain sensors, highlighting the superior combination achieved in this work (GF = 2.86, linear response up to 300 % strain). b) Relative resistance variation ($\Delta R/R_0$) of GELTG125 under increasing tensile strains (5 %, 10 %, 15 %, 20 %), showing excellent signal responsiveness and reproducibility. c) Long-term cyclic durability test of GELTG125 under 10 % strain for 1000 cycles. Inset: zoomed-in region displaying stable and repeatable response. d) Signal retention during 5000 stretch/release cycles, confirming minimal fatigue and consistent performance. e) Proof-of-concept demonstration of Morse code detection using GELTG125, showing clear signal distinction for the sequences "HARE" (yellow) and "TORTOISE" (purple). The finger was bent by 90° to produce the spike signals shown.

ambient humidity, due to the absence of mobile salts or hygroscopic dopants. Multiscale characterization confirms that these features stem from a finely balanced network architecture—moderately crosslinked and structurally optimized—to provide both mechanical resilience and dynamic ionic mobility.

This study underscores the power of enzyme-guided crosslinking to tune macroscopic functionality through precise structural control. By uniting performance, reproducibility, and eco-compatibility in a single edible matrix, this platform lays the foundation for a new class of wearable, implantable, and ingestible soft electronics—where sustainability, safety, and performance converge.

4. Experimental Section

Materials: Gelatin from porcine skin (Product code G2625, type A, gel strength ≈ 175 g Bloom; pH of a 2% (w/v) aqueous solution is equal to 5.01) and glycerol (BioXtra, $\geq 99\%$) were provided by Sigma Aldrich. Food-grade transglutaminase formulation was purchased from Bindly (Product n. 8437020422024, activity = 125 U g^{-1}). Deionized water was used for all solution preparations. All reagents were used without further purification.

TG-Crosslinked Organohydrogels Preparation: Organohydrogel samples were prepared by mixing 5 mL of a 20% (w/v) gelatin solution in a glycerol:water (1:2) mixture with 1 mL of transglutaminase (TG) solution at various concentrations (0.000, 0.025, 0.125, or 0.250 g mL^{-1} in deionized water). The compositional details are reported in Table S4 (Supporting Information). 5 mL of the resulting mixture (6 mL) was poured into a PMMA mold ($9.5 \text{ cm} \times 3.0 \text{ cm}$), and the samples were incubated at 60°C for 2 h to allow enzymatic crosslinking to proceed. After cooling to room temperature, the gels were demolded and cut into rectangular slides ($4.5 \text{ cm} \times 1.0 \text{ cm}$). Samples were coded as GELTGXXX, where XXX is 000 (Blank), 025, 125, or 250, with obvious meaning. The thickness, measured with a Mitutoyo digimatic micrometer, is $\approx 630 \mu\text{m}$ for all the samples (see Table S1, Supporting Information). As illustrated in Figure S1 (Supporting Information), the preparation method is readily scalable—using a $25 \text{ cm} \times 15 \text{ cm}$ mold.

Characterization Techniques—UV-Vis Spectrophotometry: Absorbance spectra of the organohydrogels were acquired using a Cary UV-vis multi-cell spectrometer (Agilent) across the 300–800 nm range.

Fourier-Transform Infrared Spectroscopy (FTIR): FTIR spectra of the dried GELTGXXX samples were acquired in ATR (Attenuated Total Reflectance) mode with a Thermo Nicolet Nexus 870 FT-IR spectrophotometer (Thermo Fisher Scientific, Waltham, MA, United States) equipped with a Golden Gate accessory. All the spectra were recorded with a resolution of 2 cm^{-1} , averaging 128 scans for measurement, in the range 4000–650 cm^{-1} .

X-Ray Photoelectron Spectroscopy (XPS): X-ray Photoelectron Spectroscopy was performed on air-dried samples by a Thermo Scientific K-Alpha X-ray photoelectron spectrometer, equipped with an aluminum X-ray source (energy 1.4866 keV) at a vacuum level of 10^{-8} – 10^{-9} mbar in the main chamber. The spot size of the X-ray beam was fixed at 400 μm . All XPS spectra were calibrated to the C 1s peak at 284.8 eV.

Differential Scanning Calorimetry (DSC): DSC measurements were performed using a Discovery DSC 2500 (TA Instruments). All samples were sealed in Tzero aluminum hermetic pans and analyzed under two different protocols. To determine the glass transition temperature (T_g), samples were heated from 5 to 70°C at $10^\circ\text{C min}^{-1}$. To assess the water state, samples were first cooled from 5 to -60°C and then heated from -60 to 25°C at the same rate. All samples were pre-equilibrated at 40% relative humidity. Data were processed using Trios software (v5.1.1.46572, TA Instruments).

Thermogravimetric Analysis (TGA): TGA was carried out using a Discovery SDT650 (TA Instruments). For degradation profile analysis, sam-

ples equilibrated at 40% RH were heated from room temperature (RT) to 950°C at $10^\circ\text{C min}^{-1}$ under an air flow of 100 mL min^{-1} in alumina crucibles. To quantify water content, a separate ramp from RT to 110°C was applied ($10^\circ\text{C min}^{-1}$), followed by a 20-min isothermal step, under nitrogen flow (100 mL min^{-1}) in aluminum pans. All results were processed with Trios v5.1.1.46572.

Small-Angle X-Ray Scattering (SAXS): SAXS measurements were performed using a Xeuss 3HR system equipped with a GENIX-Fox 3D Cu K α microfocus source ($\lambda = 1.542 \text{ \AA}$, 30 W) and an Eiger 1 M hybrid pixel detector (Dectris). Data were collected at sample-to-detector distances of 400 and 1800 mm, covering a q-range of 0.005 – $0.5 \text{ \AA}^{-1}$.

Scanning Electron Microscopy (SEM): To assess gel morphology, samples were immersed in 100 mL deionized water for 6 h to remove glycerol, freeze-dried, and sputter-coated with a 10 nm gold layer. Micrographs were acquired using a FEI Quanta FEG 650 microscope with a 30 kV accelerating voltage, a sample–detector distance of $\approx 10.2 \text{ mm}$, and secondary electron detection.

Swelling Experiments: The swelling behavior of GELTGXXX was evaluated by immersing $4.5 \times 1.0 \text{ cm}$ strips in 100 mL of deionized water. At predefined time intervals, the samples were removed, gently blotted with a paper towel to eliminate surface moisture, and then weighed. The Swelling ratio (SR) was calculated using the following equation:^{17b}

$$SR = (W_t - W_0) / W_0 \quad (1)$$

where W_t and W_0 are the mass of the swollen gel at time t and at the beginning of the experiment (i.e., dry), respectively.

Mechanical Characterization: Tensile mechanical properties were evaluated using a Mark-10 M7-025E digital force gauge mounted on a Mark-10 ESM-303E motorized test stand. Gel strips were clamped at the edges, with a stretchable region of 3.5 cm. For the cycling mechanical tests, an Instron universal testing machine (Model 68TM) was used, equipped with a 100 N load cell and compression plates and pneumatic clamps for compression and tensile tests, respectively.

Temperature Sensitivity Measurements: Temperature-dependent conductivity was assessed by placing gel samples on a Peltier heating plate connected to a Keithley 2636B source meter. The temperature gradually increased from 20 to 50°C while recording I vs V curves under a constant 0.2 V bias. For each formulation, three independent samples were tested, and one was measured in triplicate to assess reproducibility.

Humidity Sensitivity Measurements: Humidity responsiveness was evaluated using $36 \text{ mm} \times 2 \text{ mm}$ gel strips connected to a PCB board via iron crocodile clips. Samples were placed inside a custom-built humidity chamber, where RH was varied from 20% to 80% using wet or dry air from a commercial humidifier. Humidity was monitored with a Sensirion SMART sensor. Electrical response was measured with a Keithley 2636B under 0.2 V bias. Each formulation was tested on three samples, one of which was measured in triplicate.

Strain Sensitivity Measurements: Strain-sensing performance was measured using the same Mark-10 tensile setup. Gel samples (3.5 cm gauge length) were connected to the Keithley 2636B system, and current changes were recorded as I – t curves under an applied 1.0 V bias. Measurements were performed in triplicate.

Probe Penetration Test: GELTGXXX stripes ($4.5 \times 1.0 \text{ cm}$) were placed on copper tape attached to a thermoelectric module. A conductive probe was positioned on top of the gel. Upon heating, the gel softened, allowing the probe to penetrate and contact the copper tape, completing the circuit (see Figure S15, Supporting Information). The electrical signal was recorded to monitor the temperature-dependent conductivity response using a digital multimeter.

Biocompatibility assessment: In vitro cytocompatibility was conducted according to ISO 10993 with the extraction method. L929 mouse fibroblasts were cultured in RPMI medium supplemented with 10% fetal bovine serum, 1% L-glutamine, and 1% penicillin-streptomycin (defined as complete RPMI culture medium) at 37°C and 5% CO_2 . Samples were sterilized under UV light for 15 min per side.

For the extract preparation, samples of $15 \times 10 \text{ mm}$ were incubated in PBS for 1 h and after in 1 mL of complete RPMI culture medium at

37 °C for 24 h with agitation (40 rpm). A copper sample (15 × 10 mm) and an aliquot of complete RPMI culture medium with no added material were incubated in the same conditions described above and considered as positive and negative controls of toxicity, respectively.

L929 mouse fibroblasts were seeded in 96-well plates at 8 × 10³ cells per well. After 24 h of seeding, the medium was replaced with the sample extracts and controls (200 µL per well). Following an exposure time of 24 h, the MTT assay was performed for cell viability quantification. The MTT is based on the reduction by viable cells with active mitochondria of 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT). Briefly, 20 µL per well of the MTT reagent (0.5 mg mL⁻¹ in PBS) was added, and the plate was incubated at 37 °C for 3 h. The supernatant was gently removed and replaced with DMSO (100 µL per well) to solubilize the MTT tetrazolium dye. The absorbance was measured at 550 nm wavelength using a microplate reader (Spectrafluor Plus, TECAN Austria GmbH, Grödig, Austria). The percentage of cell viability was related to the negative control, assumed as 100%.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P.T., A.T., Y.J., M.B., and P.S. conceived the experiments and designed the study. P.T. performed the physicochemical characterization. P.T. and A.T. performed the electrical characterization. B.H. performed the XPS analysis. T.A.K. and A.C. performed the biocompatibility assessment. P.T., A.T., Y.J., M.B., and P.S. discussed the results and contributed to the interpretation of data. P.T., A.T., Y.J., M.B., and P.S. cowrote the paper with input from all co-authors.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

biopolymer materials, enzymatic crosslinking, gelatin, organohydrogels, strain sensing, wearable sensors

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Mimicking Synaptic Plasticity: Optoionic MoS₂ Memory Powered by Biopolymer Hydrogels as a Dynamic Cations Reservoir

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Neuromorphic devices are emerging as key components for next-generation computing, driven by the rapid growth of digital technology. To meet growing demand for energy-efficient logic operations, photonic synaptic devices have become a focal point of interest. Here, a novel molybdenum disulfide (MoS₂)-based synaptic memory field-effect transistor (FET) is presented, exploiting the photo-induced ionic gating effect through Janus functionalization with ion-conductive sodium alginate (SA) and ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)]. The integration of SA as a dynamic cations reservoir enables ion migration and corresponding modulation of persistent photoconductivity on MoS₂, emulating synaptic plasticity including sensory, short-term, and long-term memory operation. The SA/MoS₂ FET demonstrates over eight multilevel states adjustable by light irradiation conditions. The device also exhibits excellent visible-range photodetection (455–680 nm), with a high photoresponsivity of 20 kA W⁻¹ and a fast response time of 120 ms under 20 V gate bias and 680 nm LED illumination. Further functionality is endowed by decorating MoS₂ bottom face with P(VDF-TrFE), realizing 60 photo-induced multilevel states, and independent conductivity modulation via ferroelectric gating. This Janus SA/MoS₂/P(VDF-TrFE) configuration supports near-infrared detection governed by ferroelectric polarization. These findings highlight the transformative potential of integrating sustainable biopolymers with 2D materials for environmental-friendly neuromorphic 2D optoelectronics.

1. Introduction

As the global demand for data-intensive technologies like artificial intelligence, the Internet of Things, and Big Data continues to grow, conventional computing systems face an urgent bottleneck due to the energy-inefficient data shuttling between processing and memory units in traditional von Neumann architectures. This “von Neumann bottleneck” not only limits speed but also threatens the sustainability of modern computing. For decades, researchers have explored innovative memory devices to overcome the energy inefficiencies of traditional computing systems.^[1,2] Among these, neuromorphic devices have gained significant interest because of their ability to blur the boundaries between processing and memory functions, mimicking the architecture and functions of the human brain.^[3–5] An important category of neuromorphic devices focuses on synaptic memory, designed to emulate biological synapses—the neural connections responsible for learning and storing data in the human brain. By leveraging synaptic plasticity, these devices dynamically modulate

synaptic weights, enabling efficient, adaptive, and parallel information processing.^[6,7] In particular, using light as an input stimulus in optoelectronic synaptic devices offers additional advantages such as non-contact operation, high-speed signaling, and potential for wavelength-multiplexed processing. These unique features make optoelectronic synaptic devices a promising platform for building more scalable, energy-efficient, and multifunctional neuromorphic systems.^[8–10] To realize these functionalities, a range of semiconductors have been proposed as active materials for optoelectronic synaptic transistors.^[11–17] These cutting-edge devices promise to revolutionize computation-intensive fields including artificial neural networks, low-power electronics, and reconfigurable neuromorphic hardware, paving the way for next-generation intelligent systems.^[18–20]

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have garnered significant attention for their strong electrostatic sensitivity and exceptional light-matter interactions, making them ideal building blocks for optoelectronic synaptic

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devices.^[21–26] Recent advancements include the development of optical memory devices leveraging persistent photoconductivity (PPC)^[27–30] and hybrid structures utilizing charge trapping and de-trapping mechanisms at the interfaces.^[31–36] For example, molybdenum disulfide (MoS₂)-based field-effect transistors (FETs) incorporating zero-dimensional (0D) quantum dots have demonstrated photonic multilevel memory characteristics.^[37,38] However, these devices fail to capitalize on the intrinsic broad absorption spectrum of MoS₂ as their operational wavelength is limited by the narrower absorption characteristics of the 0D quantum dots. Moreover, many existing systems rely on toxic metals, such as cadmium- and lead-based quantum dots, underscoring the urgent need for sustainable, biocompatible, and environmentally friendly applications. As a second promising approach, electrolyte-gate transistors using the electrical double layer (EDL) enable ultralow energy consumption, making them attractive for neuromorphic systems.^[39–42] However, these devices typically suffer from poor memory retention, as low operating voltages must be maintained to avoid undesirable electrochemical reactions or ion intercalation into TMD layers. Additionally, most electrolyte-gate transistors rely exclusively on electrical stimuli to form the EDL, with no demonstrated applicability toward synaptic devices responding simultaneously to multiple independent stimuli, such as ion concentration and light with the latter offering high spatio-temporal control over a broad range of incident wavelengths. In particular, the synaptic plasticity including both short- and long-term memory operation has yet to be realized solely by photons in 2D iontronics.

Addressing these limitations requires innovative approaches combining environmental sustainability with advanced functional performance. Nature-inspired materials such as biopolymers hold immense potential for this purpose, as they offer simultaneously flexibility, stretchability, and biocompatibility, which are essential for applications in intelligent robotics, wearable technology, smart chips, and health monitoring. Among these materials, alginate—a biocompatible and biodegradable anionic polysaccharide extracted from brown algae—stands out for its exceptional film-forming capabilities, ionic affinity, and environmental sustainability.^[43,44] The —OH and —COO— functional groups in alginate's mannuronate and guluronate units enable coordination with various metal cations,^[45] broadening its application across multiple fields, including sensors and energy storage.^[46]

Building on these considerations, we report an unprecedented MoS₂-based optoionic synaptic memory FET through asymmetric, supramolecular Janus functionalization of its surfaces with ion-conductive sodium alginate (SA) and ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)]. By optimizing the concentration of SA, we uncover a novel photo-induced ionic gating effect on 2D semiconductors, where the photogating effect on MoS₂ induces ion migration in the dynamic cations reservoir provided by the SA layer, tuning the PPC behavior. This ion-mediated PPC enables the emulation of synaptic plasticity (including sensing, short-term potentiation, and long-term potentiation) in response to a 680 nm LED frequency, a capability that surpasses most 2D artificial synapses, which rely predominantly on charge trapping at hybrid interfaces (Table S1, Supporting Information). Intriguingly, the SA/MoS₂ memory FET exhibits over eight tunable multilevel states, ad-

justable through the intensity and exposure time of the incident light. While the device exhibits synaptic functionality without the need for gate bias, applying a gate voltage further enables its use as a high-performance photodetector, demonstrating a photoresponsivity of 20 kA W^{−1} and a response time of 120 ms under 680 nm LED illumination at V_{GS} = 20 V, which is comparable to the literature.^[47–49] The incorporation of P(VDF-TrFE) as a ferroelectric bottom gate further expands functionality, thereby achieving 60 linear multilevel states with enhanced linearity. This Janus SA/MoS₂/P(VDF-TrFE) architecture also enables near-infrared (NIR) photon detection, modulated by ferroelectric polarization. These findings establish a new pathway for functional polymers, especially ion-conductive biopolymers, integrated with supramolecular Janus 2D materials, paving the way for a novel class of artificial optical synapses and energy-efficient computing systems.

2. Result

Figure 1a,b illustrate the three-dimensional (3D) schematic views of a MoS₂ channel FET coated with a 500 nm-thick SA top layer, highlighting the photo-induced ionic gating effect. Upon photon irradiation at $\lambda = 680$ nm, photo-excited electrons are generated in the MoS₂ channel due to a photogating effect.^[50,51] The latter determines an increase in the Fermi energy of MoS₂, which drives the migration of cations within the SA layer toward the MoS₂ surface. The proposed mechanism behind this effect, which relies on the role of the SA as cations reservoir, is discussed further in the following section. A 2D hexagonal boron nitride (h-BN) layer was adopted to ensure a defect-less dielectric surface compared to hydrophilic silicon dioxide (SiO₂), thereby reducing the trap densities at the channel/gate insulator interface. Atomically-thin MoS₂ crystals are particularly vulnerable to interfacial traps, and the hydrophilic nature of SiO₂ can significantly complicate the photoresponse of MoS₂-based devices.^[50,51] A detailed comparison on the photoresponse between MoS₂ FETs with and without h-BN is portrayed in Figure S1 (Supporting Information). The h-BN layer's advantages are evident under 680 nm illumination at 0.03 mW cm^{−2}, where the photocurrent (*I*_{PHOTO}) of the MoS₂/h-BN FET was 20 times higher, and its overall photoswitching speed was 3 times faster than that of the control MoS₂ FET supported on SiO₂. Atomic Force Microscopy (AFM) height profiles of Figure S2 (Supporting Information) confirmed that MoS₂ and h-BN crystals were ≈6 nm- and 25.5 nm-thick, respectively. For a reliable photodetecting performance of MoS₂ FET (Figure S1c, Supporting Information and gray dots of Figure 1e), h-BN flakes were placed underneath the MoS₂ crystal for all the SiO₂ bottom gate devices. Next, the top surface of MoS₂ supported on h-BN was decorated with SA. The latter not only provides functionality but also acts as a protective layer for the underlying device components, as suggested by its high thermal stability (220 °C, see the thermogravimetric analysis results in Figure S3a, Supporting Information). By making use of the photo-induced ionic gating effect of our SA/MoS₂ FET, it has been possible to mimic a biological synapse, where parallel processing is achieved by analog-like modulation in synaptic efficacy. When action potentials (analogous to photon stimuli in our artificial synapse) trigger neurotransmitter release into the synaptic cleft, the connection between the presynaptic and

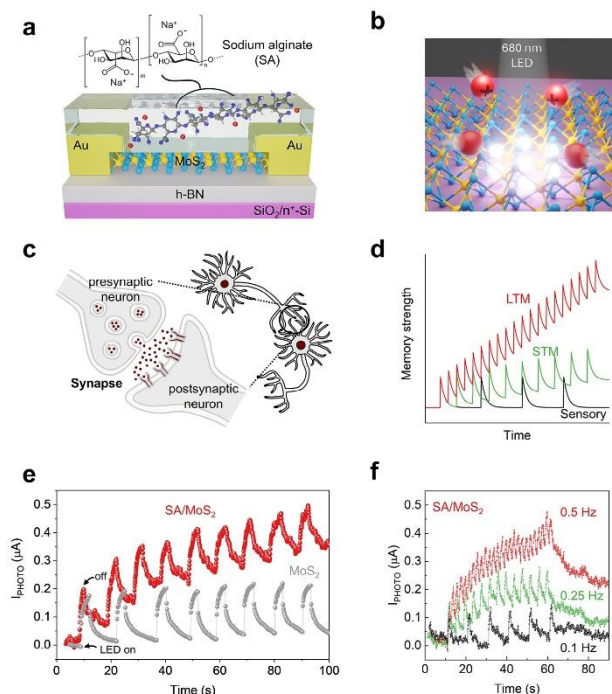


Figure 1. Optoionic synaptic plasticity of SA/MoS₂ FET. a) 3D schematic view of a MoS₂ synaptic memory FET with a 500 nm thick-SA layer. b) Cartoon of the photo-induced ionic gating effect at magnified van der Waals heterojunction between SA and MoS₂ under 680 nm LED illumination. c) Schematic illustration of a biological synapse in the human neural system. d) Memory model of the artificial synaptic device as a function of stimulus frequency, illustrating sensory memory (SM) in black, short-term memory (STM) in green, and long-term memory (LTM) in red. These correspond to the transient response, short-term plasticity (STP), and long-term plasticity (LTP) of biological synapses, respectively. e) Time-resolved photoresponse of the SA/MoS₂ synaptic memory and control sample under 680 nm LED illumination at V_{GS} = 0 V and V_{DS} = 1 V. f) Time-resolved photoresponse of SA/MoS₂ synaptic memory under 680 nm LED illumination at frequencies of 0.1, 0.25, and 0.5 Hz with V_{GS} = 0 V and V_{DS} = 1 V, demonstrating SM (black), STM (green), and LTM (red) operations, respectively.

postsynaptic neurons is modified (Figure 1c). This modification can either strengthen or weaken the connection, corresponding to potentiation and depression, respectively. Potentiation, which is associated with learning/memory, is a key characteristic of biological synapses. Figure 1d displays a memory model characterized by different frequencies of stimulus, emulating various memory behaviors, including sensory memory (SM), short-term memory (STM), and long-term memory (LTM), as represented with black, green, and red curves. Interestingly, the SA/MoS₂ FET exhibited photonic multilevel memory characteristics (red dots in Figure 1e) when kept under continuous 680 nm LED illumination (0.03 mW cm⁻²). Remarkably, more than eight distinct mem-

ory states were achieved solely through optical stimulation, without the need for any electrical input signals. It is also noteworthy that the first I_{PHOTO} of both SA/MoS₂ and pristine MoS₂ FET approached ≈ 200 nA, indicating that 500 nm-thick SA does not hinder the propagation of 680 nm light. In order to confirm the transparency of SA in the visible range, ultraviolet-visible (UV-vis) spectroscopy of SA was conducted and reported in Figure S4 (Supporting Information). More interestingly, all three SM, STM, and LTM can be generated by modulating the light stimulus frequency to 0.1, 0.25, and 0.5 Hz, respectively, with consistent light intensity (0.01 mW cm⁻²) and exposure time. The three operating modes of the SA/MoS₂ FET denote a unique photonic synaptic

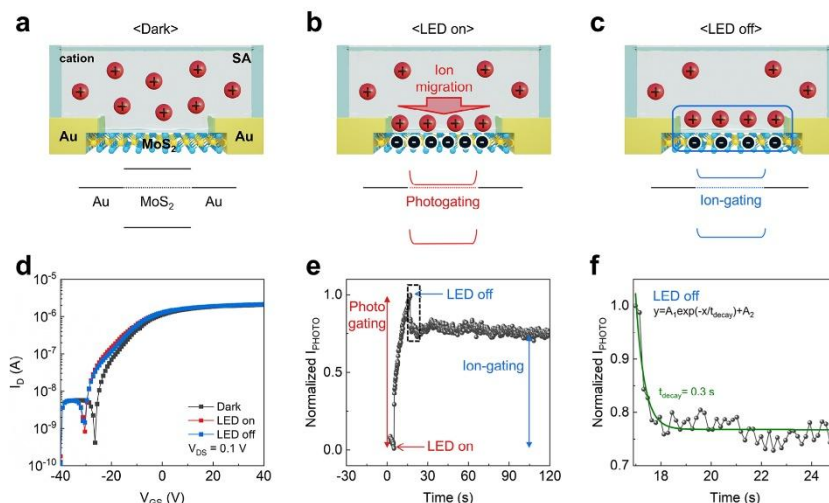


Figure 2. The working mechanism of PPC in SA/MoS₂ FET. 2D schematics of the SA/MoS₂ FET and corresponding energy band diagrams of Au-MoS₂-Au under different conditions: a) equilibrium in the dark, b) photogating effect under 680 nm LED illumination, and c) photo-induced ionic gating effect after LED off, leading to PPC in the SA/MoS₂ FET via electron-cation attraction. d) Transfer curves of the SA/MoS₂ FET, showing PPC after 680 nm LED illumination at $V_{DS} = 0.1$ V. e) Time-resolved photoresponse of the SA/MoS₂ FET under 680 nm LED illumination, and f) its I_{PHOTO} decay over time, with a decay time constant of 0.3 s. Experimental data (black dots) were fitted using an exponential decay function to determine the decay time constants.

plasticity that effectively emulates the transient response, STP, and LTP of biological synapses.

Intriguing synaptic STM and LTM operations of the SA/MoS₂ FET can be elucidated with the movement of cations in the SA layer under and after light illumination. **Figure 2a–c** illustrates the 2D schematics of the van der Waals interface between MoS₂ and SA, along with the corresponding band diagrams. Electron-dominant band diagrams are established as a consequence of intrinsic sulfur vacancies of MoS₂ and the Fermi-level pinning between MoS₂ and thermally evaporated Au, as displayed in Figure 2a.^[32,53] Upon exposure to 680 nm LED, a photogating effect occurs, as reported previously, which causes electron doping in MoS₂ (Figure 2b).^[59,54–56] Driven by the photo-excited electron accumulation in MoS₂, electrostatic force can result in the migration of cations in SA toward the interface of SA/MoS₂. To make sure that no intercalation of sodium ions into MoS₂ layers occurs when 0.25 wt.% of SA was used, Raman spectroscopy and XPS measurements were conducted (Figures S5 and S6, Supporting Information). Even after turning off the LED, MoS₂ retains accumulated electrons due to the ion-electron attraction, leading to PPC in the SA/MoS₂ FET. The anionic character of alginate is essential in this process, as it retrieves sodium ions progressively and redistributes them within its network once the light is turned off. This dynamic ionic redistribution, whose kinetics can be finely tuned by modulating the SA loading on the top

of the channel, ensures the reversibility of the PPC effect, contributing to the stability and repeatability of the device's synaptic behavior. It is noteworthy that this photo-induced ionic gating effect is fundamentally different from previously reported PPC effects in MoS₂ caused by trapped charges upon strong UV light irradiation.^[29,30] While MoS₂ can exhibit both photogate and PPC effects under visible and UV light due to intrinsic defects in the crystal, the presence of mobile ions in our system introduces an electrostatically driven mechanism distinct from conventional defect-induced PPC. This ionic contribution enables a strong yet reversible PPC effect. The transfer curves of Figure 2d reveal that the SA/MoS₂ FET exhibits a strong PPC effect under 680 nm of visible photon stimulus. Compared to a dark condition (black square in Figure 2d), the transfer curve (red square) under 680 LED illumination showed 4 V of the threshold voltage shift toward the negative side, which indicated electron doping in MoS₂ by photogating effect. After turning off the LED, the transfer curve maintained electron accumulations, demonstrating the strong PPC effect governed by ion-electron attractions (blue square). Conversely, transfer characteristics of pristine MoS₂ FET without SA in the same device architecture showed a typical photoresponse, with the absence of the PPC effect as evidenced in supporting Figure S7b (Supporting Information). The pronounced PPC effect of SA/MoS₂ FET can be directly observed not only in the static transfer curves (Figure 2d)

but also in the time-resolved photoresponse after irradiation with 0.5 mW cm^{-2} of 680 nm LED (Figure 2e). After a fast decay of I_{PHOTO} with a time constant of 0.3 s, due to electron-hole recombination in MoS_2 (Figure 2f), PPC induced by ionic gating was retained for over 100 s. Moreover, the decay time constant ($\approx 4 \text{ s}$) of a pristine MoS_2 FET without SA shown in Figure S7c,d (Supporting Information) is ≈ 10 times slower than the one observed in the SA/ MoS_2 FET. This difference represents the unambiguous demonstration that the PPC effect in our SA/ MoS_2 hybrid system is ruled by a photo-induced ionic gating effect, realizing STM and LTM. Such a prolonged retention time exceeding 100 s clearly falls within the time scale typically associated with LTM in artificial synaptic devices,^[57] and is also comparable to the retention characteristics reported in previous organic/2D TMD-based synaptic hybrid devices.^[24,58] Figure S8 (Supporting Information) displays the transfer curves and time-resolved photoresponse of the SA/ MoS_2 FET under vacuum (1.3 mbar). In such an environment, where cations in SA are immobile due to the absence of freely diffusing water within the polymer matrix, the SA/ MoS_2 FET exhibited no PPC effect. The matrix contains 17.7% (wt/wt) at RH = 40% (see Figure S3b, Supporting Information), which strongly interacts with both ions and alginate's functional groups, as evidenced by the absence of peaks in the Differential Scanning Calorimetry (DSC) thermogram in Figure S3c (Supporting Information). The I_{OFF} of the transfer curves in Figure S8a (Supporting Information) lowers from nA in ambient condition to pA under vacuum—confirming that cations are immobilized—providing further evidence that the PPC effect driven by ion-electron interaction can occur in ambient conditions. Figure S9 (Supporting Information) highlights the importance of SA concentration in ensuring a reliable photo-induced ionic gating effect. A high concentration of SA (2.5 wt.%)—and therefore of Na^+ —caused uncontrollable electrostatic doping in the MoS_2 channel, preventing the observation of the photo-induced ionic gating effect. On the other hand, a low concentration of SA (0.025 wt.%) failed to provide sufficient cations, as revealed by $I_{\text{D,OFF}}$ of 1 pA, similar to pristine MoS_2 FET.

Next, the multilevel memory characteristics of the SA/ MoS_2 device were assessed by varying the measurement conditions, such as light intensity, exposure time, LED wavelengths, and V_{GS} . Figure 3a shows the gradual increase in I_{PHOTO} upon growing the light intensity. The $I_{\text{MAX,PHOTO}}$ reached up to 820 nA upon exposure to 0.50 mW cm^{-2} of 680 nm LED. Interestingly, not only $I_{\text{MAX,PHOTO}}$ but also the persistent photocurrent (I_{PPC}) increased up to 350 nA. This indicates that, as the light intensity increases, the degree of photogating also increases, leading to a higher I_{PPC} . It was also found that the transition from SM to LTM can be achieved by adjusting the light intensity. Upon applying a light stimulus exceeding 0.03 mW cm^{-2} both STM and LTM are observed, whereas only a transient conductivity change can be induced upon illumination at 0.01 mW cm^{-2} , serving as SM in an artificial synapse. (Figure 3a) By taking advantage of robust LTM operation under a high light intensity of 0.50 mW cm^{-2} , a step-wise increase in I_{PPC} depending on the exposure time can be also generated, as shown in Figure 3b. From now on, unless specified otherwise, the light intensity was fixed at 0.50 mW cm^{-2} for all the measurements. The device exposed for a total of 20 s (5 s $\times$ 4 times) showed an I_{PPC} of 620 nA, and for 9 s (1.5 s $\times$ 6 times), the I_{PPC} converged to 410 nA, as presented in Figure 3b. This means

that I_{PPC} exhibits a positive correlation not only with light intensity but also with exposure time, as shown in Figure 3c. Even if SA/ MoS_2 could dynamically create STP and LTP, the number of non-volatile memory levels in LTP is limited due to the abrupt I_{PPC} change mediated by the superior photogating effect of MoS_2 , exhibiting a non-linear curve (black square in Figure 3c). Interestingly, the nonlinear relationship between I_{PPC} and exposure time under $V_{\text{GS}} = 0 \text{ V}$ can be mitigated with the help of V_{GS} . In the case of $V_{\text{GS}} = -20 \text{ V}$ (represented by triangles in Figure 3c), the absolute magnitude of I_{PPC} decreased; however, the linearity, which is one of the crucial parameters for synaptic devices, improved to an ideal level. Suppressing the photogating effect of MoS_2 with negative V_{GS} ^[50] enables delicate control of the number of cations migrating on MoS_2 surface. On the other hand, at $V_{\text{GS}} = 20 \text{ V}$, there is no photo-induced ionic gating effect, and only the typical photodetection with fast-photoswitching speed (rise/fall time of 120/120 ms) is observed, as revealed in Figure S10 (Supporting Information). This phenomenon can be ascribed to the accumulation of cations at the SA/ MoS_2 interface driven by electrostatic gating on MoS_2 , which induces a saturated current state. In other words, applying V_{GS} improves multilevel characteristics ($V_{\text{GS}} < 0$) as well as it endows multifunctionality on SA/ MoS_2 FET, serving also as a photodetector ($V_{\text{GS}} > 0$). At $V_{\text{GS}} = 20 \text{ V}$, photoreponsivity (R) of SA/ MoS_2 FET becomes 20, 37, and 100 kA W^{-1} upon 680, 530, and 455 nm LED irradiation, respectively. The detailed estimation of R is provided in Figure S11 (Supporting Information). Figure 3d reveals that our SA/ MoS_2 FET exhibits photonic multilevel behavior also when exposed to different visible wavelengths. (Figure 3a–e were obtained from two different devices. Device 1 was used for Figure 3a–c, and Device 2 was used for Figure 3d,e. The difference in $I_{\text{MAX,PHOTO}}$ values under identical light exposure conditions can originate from the variation in channel areas. Supporting Figure S12 (Supporting Information) provides optical microscopy images and responsivity estimation for each device. Such a broad absorption characteristic is guaranteed by the capacity of our device to fully exploit the inherent optoelectronic properties of MoS_2 , in stark contrast to previous photonic memory studies that were limited to specific wavelengths of incident light.^[29,30,37,38] More interestingly, a system reset, analogous to an auto-refresh of cache data, can be achieved by turning off the V_{DS} , which interrupts electron injection from the source and allows the previously accumulated Na^+ ions at the SA/ MoS_2 interface to diffuse back into the alginate matrix. This ion redistribution effectively restores the device to its initial state without the need for external voltage pulses. Compared to other previous reports where high voltages were required to remove trapped charges,^[29,30,37,38,40–42] the photo-induced ionic gating effect provides extraordinarily energy-efficient device operation through the van der Waals ion-electron interactions. Measurements in Figure 3e provide unambiguous evidence that the reset can be achieved without the need to use high voltages, also confirming the applicability of the SA layer as a dynamic cations reservoir operating under successive light pulses. To confirm the repeatability of the switching behavior enabled by this distinctive reset process, an endurance test was performed and included in Figure S13 (Supporting Information).

As discussed in Figure 3c, linearity in LTM behavior can be achieved upon applying a controlled voltage to the bottom gate compared to adjusting the exposure time. However, applying a

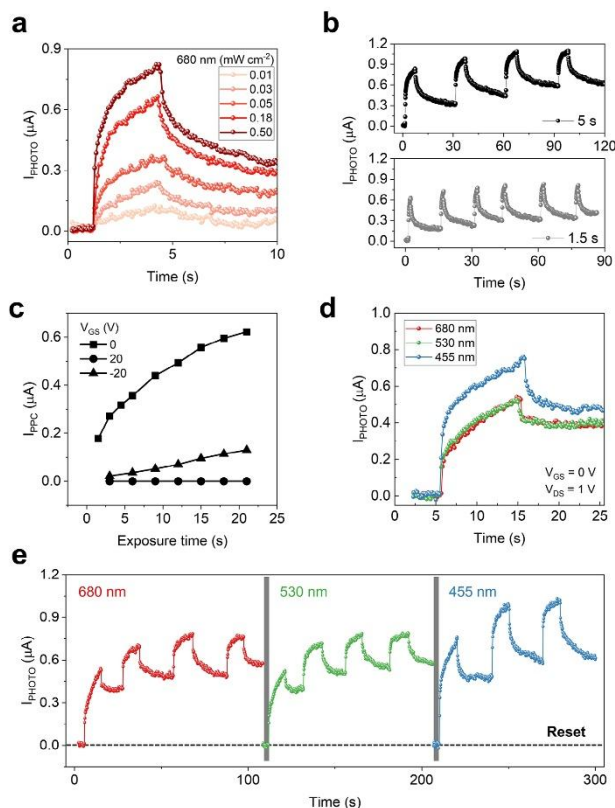


Figure 3. Optoelectrical characteristics of SA/MoS₂ photonic-multilevel memory. a) Time-resolved photoresponse of the SA/MoS₂ FET under 680 nm LED illumination with varying light intensities from 0.01 to 0.50 mW cm⁻² at V_{GS} = 0 V and V_{DS} = 1 V. b) Time-resolved photoresponse of the SA/MoS₂ FET under 680 nm LED, comparing maximum I_{ppc} values for exposure times of 20 s (top) and 9 s (bottom) at V_{GS} = 0 V and V_{DS} = 1 V. c) I_{ppc} of SA/MoS₂ FET as a function of exposure time at different V_{GS}. d) Time-resolved photoresponse upon exposure to visible LED illumination at three different wavelengths. e) Photoresponse upon device exposure at successive light pulses at V_{GS} = 0 V and V_{DS} = 1 V, demonstrating that the device returns to its idle (reset) state once the voltage sources are disconnected. Voltage disconnection, represented by gray segments between measurements, resets the device.

constant voltage for all device operations will result in high power consumption, making it undesirable for energy-efficient computing systems. In order to impart a permanent ferroelectric gating effect on 2D MoS₂, the bottom surface of MoS₂ was decorated with 200 nm-thick P(VDF-TrFE) layer, as shown in Figure 4a. Due to the large surface roughness of crystalline P(VDF-TrFE), all reported MoS₂ ferroelectric FETs (FeFETs) have utilized P(VDF-

TrFE) as a top gate.^[59,60] However, by transferring the flake onto the spin-coated P(VDF-TrFE) with a relatively flat surface compared to that after curing for crystallization,^[61,62] we successfully transferred a 6 nm thin MoS₂ flake and fabricated an MoS₂-based bottom gate FeFET with a 10 μm channel length. The details on FeFET device fabrication and optical and AFM examination of MoS₂ supported on crystalline P(VDF-TrFE) are given in

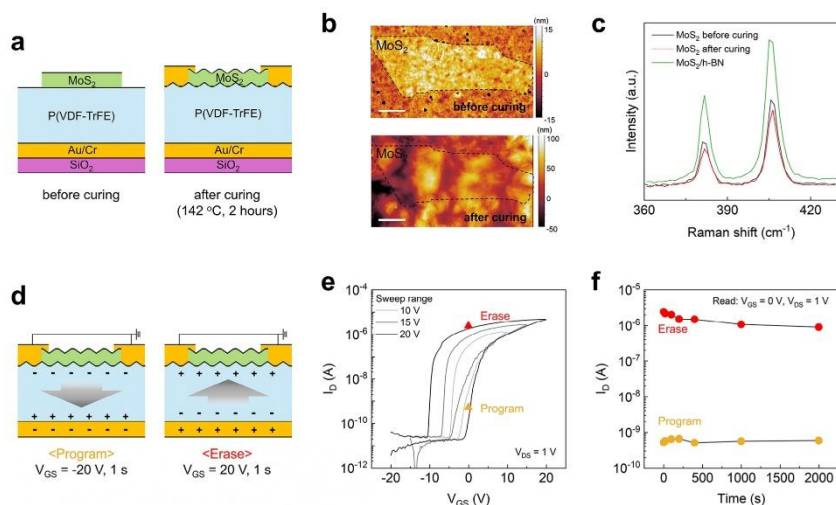


Figure 4. Non-volatile MoS₂ memory FET using ferroelectric P(VDF-TrFE). **a**) Side-view scheme of the MoS₂/P(VDF-TrFE) heterojunction before and after curing. **b**) Topographical AFM image of MoS₂/P(VDF-TrFE), showing significant changes in the root-mean-square roughness (R_{RMS}) before and after curing. The scale bar represents 2 μm. **c**) Raman spectra of MoS₂ crystals supported on different insulators: black (before curing of P(VDF-TrFE)) and red (after curing of P(VDF-TrFE)) and green (h-BN). **d**) Side-view scheme of a MoS₂ FET to describe ferroelectric dipole alignment in P(VDF-TrFE) under Program state after V_{GS} = -20 V, 1 s pulse and Erase state after V_{GS} = +20 V, 1 s pulse. **e**) Transfer curves of the MoS₂ FET at V_{DS} = 1 V, showing a maximum ferroelectric hysteresis of 10 V depending on the gate voltage sweep. Program and Erase states are measured at V_{GS} = 0 V and V_{DS} = 1 V after applying -20 V and 20 V pulses. **f**) Memory retention properties of the non-volatile MoS₂ FET for 2000 s.

Figure S14 (Supporting Information). To confirm the crystalline β -phase responsible for the ferroelectricity of P(VDF-TrFE), X-ray diffraction analysis was conducted and included in Figure S15 (Supporting Information). Figure 4b shows the topographical AFM images of MoS₂ on the P(VDF-TrFE) before and after curing (for crystallization), revealing that the curing process is accompanied by a notable increase in the root-mean-square roughness (R_{RMS}) from 2.1 to 12.5 nm as estimated on a MoS₂ region of $2 \times 2 \mu\text{m}^2$. The strain caused by crystallization hardly changed the in-plane vibrational mode of MoS₂, as shown in Figure 4c, where the MoS₂ Raman spectra remain the same regardless of the state of the bottom insulator. Considering the thickness of the 200 nm P(VDF-TrFE) layer and its coercive electric field of 80 MV m^{-1} , we applied a -20 V, 1 s pulse to the bottom Au electrode for the Program state and a +20 V, 1 s pulse for the Erase state to fully align the dipoles, as shown in Figure 4d. Figure 4e shows the transfer characteristics of our non-volatile MoS₂ FET, achieved under different V_{GS} sweep ranges from 10 to 20 V to access intermediate polarization states. The memory hysteresis window increases from 5 V (-10 to 10 V sweep) to 10 V (-20 to 20 V sweep), and the Program/Erase states are clearly distinguished at V_{GS} = 0 V after the Program and Erase pulses, as indicated by triangular-shaped points. The retention properties of the Program/Erase states are maintained for at least 2000 s,

with a ratio of 1000 throughout the entire duration, as shown in Figure 4f.

As a final device application, we integrated SA into the MoS₂ FET to develop a Janus MoS₂ FET toward an energy-efficient photonic artificial synapse device, as illustrated in Figure 5a. The conductivity of the Janus MoS₂ FET can be independently modulated through two different remote controls, by either applying electrical or photonic pulses. The electrical control is achieved via pulse-induced ferroelectric modulation on the bottom P(VDF-TrFE) layer, while the photonic control is achieved through photo-induced ionic gating on the top SA layer. The transfer curves of the Janus MoS₂ FET in Figure 5b reveal that the memory hysteresis window of 10 V is retained even after the SA deposition. In fact, the Program/Erase current ratio (over 1000), measured after applying a 1 s pulse of V_{GS} = ± 20 V, remains similar to that before SA deposition. Beyond the static memory hysteresis, the device exhibits robust retention properties for over 10 000 s. This stability denotes that the ferroelectric gating predominantly modulates the MoS₂ conductivity without contributing to cation migration within the SA layer. Finally, our Janus SA/MoS₂/P(VDF-TrFE) device has been adapted to emulate a photonic synaptic device through a combination of ferroelectric and photo-induced ionic gating. As demonstrated in Figure 3, it operates in both SM and LTM modes, suggesting that multifunctionality can be also

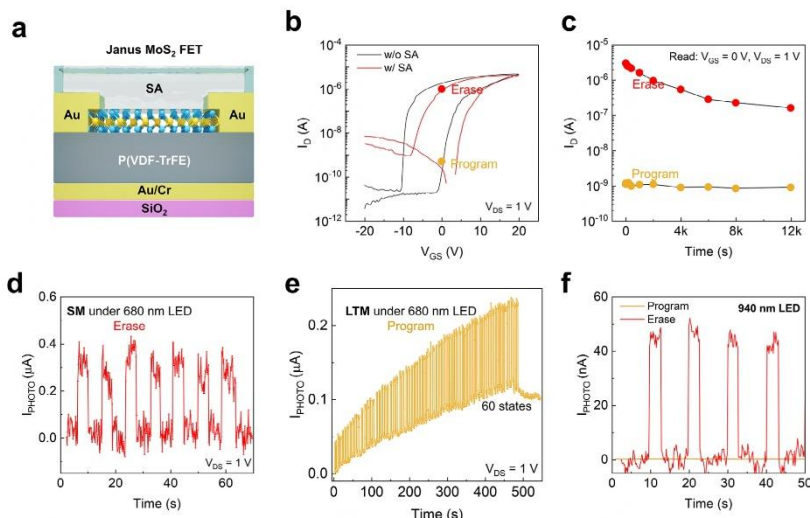


Figure 5. Asymmetric supramolecular functionalization of 2D MoS₂ FET with SA and ferroelectric polymer. a) Side-view scheme of the Janus MoS₂ FET achieved by interfacing SA with the MoS₂ FeFET. b) Transfer curves of the MoS₂ FeFET (black) and Janus MoS₂ FET (red) at V_{DS} = 1 V, showing a maximum ferroelectric hysteresis of 10 V, regardless of the presence of SA. c) Memory retention properties of the Janus MoS₂ FET over 12 000 s. Time-resolved photoresponse of the Janus MoS₂ at V_{GS} = 0 V and V_{DS} = 1 V, demonstrating d) sensory memory (SM) under 680 nm LED illumination at the ferroelectric Erase state, e) synaptic LTM under 680 nm LED illumination at the ferroelectric Program state, and f) SM by leveraging the ferroelectric Erase state under NIR LED illumination.

achieved through non-volatile ferroelectric gating rather than applying high gate voltage, thus securing energy-efficient operation. For a quantified comparison, we estimated the power consumption of both the h-BN and P(VDF-TrFE) supported MoS₂ synaptic FETs (Figure S16, Supporting Information). We found that SA/MoS₂/h-BN FET exhibits an average gate power consumption (P_G) of 0.2 nW at V_{GS} = −20 V for 80 s, while the SA/MoS₂/P(VDF-TrFE) FET features P_G = 0 nW at V_{GS} = 0 V. Although the sub-nW P_G of the SA/MoS₂/h-BN FET appears insignificant compared to the tens of nW of drain power consumption (P_D), the complete elimination of P_G is a critical factor, reducing the burden of heat dissipation and facilitating continued device downscaling. For SM operation, shown in Figure 5d, the MoS₂ is in a high-conductive Erase state, whereas the Janus MoS₂ FET in its low-conductive Program state can display up to 60 linear multilevel states (Figure 5e). The resolution of each conductance state is ≈2 nA, with the total device conductance ranging from 0 to 120 nA. Further details and supporting data are provided in Figure S18 (Supporting Information). Additionally, in the Erase state, the photodetection wavelength range extends up to 940 nm, covering the NIR spectrum (Figure 5f). Although NIR photodetection of MoS₂ has already been reported under bottom gating,^[63,64] the significance of our findings lies in applying nonvolatile memory characteristics to the photodetec-

tor via molecular functionalization, effectively reducing energy consumption.

3. Conclusion

In summary, we have successfully fabricated an optoelectronic artificial synapse that responds to a broad wavelength range within the visible spectrum (455–680 nm) through the photo-induced ionic gating effect between MoS₂ and ion-conductive sodium alginate (SA), an abundant and sustainable biopolymer acting as a dynamic cations reservoir. This novel mechanism enables emulating synaptic plasticity, including SM, STM, and LTM. By tuning light intensity and exposure time, the SA/MoS₂/h-BN multilevel memory device exhibited over eight distinct states using solely photon stimulation as a remote control. Importantly, unlike previous optoelectronic multilevel memories based on trap/de-trap mechanisms, our device achieves a reset state through a simple voltage disconnection, eliminating the need for a high reset voltage. To further enhance the device functionality, we developed a novel Janus MoS₂ assembly by decorating also the bottom surface of MoS₂ with nonvolatile ferroelectric P(VDF-TrFE). This configuration enables independent modulation of conductivity via electronic pulses and photons, resulting in a multifunctional photonic memory device with 60 distinct states and ideal

linearity for energy-efficient LTM operations. By leveraging the non-volatile ferroelectricity, the device works without constant back-gating, offering a significant step forward in energy-efficient neuromorphic systems. Additionally, our Janus MoS_2 device demonstrated broad-spectrum photodetection capabilities, extending from visible to NIR wavelengths of 940 nm. These findings underscore the transformative potential of supramolecular functionalization of MoS_2 with ionic-conductive biopolymers, introducing a sustainable, versatile platform for high-performance, multifunctional 2D Janus synaptic devices. With their unique combination of photonic memory, synaptic behavior, and energy-efficient design, such devices pave the way for innovations in neuromorphic computing, optoelectronic systems, and beyond.

4. Experimental Section

Materials: Bulk 2H- MoS_2 and h-BN crystals were purchased from HQ Graphene. Sodium Alginate was purchased from CARLO ERBA [Product code: 366551; the Mannuronate/Gulonate (M/G) ratio was determined to be 1.17 using FT-IR spectroscopy (Figure S17 and Table S2, Supporting Information)],^[65,66] the molecular weight—calculated through viscosimetric analysis—was ≈ 317 kDa (Table S3, Supporting Information).^[65,67] The Na^+ content (determined through ICP-AES analysis) was 6.1% of the weight of the dried SA powder. P(VDF-TrFE) and 2-butanone were purchased from Sigma-Aldrich (Product codes: 900904 and 360473).

Device Fabrication— $\text{MoS}_2/\text{h-BN}$ FET: SiO_2 (270 nm)/ $\text{n}^+\text{-Si}$ substrates (Fraunhofer Institute IPMS) were cleaned sequentially with acetone and ethanol in an ultrasonicator for 30 min each. Few-layer h-BN flakes were mechanically exfoliated using polydimethylsiloxane (PDMS, SYLGARD 184 Kit). Subsequently, another PDMS stamp was used to exfoliate few-layer h-BN crystals from the original PDMS surface. The exfoliated h-BN was inspected under an optical microscope to select flakes with optimal lateral size and uniformity. Thereafter, they were transferred onto the $\text{SiO}_2/\text{n}^+\text{-Si}$ substrates. The semiconducting MoS_2 flakes were exfoliated through the same mechanical exfoliation process. The alignment of the MoS_2 flake on the PDMS stamp with the h-BN/ $\text{SiO}_2/\text{n}^+\text{-Si}$ substrate was accomplished using the optical microscope and a CCD camera-equipped microaligner. The MoS_2 flake was then transferred onto the h-BN surface by applying vertical pressure. (The thickness of all h-BN and MoS_2 flakes used in this study ranged from 20 to 30 nm and 5 to 10 nm, respectively.) Source/Drain (S/D) electrodes of Au (50 nm) were patterned via photolithography (laser writer LW405B from Microtech, AZ1505 photoresist), thermal evaporation, and a lift-off process. The prepared samples were mildly annealed at 150 °C for 2 h in a nitrogen-filled glovebox to enhance contacts and minimize S-defect formation.

Device Fabrication— $\text{MoS}_2/\text{P(VDF-TrFE)}$ FeFET: The Au/Cr (12 nm/3 nm) bottom gate electrodes were patterned on the $\text{SiO}_2/\text{n}^+\text{-Si}$ substrates using the previously described electrode fabrication method. P(VDF-TrFE) was dissolved in 2-butanone solvent to prepare a 3 wt.% solution. This solution was spin-coated onto the bottom gate electrodes, followed by thermal annealing on a hot plate at 100 °C for 1 min. The semiconducting MoS_2 channel was transferred onto the P(VDF-TrFE)/Au layers using the PDMS stamping method, followed by curing at 142 °C on a hot plate for 2 h in a nitrogen-filled glovebox to crystallize P(VDF-TrFE). Finally, S/D electrodes of Au (50 nm) were patterned using the same methods as for the bottom gate. The FeFET samples were annealed at 100 °C for 2 h in a nitrogen glovebox to improve contact quality.

Device Fabrication—SA Deposition: The 250 mg of SA was dissolved in 100 mL of Milli-Q water under gentle stirring for 1 h at room temperature. A 2 μL aliquot of the 0.25 wt.% SA solution was drop-casted onto the MoS_2 channel for both $\text{MoS}_2/\text{h-BN}$ FET and $\text{MoS}_2/\text{P(VDF-TrFE)}$ FeFET devices, respectively. Excess water was removed using an N_2 gun, leaving an SA hydrogel on the MoS_2 channel.

Optoelectronic Measurements: Electrical measurements were performed using a Keithley dual-channel 2636A and 4200A SCS semiconductor

parameter analyzer under ambient atmosphere and dark conditions. Electrical transport characteristics in low vacuum (≈ 1.3 mbar) were measured using the 4200A SCS in a Lakeshore probe station. Photoresponse measurements of the transistors were conducted under the illumination of 740, 680, 530, and 455 nm LEDs.

Material Characterization—Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES): The amount of Na^+ contained in the used sodium alginate was determined by means of an Agilent 720-ES Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) equipped with a pneumatic nebulizer and a cyclonic spray chamber. Sodium alginate solutions 0.1% (w/v) in MilliQ were analyzed. The calibration lines were obtained by preparing the standard solutions starting from commercial standards certified at 1000 ppm. Sodium absorbance was evaluated at 589.592 nm. Measurements were performed in quadruplicate. After each measurement, the system was washed with a 2% HNO_3 solution.

Material Characterization—Thermogravimetric Analysis (TGA): TGA was carried out with a Discovery SDT650 from TA Instruments, using an alumina pan under air flux (100 mL min^{-1}). A heating ramp from room temperature (RT) to 950 °C, with a rate of 10 °C min^{-1} , was applied. For water content determination, samples were heated to 120 °C at the same rate, followed by a 10 min isotherm. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Samples were all equilibrated at RH = 40% prior to measurement.

Material Characterization—Differential Scanning Calorimetry (DSC): DSC analysis was carried out by means of Discovery DSC 2500 (TA Instruments). In order to define the state of the water in the samples, the latter were subjected to a cooling ramp from 5 to -60 °C, followed by a heating ramp from -60 to 25 °C (in both cases with a heating rate of 1 °C min^{-1}). Tzero Aluminum Hermetic pans (TA Instruments) were used. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). Measurements were performed in duplicate. Samples were all equilibrated at RH = 40% prior to measurement.

Material Characterization—X-Ray Photoelectron Spectroscopy (XPS): XPS measurements (Thermo Scientific K-Alpha) were performed at a base chamber pressure of $\sim 10^{-9}$ mbar using an Al K α X-ray source (1486 eV). Spot sizes of 400 μm and pass energies of 200 eV (for wide scans) and 10–20 eV (for high-resolution scans) were used. All XPS spectra were calibrated to the C 1s peak at 284.8 eV.

Material Characterization—Atomic Force Microscopy (AFM): For AFM imaging, scan-assist mode atomic force microscopy was performed in the air using a Bruker Dimension Icon. The tip model was SCAN-ASSIST-AIR with a stiffness constant $K = 0.4$ N m^{-1} .

Material Characterization—UV-Vis Spectrophotometry: UV-Vis absorbance spectra of the gels were collected using a Cary UV-Vis multi-cell spectrometer (Agilent) in the 200–1000 nm range. Gels were adhered to the wall of a quartz cuvette, perpendicular to the light path.

Material Characterization—Confocal Raman Microscopy: Confocal Raman microscopy was carried out using a Renishaw InVia Qontor confocal microRaman system equipped with a front-illuminated CCD camera and a research-grade Leica DM 2700 microscope. Spectra were collected by using a 100 $\times$ and a laser operating at 532 nm with a power of 100 mW and a grating of 2400 lines per mm. Spectra were processed with the Renishaw software WIRE 5.5, and corrected for cosmic rays, baseline, and noise.

Material Characterization—X-Ray Diffraction Analysis: The crystallinity of ferroelectric P(VDF-TrFE) polymer was investigated by X-ray diffraction patterns (Bruker D8 X-ray diffractometer).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Y.J. and P.T. contributed equally to this work. Y.J., P.T., M.B., and P.S. conceived the experiments and designed the study. Y.J. and P.T. performed all optoelectrical and materials characterization. B.H. performed the XPS measurement. A.T. performed AFM measurement. Y.J., P.T., A.T., B.H., M.B., and P.S. discussed the results and contributed to the interpretation of data. Y.J., P.T., and P.S. co-wrote the paper with input from all co-authors.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

ionic gating, MoS_2 synaptic memory, P(VDF-TrFE), persistent photoconductivity, sodium alginate

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Appendix III

The following papers derive from my Master's degree research and are reported in the next pages in the Publisher's Main Text PDF version.

Paper I: P. Tordi; F. Ridi; M. Bonini, A Green and Sustainable Approach for the Preparation of Cu-Containing Alginate Fibers, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2023**, 677, 132396.

Paper II: P. Tordi; F. Ridi; M. Bonini, A Bioinspired and Sustainable Route for the Preparation of Ag-Crosslinked Alginate Fibers Decorated with Silver Nanoparticles, *Carbohydrate Polymers*, **2024**, 326, 121586.

Paper III: P. Tordi; R. Gelli; S. Tamantini; M. Bonini, Alginate Crosslinking Beyond Calcium: Unlocking the Potential of a Range of Divalent Cations for Fiber Formation, *International Journal of Biological Macromolecules*, **2025**, 306, 141196.



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A green and sustainable approach for the preparation of Cu-containing alginate fibers

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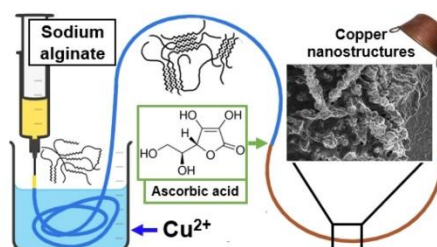
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HIGHLIGHTS

- Cu²⁺-alginate fibers obtained through a facile extrusion and crosslinking process.
- Ascorbic acid to reduce Cu²⁺ ions *in situ*.
- Fibers decorated with homogeneously distributed copper-based nanostructures.
- Properties of the fibers finely tuned as a function of the preparation conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

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ABSTRACT

The development of biopolymer fibers is attracting considerable interest due to the need to reduce the environmental impact of the petroleum-based industry. With the aim to foster the use of biopolymer-based antimicrobial fibers, a green and sustainable preparation route for alginate fibers containing copper-based nanostructures is reported. Its strong antimicrobial properties and affinity for alginate make copper the ideal candidate for the preparation of products suitable for various applications. In this work alginate is extruded and crosslinked in a Cu²⁺ aqueous bath, producing a filiform hydrogel structure. Ascorbic acid was then used to reduce the metal ions and to form the aforementioned nanostructures. This *in situ* strategy for the reduction of coordinating Cu²⁺ ions is unprecedented and leads to a homogeneous distribution of the inorganic structures in the polymeric network. The entire process can be monitored through infrared spectroscopy and the performances (e.g., thermal stability, morphology, swelling, water retention, mechanical properties) of the obtained products are tunable as a function of the duration of each preparation step. The great affinity for water and the small

Abbreviations: Alg, Alginate; Cu, Copper; CuAlg, Copper-crosslinked Alginate; AA, Ascorbic acid; Lyo, Lyophilized; FT-IR, Fourier transform - infrared spectroscopy; SEM, Scanning Electron Microscopy; EDX, Energy dispersive X-Ray spectroscopy; TGA, Thermogravimetric analysis; DSC, Differential scanning calorimetry; SR, Swelling Ratio; ICP-OES, Inductively coupled plasma-optical emission spectroscopy.

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amount of Cu^{2+} released as a function of time suggest promising perspectives for the use of these fibers in antimicrobial applications.

1. Introduction

In recent years, the use of composite materials has provided significant impetus to research in various sectors. Sensors, antimicrobial matrices, and scaffolds for tissue regeneration can be successfully designed with relative simplicity taking advantage of organic-inorganic composites [1]. A biopolymer with considerable potential for the production of functional materials is alginate, an anionic polysaccharide extracted from brown algae and consisting of linear copolymer blocks made of D-mannuronate and L-guluronate residues (MW Guluronate/Mannuronate unit = $193.13 \text{ g mol}^{-1}$) [2]. In particular, guluronate units (G-blocks) are believed to be the main actors in the coordination of divalent cations (e.g. Ca^{2+}). Alginate is considered safe by the FDA (Food and Drug Administration) [3] and it has found a large number of applications in medicine, food and agriculture. It is frequently used in polymeric formulations to encapsulate actives, enhance solubility and improve mechanical properties [3]. In the food industry, alginate is used as an emulsifier, thickener and stabilizer [3]. The presence of carboxylate groups on its backbone provides a peculiar reactivity towards divalent cations to form “egg box” type structures [4]. There is an extensive bibliography on the study of alginate hydrogels crosslinked with divalent cations, belonging to the families of alkaline-earth metals (Ca^{2+} , Ba^{2+} and Sr^{2+}) and transition metals (Cu^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Cd^{2+} , Pb^{2+} and Ni^{2+}) [5].

Calcium appears to be the element of choice for the preparation of alginate hydrogels, since it is cheap and effectively produces biocompatible cross-linked materials [4]. The technique adopted to prepare such structures involves the dripping of an aqueous alginate solution into a solution of a calcium salt in water: in fact, crosslinking is almost instantaneous and leads to the formation of insoluble polymeric structures. The possibility of varying multiple preparation parameters (i.e., concentration and type of alginate, calcium ion concentration and counterions, crosslinking time) allows for the preparation of hydrogels with tunable properties. For instance, Ca^{2+} -alginate hydrogels can be successfully used in the biomedical field as carriers for the release of drugs [6] and as scaffolds for tissue regeneration [7].

Copper is another element that has attracted considerable interest in terms of its interaction with alginate. Compared to Ca^{2+} , it is considered less selective towards the coordination of carboxylate groups, assuming unpredictable coordination arrangements [8]. Although most of the alginate hydrogels crosslinked with Cu^{2+} ions are produced in the form of beads [9], some studies have recently reported about the preparation of alginate fibers by crosslinking polymer solutions immediately after their injection into a M^{2+} -containing solution [10].

Copper is well known for its antimicrobial properties. In particular, copper nanostructures are characterized by antimicrobial efficacy competitive or even superior to those based on silver [11]. The synthesis is also cheap and easy to implement. Nanoparticulate copper can assume various forms depending on the adopted synthetic strategy: CuO , Cu_2O and Cu . The mechanism of antibacterial action of these products is believed to involve the generation of ROS capable of damaging bacterial membranes and viral proteins [12]. In the past, copper-based nanoparticles were often synthesized using toxic reagents (e.g., NaBH_4). In the last decade, their replacement with natural molecules (e.g., polysaccharides and plant extracts) has grown exponentially, encouraged by the need to maximize both biocompatibility and sustainability. It is interesting to note that synthetic methodologies based on polysaccharides show excellent results in the preparation of nanoparticles [13]. Plant extracts containing polyphenols and other reactive molecules such as ascorbic acid can also be used to replace hazardous chemicals: these substances, in addition to being cheap and sustainable,

have remarkable antioxidant properties [14,15]. The introduction of copper nanoparticles into polymeric matrices allows to exploit the antibacterial capabilities in many sectors, including membranes for water purification [16] and composites for wound healing [17].

The aim of this paper is the preparation and characterization of alginate fibers crosslinked with copper ions and containing copper-based nanoparticles. The filiform structure of the products, important towards their applicability in many sectors, can be easily imparted by extrusion and immediate ionic crosslinking of the polymer. In order to decorate the fibers with nanoparticles, a reducing agent of natural origin such as ascorbic acid was used. The aforementioned composite material therefore aims to be attractive for its antimicrobial properties in sectors that require high biocompatibility (e.g., wound healing and water/air purification) and sustainability. The *in situ* synthesis of the nanoparticles directly in the crosslinked substrate (an approach not previously reported) favors a homogeneous distribution in the polymeric matrix and considerably simplifies a possible production process at the industrial scale. Multiple parameters (concentration of the polymeric solution, rate of extrusion, concentration of the crosslinking and reducing solutions, duration of each preparation step, etc.) have been optimized in order to obtain hydrogels with good mechanical properties and maximize the copper content. The Scanning Electron Microscopy (SEM) analysis of the fibers provided useful information regarding distribution and oxidative state of copper in these systems, both of which are relevant for the determination of antimicrobial efficacy. Thermal analysis (by means of thermogravimetric analysis, TGA, and differential scanning calorimetry, DSC) made it possible to appreciate how the preparatory steps modify the properties of the starting polymer, while at the same time defining the limits of use of the fibers. Aiming at the use of fibers in water purification systems, water absorption and retention properties were investigated. The mechanical properties of the fibers were evaluated by extensional tests. The amount of copper released by the fibers in contact with water was assessed by inductively coupled plasma-atomic emission spectrometry (ICP-OES), in order to evaluate that it could be tuned above the minimum amount needed to provide antimicrobial effectiveness, but well below the maximum amount imposed by law.

2. Experimental section

2.1. Reagents

Sodium alginate was purchased from Sigma Aldrich, while cupric sulfate anhydrous (CuSO_4 , > 98 %) was obtained from Carlo Erba. Ascorbic acid (AA, Assay ≥ 99.0 %) and hydrogen chloride solution (HCl, Standard 0.1 M) were provided by Fluka. Controlled relative humidity conditions were obtained by using KNO_3 (Merck, min. 99 %). Deionized water was used to prepare sodium alginate, copper sulfate and ascorbic acid solutions. All reagents were used without any further purification.

2.2. Preparation of crosslinked alginate fibers containing Copper-NPs

A 4% (w/v) sodium alginate water solution was extruded through a needle (0.9 mm of internal diameter) in 9 mL of CuSO_4 1 M. The extrusion flux was equal to 5.76 mL/min: 0.67 mL of polymeric solution were extruded for each sample. The instantaneously formed structure was kept in the cupric sulfate solution for 1 h. The hydrogel was transferred in 100 mL of deionized water and kept there for 1.5 h to remove the excess of copper. Markovic's work provided an insight into the implementation of the reductive process [18]. A 4.5 cm long fiber was dipped into 8 mL of ascorbic acid (AA) 0.5 M maintained at 50 °C.

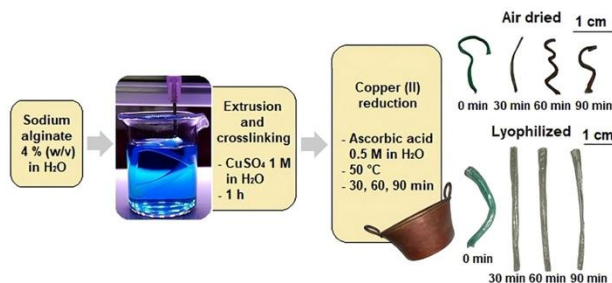


Fig. 1. Scheme of copper-alginate fibers preparation process.

Table 1

Preparation parameters and nomenclature of the prepared samples (see Fig. 1).

Sample	Dehydration mode	AA treatment (mins)
CuAlg	Air drying	0
CuAlg1y0	Lyophilization	0
CuAlg30	Air drying	30
CuAlg30Ly0	Lyophilization	30
CuAlg60	Air drying	60
CuAlg60Ly0	Lyophilization	60
CuAlg90	Air drying	90
CuAlg90Ly0	Lyophilization	90

The treatment was extended for 30, 60, and 90 min. Then the fibers were kept in 40 mL of deionized water for 30 min. After this, samples were either air dried or lyophilized. Fig. 1 illustrates the preparation process. The prepared crosslinked alginate fibers containing Copper-NPs were coded as shown in Table 1.

2.3. Alginic acid synthesis

Alginic acid was prepared and used as a reference. HCl 0.1 M was added to a solution of sodium alginate 4 % (w/v), until the precipitation of the polysaccharide occurred ($\text{pH} < 2$). The precipitate was filtered and washed several times with deionized water. When the pH of the washing water was close to 7, the material was air dried for 24 h. The obtained product was coded as Alginic acid.

2.4. Equilibration at specific relative humidity conditions

The air-dried samples were equilibrated at 95% relative humidity. For this purpose they were placed in airtight boxes containing supersaturated KNO_3 solutions [19]. Equilibrated samples acquire the suffix RH95.

2.5. Extrusion of the polymeric solution

The HYREL 3D Engine SR injection 3D printer was employed to extrude the 4 % (w/v) alginate solution in deionized H_2O . To achieve this, it was equipped with an SDS-10 print head equipped with an electric motor (model LDO-28STH51-0674A) and a 10 mL syringe. The polysaccharide solution was extruded, with a flow of 5.76 mL/min, through a cylindrical needle having an internal diameter of 0.9 mm.

2.6. Scanning electron microscopy (SEM)

CuAlgLy0, CuAlg30Ly0, CuAlg60Ly0, CuAlg90Ly0, CuAlg, CuAlg30, CuAlg60 and CuAlg90 samples were analyzed by means of Scanning

electron microscopy. The SEM images were obtained using a Zeiss Sigma scanning electron microscope, equipped with a Gemini column and a field emission gun (FEG) source. Secondary electrons were collected using an InLens detector. The applied acceleration voltage (EHT) was kept fixed at 1 kV. Images were analyzed using “ImageJ” software.

2.7. Energy dispersive X-ray spectroscopy (EDX)

Energy dispersive X-Ray spectroscopy (EDX) was carried out using X-act Silicon Drift Detector (Oxford Instruments). The accelerating voltage and the working distance were kept constant, respectively, at 10 kV and ~8.5 mm for all the measurements.

2.8. Fourier transform - infrared spectroscopy (FT-IR)

Sodium alginate, CuAlg, CuAlg30, CuAlg60, CuAlg90 and Alginic acid samples were analyzed by means of Fourier transform-infrared spectroscopy (FT-IR) using a Thermo Nicolet Nexus 870 FT-IR spectrophotometer equipped with an ATR (Attenuated Total Reflectance) Golden Gate accessory. All the spectra were recorded at room temperature within the of 4000–650 cm^{-1} wavenumber range with a spectral resolution of 2 cm^{-1} and recording 128 scans for measurement.

2.9. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed on Sodium alginate RH95, CuAlgRH95, CuAlg30RH95, CuAlg60RH95, CuAlg90RH95 and Alginic acid RH95 samples using a Discovery SDT650 (TA Instruments). A heating ramp from room temperature to 1000 °C, with a rate of 10 °C/min, was applied to all the samples. Measurements were performed under N_2 flux, using alumina pans. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments).

2.10. Differential scanning calorimetry (DSC)

DSC analysis was carried out by means of Discovery DSC 2500 (TA Instruments). Tzero Aluminum Hermetic pan (TA Instruments) were used for all the measurements. Sodium alginate, CuAlg, and CuAlg90 samples were analyzed by applying a heating ramp from room temperature to 100 °C, with a heating rate of 10 °C/min. In order to determine the presence of freezable water in the sample, CuAlg30RH95 was investigated using an initial cooling ramp (from 5 °C to −60 °C) and a subsequent heating one (from −60 °C to 25 °C), with a 1 °C/min rate. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments).

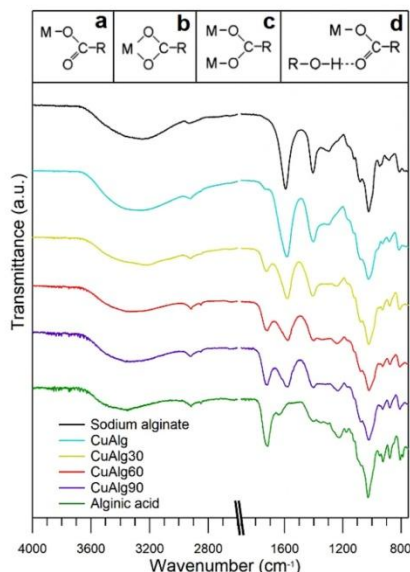


Fig. 2. FT-IR spectra of Sodium alginate, CuAlg, CuAlg30, CuAlg60, CuAlg90 and Alginate acid. Spectra were normalized to the $\nu(\text{COO}) + \delta(\text{CCO}) + \delta(\text{CC})$ peak (Table S1). In the panels on top, the different coordination geometries of metal-carboxylate complexes are shown: monodentate (a), bidentate chelating (b), bidentate bridging (c) and pseudo-bridging monodentate (d).

2.11. Swelling tests

The swelling properties of CuAlg, CuAlg30, CuAlg60 and CuAlg90 samples were analyzed. Each dry fiber was placed in 20 mL of demineralized H_2O , after being weighted. Mass measurements were then acquired at regular intervals (over a period of 335 min), extracting the samples from the fluid and removing the excess surface of the same using absorbent paper. Data were analyzed with "Igor Pro 6.1.0.9" software.

2.12. Inductively coupled plasma-atomic emission spectrometry (ICP-OES)

The copper-release properties in water of CuAlg, CuAlg30 and CuAlg90 were determined by means of an Agilent 720-ES Inductively coupled plasma atomic emission spectrometer (ICP-OES) equipped with a pneumatic nebulizer and a cyclonic spray chamber. 10 mg of each sample was kept in 15 mL of MilliQ water for 24 h. Aliquots of the

solution (6 mL) were withdrawn and acidified with HNO_3 prior to the analysis. The calibration lines were obtained by preparing the standard solutions starting from commercial standards certified at 1000 ppm. Copper absorbance was evaluated at 324.754 nm. After each measurement, the system was washed with a 2 % HNO_3 solution.

2.13. Mechanical properties

The mechanical properties of the fibers were evaluated using a Discovery DHR-3 rheometer (TA Instruments). The fibers were fixed to a paper support using glue and clamped (similarly to the work of Fidellis et al. [20]), applying a force equal to 30 cN·m. The traction test was performed with a 25 $\mu\text{m/s}$ rate. Measurements were performed in triplicate. Data were analyzed using Trios v5.1.1.46572 software (TA Instruments).

3. Results and discussion

3.1. FT-IR spectroscopy

FT-IR spectra of Sodium alginate, CuAlg, CuAlg30, CuAlg60, CuAlg90 and Alginate acid samples are reported in Fig. 2. Table 2 shows the assignment (based on literature data [21,22]) of the infrared absorption bands of the examined samples in the 1750 cm^{-1} - 1350 cm^{-1} region. The complete assignment is reported in Table S1. From the observation of the spectra, some significant differences are evident, especially in the $-\text{COO}$ stretching bands. The evaluation of the CuAlgX samples absorption in the region between 1750 cm^{-1} and 1500 cm^{-1} suggests that the treatment with ascorbic acid partially convert the carboxylate groups on the alginate backbone into carboxylic groups: CuAlg30, CuAlg60 and CuAlg90 spectra show a band at 1725 cm^{-1} , present in the Alginate acid spectrum and attributable to $\nu(\text{COOH})$. Sodium alginate, on the other hand, shows a single band at 1594 cm^{-1} related to the asymmetric $-\text{COO}$ stretching of the carboxylate unit in the aforementioned region. With the exception of Alginate acid, all the investigated samples show such a band, characterized by a more or less pronounced shift.

Considering that the FT-IR spectra were acquired in ATR mode, it is not possible to use the data to quantitatively compare the amounts of carboxylic and carboxylate groups present in each sample. However, it is possible to compare the relative amounts of carboxylic and carboxylate groups of each spectrum by evaluating the intensities of the bands attributable to the $-\text{COO}$ stretchings of previously mentioned structures. Eq. 1 was used to determine (approximate) molar ratios between carboxylic groups and carboxylate groups ($n\text{COOH} / n\text{COO}^-$) for the CuAlg30, CuAlg60 and CuAlg90 samples, resulting in 0.53, 0.82 and 0.90, respectively.

$$\frac{n\text{COOH}}{n\text{COO}^-} = \frac{\text{Transmittance } \nu\text{COO}_{\text{asym}}}{\text{Transmittance } \nu\text{COOH}} \quad (1)$$

This evidence confirms that the treatment with ascorbic acid progressively protonates an increasing number of alginate carboxylate groups during the copper reduction process. Infrared spectroscopy is able to provide other valuable information about the interaction of carboxylate groups with Cu^{2+} ions. The carboxylate ions usually coordinate metal cations according to the three modes illustrated in Fig. 2: monodentate (Fig. 2a), bidentate chelating (Fig. 2b) and bidentate

Table 2

Assignment of the IR absorption bands (1750 cm^{-1} - 1350 cm^{-1} region) of the Sodium alginate, CuAlg, CuAlg30, CuAlg60, CuAlg90 and Alginate acid spectra in Fig. 2 (ν : stretching; error: 2 cm^{-1}).

Assignment	NaAlg (cm^{-1})	CuAlg (cm^{-1})	CuAlg30 (cm^{-1})	CuAlg60 (cm^{-1})	CuAlg90 (cm^{-1})	Alginate acid (cm^{-1})
$\nu(\text{COOH})$	-	1730	1725	1725	1725	1724
$\nu(\text{COO})_{\text{asym}}$	1594	1585	1583	1579	1579	-
$\nu(\text{COO})_{\text{sym}}$	1405	1407	1407	1404	1406	-

Table 3

Coordination geometry of the analyzed samples. For the calculation of $\Delta\nu$, the data presented in Table 2 were used.

Sample	$\Delta\nu$ (cm ⁻¹)	Coordination geometry	FIB
Sodium alginate	189	Bidentate bridging	1.00
CuAlg	178	Bidentate chelating/ <i>pseudo-bridging</i> [‡]	1.07
CuAlg30	176	Bidentate chelating/ <i>pseudo-bridging</i> [‡]	1.09
CuAlg60	175	Bidentate chelating/ <i>pseudo-bridging</i> [‡]	1.11
CuAlg90	173	Bidentate chelating/ <i>pseudo-bridging</i> [‡]	1.11

[‡]According to Nakamoto [23]. [‡]According to Deacon and Phillips [24].

bridging (Fig. 2c). Based on the work of Nakamoto [23], it is possible to determine the coordination geometry of the complex formed between Cu²⁺ and carboxylate anions by comparing the IR absorption frequencies of the asymmetrical and symmetrical -COO stretching bands of the copper-crosslinked samples and sodium alginate. Using Eq. 2 (with obvious meaning of the symbols) the values of $\Delta\nu_{Cu}$ and $\Delta\nu_{Na}$ were determined. The monodentate, bidentate bridging and bidentate chelating coordination are characterized by $\Delta\nu_{Cu}$ values higher, equal and lower (respectively) than $\Delta\nu_{Na}$ [21], Table 3 shows the $\Delta\nu$ values determined for each sample, with the corresponding coordination geometry.

$$\Delta\nu = \nu_{COO_{sym}} - \nu_{COO_{asym}} \quad (2)$$

The bidentate chelating coordination geometry is difficult to rationalize through an egg box coordination model in which the organization of the alginate chains involves not just the carboxylate groups, but also the hydroxyl ones [25]. Furthermore, $\Delta\nu$ values for this type of coordination should be higher than those listed in Table 3. The work of Deacon and Phillips [24] is useful to shed light on the topic: in fact, it pointed out that a *pseudo-bridging* monodentate coordination mode, due to symmetry, can lead to $\Delta\nu$ values that are lower than those expected for a common monodentate coordination mode (i.e., resembling the ones of the bidentate coordinations). Such structure, schematically illustrated in Fig. 2d, can occur when a metal cation is complexed with carboxylic ligands prone to forming hydrogen bonds. Considering the known tendency of uronic acids to form hydrogen bonds [21] and the experimentally obtained $\Delta\nu$ values, it is reasonable to infer that all of the Cu²⁺-crosslinked samples, regardless of the treatment, are characterized by a *pseudo-bridging* monodentate coordination modality. The collected

FT-IR data also provide information on the binding character between carboxylate groups and Cu²⁺ ions. Taking a cue from the work of Chen [26], the Fraction of Ionic Bonding (FIB) of the COO-Cu²⁺ complexes of each sample was determined using Eq. 3, where $\nu(COOH)$ is the IR absorption frequency of Alginic acid -COO stretching (typical covalent bond), while $\nu(COOCu)$ and $\nu(COONa)$ are the asymmetric -COO stretching frequencies of the copper-crosslinked samples and sodium alginate (typical ionic bond) respectively.

$$FIB = \frac{\nu(COOH) - \nu(COOCu)}{\nu(COOH) - \nu(COONa)} \quad (3)$$

Table 3 shows the obtained results. It is interesting to note that, similarly to Chen, the FIB of the Cu²⁺-crosslinked samples always exceeds unity. The lower vibration frequency of the carboxylate unit in the COO-Cu²⁺ complex compared to the COO-Na⁺ complex can be linked to a decrease in the electron density on the aforementioned group due to an electronic delocalization phenomenon. The latter is attributable to polarization or electronic retro donation events which are known to stabilize metal-complexes [26].

3.2. Morphological and elemental analysis

The SEM image of CuAlgLyso sample cross-section (Fig. 3a) shows a multilayer structure that is not identifiable in the case of CuAlg (Fig. 3b), most reasonably because of the collapse of the structure during drying. In our hypothesis the layered structure is the result of the crosslinking process: in fact, the large amount of available Cu²⁺ ions (from the 1 M CuSO₄ solution) rapidly saturates the coordination sites available in the surface of the fiber, reducing the permeability of the structure towards the diffusion of ions in the inner regions. At the same time, the presence of water released by the newly coordinated sites might be able to create

Table 4

Results of the EDX elemental analysis.

Element	CuAlgLyso atomic %	CuAlgX [‡] atomic %	CuAlgX [‡] atomic %
C	45.8	54.1	81.3
O	50.2	10.9	17.2
Cu	4.00	35.0	0.5

[‡] White square in Fig. 4b. [‡] Black square in Fig. 4b.

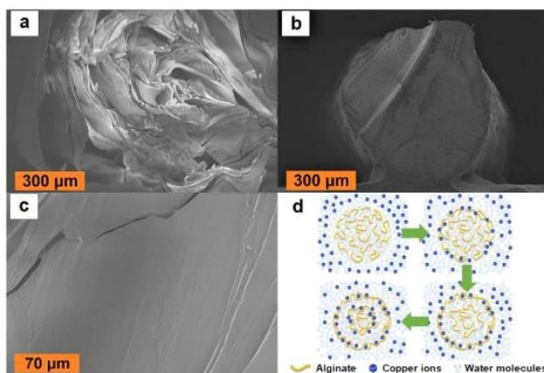


Fig. 3. SEM images of CuAlgLyso (a, c) and CuAlg (b) samples. (d) Sketch of the hypothesized crosslinking and diffusion mechanism leading to the layered structure of the fiber (green arrows indicate the evolution with time).

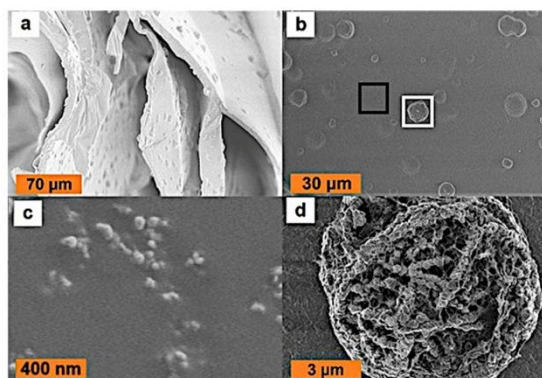


Fig. 4. SEM images of the CuAlg60 sample. Fig. 4c (large view reported in Fig. S1) highlights the presence of embedded copper nanoparticles, detected both in CuAlg30 and CuAlg60 samples. Orange bars correspond to actual sizes.

discontinuities in the hydrogel structure, generating a layered structure (Fig. 3d). This is consistent with SEM results, where the surface of the CuAlgLyo sample is smooth (see Fig. 3c). The EDX analysis of CuAlgLyo sample confirms that a significant amount of copper, about 4 % of atoms, was uploaded into the structure (Table 4).

Samples treated with ascorbic acid show a high number of surface humps, homogeneously distributed in all the layers of the fiber and clearly distinguishable in Fig. 4a. At higher magnifications, one can clearly see that the humps consist of spherical aggregates with external

diameters ranging between 4 and 10 µm embedded in the polymeric matrix.

The EDX analysis conducted in these regions (white square in Fig. 4b) highlighted the inorganic character of these structures, made up mostly of copper. Its percentage, higher than that of oxygen (Table 4), suggests that the inorganic structures are made of metallic copper. Prabhu's research group, in an attempt to synthesize copper nanoparticles, obtained clusters of metallic copper morphologically similar to the aforementioned spherical structures [15]. The color of the fibers treated with ascorbic acid, tending to brownish red, supports this hypothesis. The CuAlg30Lyo and CuAlg60Lyo samples, in contrast with CuAlg90Lyo, also show uniformly distributed copper nanoparticles with diameters ranging from 40 to 90 nm (Fig. 4c). The observation of Fig. 4d suggests that the micrometric inorganic structures are produced by the aggregation of the same nanoparticles. The EDX analysis performed in a cluster-free region (black square in Fig. 4b) highlighted a low copper concentration (lower than that of CuAlgLyo sample), coherent with a progressive migration of the metal to grow the clusters. The absence of nanoparticles in the CuAlg90Lyo sample is probably due to the depletion of the copper available for reduction within the sample. A 2-D elemental map of CuAlg90, obtained through EDX, is reported in Fig. S2. It is plausible that the copper nanoparticles formed during the ascorbic acid treatment interact with some of the carboxylate groups of the polymeric matrix, staying dispersed. As the reduction treatment proceeds, the number of carboxylate binding sites decreases due to their concomitant protonation highlighted through FT-IR Spectroscopy (see Section 3.1): nanoparticles therefore tend to aggregate, forming the nanostructured copper clusters.

3.3. Thermal analysis

TGA curves of Sodium alginate RH95, CuAlgRH95, CuAlg30RH95, CuAlg60RH95, CuAlg90RH95 and Alginate acid RH95 are discussed in this section. Samples were equilibrated at the same humidity level (*i.e.*, RH 95 %) in order to exclude possible alterations of thermal degradation profiles due to environmental factors. Table 5 shows values and temperature ranges related to each characteristic mass loss obtained by taking into account the starting and ending points of the peaks in the DTG plot (derivative of the percentage mass loss) of each sample.

The thermal degradation curve of Sodium alginate RH95 (Fig. 5a)

Table 5
Mass losses and related temperature ranges of the TGA curves shown in Fig. 5a.

Sample	Event	T range (°C)	Mass loss (%)	Norm. Mass loss (%)
Sodium alginate RH95	I	28.5 – 201.9	30.3	0
	II	201.9 – 259.6	26.3	37.7
	III	259.6 – 521.3	12.2	17.5
	IV	521.4 – 840.6	18.9	27.1
	V	840.6 – 992.5	1.5	2.2
CuAlgRH95	I	26.3 – 148.0	17.2	0
	II	148.0 – 238.9	33.8	40.8
	III	238.9 – 493.8	18.3	22.1
	IV	493.8 – 993.5	4.3	5.1
	V	-	-	-
CuAlg30RH95	I	23.5 – 142.3	13.7	0
	II	142.3 – 250.2	33.9	39.3
	III	250.2 – 495.9	18.4	21.3
	IV	495.9 – 993.4	5.6	6.5
	V	-	-	-
CuAlg60RH95	I	22.8–140.7	14.8	0
	II	140.7–249.5	29.7	34.9
	III	249.5–507.9	18.1	21.3
	IV	507.9–993.9	6.6	7.8
	V	-	-	-
CuAlg90RH95	I	22.5 – 141.3	13.5	0
	II	141.3 – 249.2	34.4	39.8
	III	249.2 – 508.2	18.4	21.3
	IV	508.2 – 993.9	5.7	6.6
	V	-	-	-
Alginate acid RH95	I	20.1–136.2	15.2	0
	II	136.2 – 233.6	39.1	46.2
	III	233.6 – 577.8	21.3	25.1
	IV	577.8 – 993.3	4.1	4.9
	V	-	-	-

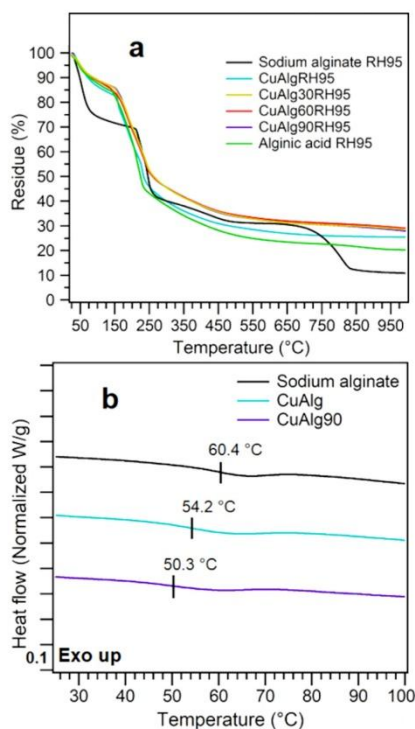


Fig. 5. TGA thermograms (a) of Sodium alginate RH95, CuAlgRH95, CuAlg30RH95, CuAlg60RH95, CuAlg90RH95 and Alginic acid RH95. DSC thermograms (b) of Sodium alginate, CuAlg and CuAlg90.

shows five significant mass losses (Table 5). The first (Event I), occurring between 28.5 °C and 201.9 °C, is due to the loss of the water contained in the sample. A first rapid degradation process (Event II) then occurs and lasts up to 259.6 °C. This event is linked to the loss of CO, CO₂ and other volatile products by the polymeric structure [27]. This is the most relevant degradation process of the entire thermogram, as it is responsible for the loss of 26.3 % of the sample mass. The second degradation event (Event III, 259.6–521.3 °C) is characterized by the release of the aforementioned products and the concomitant formation of Na₂O and NaCO₃ [27,28]. The latter compound undergoes further degradation, releasing carbon dioxide in the temperature range between 521.3 °C and 840.6 °C [27,28]. The sample loses only 1.5 % of its mass in the next temperature range, remaining in the form of carbon residue (10.8 % of the initial mass). The CuAlgRH95 sample, on the other hand, shows only four significant events in the TGA curve (Fig. 5a). The first, between 26.3 °C and 148.0 °C, is due to the loss of the water contained in the sample. Then a net degradation process occurs and extends up to a temperature of 238.9 °C, involving the release of CO, CO₂ and other volatile products by the polymeric structure [27]. This mass loss is faster than its analog in the Sodium Alginate RH95 sample. The second

degradation event (Event III, 238.9–493.8 °C) is attributable to the loss of CO₂ by the structure and to the simultaneous formation of Cu₂O and CuO [29]. The sample loses 4.3 % of its mass in the temperature range up to 993.5 °C. In this case there is no degradation of the inorganic component as copper carbonate, due to its low thermal stability (i.e., it degrades to CuO and CO₂ at only 300 °C [29], cannot be present in the sample in the investigated temperature interval. Table 5 also highlights that the introduction of copper into the network lowers the onset temperatures of all the degradation processes. TGA curves of ascorbic acid treated samples are similar to the CuAlgRH95 one: the structure of the thermogram is almost the same, except for some details. Firstly, CuAlgXRH95 samples show a lower water content (Event I in Table 5). Furthermore the degradation process of the polymer chains is slower and takes place at lower temperature with respect to CuAlgRH95. This phenomenon may be due to the inhomogeneous copper distribution highlighted by SEM analysis. A similar explanation is supported by the amount of mass lost by the sample during the event, similarly to the CuAlgRH95 sample. The second degradation event (Event III) extends up to about 500 °C, similar to the untreated crosslinked sample. The samples lose about 6% of their mass in the last section of the thermal ramp. Water content and residue are similar for all the CuAlgXRH95 samples: considering that the polymeric structure is almost the same for all samples treated with ascorbic acid, this evidence denotes that the amount of copper contained in the fibers is the same (ensuring the reproducibility of the preparation method). The duration of the reducing treatment therefore does not affect the total copper content, but only its distribution in the fibers. The TGA analysis of Alginic acid RH95 is able to provide some interesting insights on the effects of the treatment with ascorbic acid on the examined samples. The TGA curve of Alginic acid RH95 (Fig. 5a) shows four significant weight losses, similar to the Cu²⁺-crosslinked samples. The amount of water lost in the temperature range between 20.1 °C and 136.2 °C (Event I) is higher than that lost by CuAlgXRH95 (X = 30, 60, 90) samples, but lower than Sodium alginate RH95 and CuAlgRH95 sample (this is attributable to a strong hydrophobic interaction between the polymer chains, if highly protonated).

The obtained percentage mass losses were normalized for the amount of bulk water contained (Norm. mass loss in Table 5), based on the assumption that Event I mass losses are attributable only to the water present in the samples. In this way it is possible to compare data from samples that differ in the amount of water.

Analyzing the data in Table 5 it is possible to approximately quantify the copper loaded by the polymer during the crosslinking process: in fact, it is sufficient to compare the normalized mass losses of the CuAlgRH95 and Alginic acid RH95 samples. The method is based on three assumptions: *i.* the quantity of sodium in the Alginic acid RH95 sample is negligible; *ii.* the polymeric component of the CuAlgRH95 sample does not reach a higher level of degradation than that present in the Alginic acid RH95 sample; *iii.* all of the copper contained in the CuAlgRH95 sample is oxidized to CuO during the heating process. The “Normalized mass loss” values in Table 5 reveal that the percentage (scaled for water) of polymeric residue in the Alginic acid RH95 sample is equal to 23.8 % of the starting one, while the percentage “CuO + polymer” in the form of residue for the sample CuAlgRH95 is equal to 32.0 %. Approximately 6.55% of the weight of the CuAlgRH95 (dry) fiber is therefore due to copper. Considering a molecular weight of 193.13 g mol⁻¹ for the manuronate (or guluronate) unit, a 4.69 molar ratio [glycosidic units/Cu²⁺ ions] was calculated. This result suggests that the copper can be fully coordinated by the polysaccharide structure according to the canonical egg box model.⁴ A value of the ratio close to 4 also suggests that the copper present in the structure is sufficient to saturate the coordination sites. DSC analysis also provided information on the order of polymer chains. The Sodium alginate thermogram (Fig. 5b) shows a glass transition (*T_g*) at a temperature of 60.4 °C, confirming the presence of amorphous domains within the polymer. The analysis was extended to CuAlg and CuAlg90 samples in order to highlight the effect of crosslinking and reduction treatment on the thermal

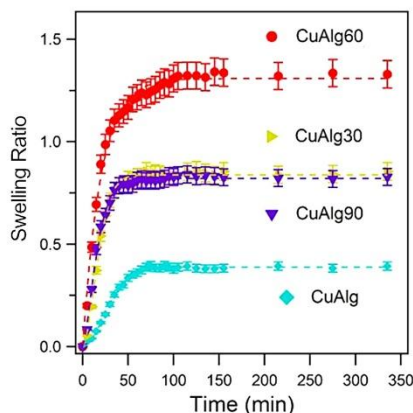


Fig. 6. Swelling Ratios of CuAlg, CuAlg30, CuAlg60 and CuAlg90 samples with the respective fitting curves according to the Weibull model.

properties. CuAlg shows a T_g at 54.2 °C, suggesting that copper introduction increases the polymer chains mobility in the amorphous domains. The egg box coordination geometry probably decreases the packing ability of the polymer chains, reducing hydrogen bonding interactions and, consequently, their resistance to the transition. CuAlg90 shows a T_g at a lower temperature (50.3 °C) than CuAlg. This behavior could be explained with the increase in the number of protonated carboxylate groups, unable to efficiently coordinate the cations present in the network. The DSC analysis was performed on CuAlg30RH95 in order to determine the state of the water contained in the fiber (13.7 % from TGA analysis): the sample was subjected to a cooling ramp (from 5 °C to −60 °C) and to a subsequent heating ramp (from −60 °C to 25 °C) with a 1 °C/min rate. The obtained thermogram (Fig. S3) does not show peaks related to water phase transitions, proving that all the water present in the sample is closely linked to the polymer chains [30].

3.4. Swelling and retention properties

The swelling properties of CuAlg, CuAlg30, CuAlg60 and CuAlg90 samples were tested to evaluate the influence of the treatment with ascorbic acid. The Swelling Ratio (SR) of each sample was calculated as a function of time using Eq. 4, in which W_s and W_d are the masses of the swollen hydrogel and of the dry hydrogel, respectively. The related swelling curves are shown in Fig. 6.

$$SR = \frac{W_s - W_d}{W_d} \quad (4)$$

The fibers treated with ascorbic acid have a higher swelling capacity than the untreated one. This phenomenon is attributable to the decrease in the amount of Cu^{2+} ions linked to the polymer chains and the consequent increase in their degrees of freedom. Interestingly, the sample that has undergone an intermediate treatment in ascorbic acid (i.e., CuAlg60) is able to absorb a larger volume of water. Such behavior can be justified considering the swelling capacity as resulting from two competitive contributions: percentage of reduced copper (favorable) and percentage of protonated carboxylate groups (unfavorable). The first is responsible for a lower structural rigidity, while the second involves a reduction in the affinity of the polymer towards water (stronger hydrophobic intra/inter-chain interactions [31]). This latter

Table 6
Weibull fitting parameters for SR curves in Fig. 6.

Parameter	CuAlg	CuAlg30	CuAlg60	CuAlg90
M_{∞}	0.387 ± 0.002	0.838 ± 0.003	1.31 ± 0.01	0.821 ± 0.003
k ($\bullet 10^{-3}$)	(1.37 ± 0.25)	(5.90 ± 1.04)	(47.1 ± 6.8)	(15.7 ± 2.5)
n	1.86 ± 0.05	1.70 ± 0.06	1.02 ± 0.05	1.44 ± 0.05

Table 7
Results of the ICP-OES and mechanical analysis conducted on CuAlg, CuAlg30 and CuAlg90 samples. The percentage of Cu^{2+} released by the fibers (i.e., Cu^{2+} rel. (%)) was calculated taking into account the copper content of the CuAlg sample determined from TGA (see Section 3.3). Young's modulus and ultimate tensile strength were determined from the stress (σ) vs strain (ϵ) curves reported in Fig. S6.

Sample	Cu^{2+} rel. / mg of fiber (μg)	Cu^{2+} rel. (%)	Young's modulus (GPa)	Ultimate tensile strength (MPa)
CuAlg	0.28	0.43	1.25 ± 0.06	31 ± 2
CuAlg30	1.32	2.02	1.31 ± 0.07	22 ± 1
CuAlg90	1.20	1.84	0.95 ± 0.05	15 ± 1

contribution, as evidenced by FT-IR analysis, constantly increases during the treatment with ascorbic acid. The percentage of reduced copper shows a different trend: in fact, the presence of non-aggregated copper nanoparticles (SEM, Fig. 4) suggests the availability of Cu^{2+} ions for reduction only for the CuAlg30 and CuAlg60 samples. CuAlg90 shows only micrometric clusters due to the aggregation of the nanoparticles formed in the first hour of treatment in ascorbic acid. In this case, the prolongation of the reduction process does not involve an increase in the mobility of the polymer chains, but just an increase in the number of protonated carboxylate groups. The marked tendency for the absorption of water by the CuAlg60 sample had already been observed through the TGA analysis of the CuAlg60RH95 sample (Event I in Table 5). A Weibull diffusion model was used to fit the swelling data [32], according to Eq. 5, in which M_t and M_{∞} are the mass of water absorbed at time t and time $t = \infty$ respectively. k is a constant related to the time scale of the



Video 1. A video clip is available online. Supplementary material related to this article can be found online at doi:10.1016/j.colsurfa.2023.132396.

diffusion process (higher k , fastest water uptake) and n indicates the type of diffusion of a water molecule in the polymeric matrix. The obtained results are reported in Table 6.

$$\frac{M_t}{M_{\infty}} = 1 - \exp(-kt^n) \quad (5)$$

The obtained k values highlight that the treatment with ascorbic acid accelerates the water uptake process by the network. It is also possible to state that the water diffuses in the samples according to a Supercase II type kinetics, except in the case of CuAlg60 (Case II diffusion) [33]. The water retention properties of the fibers were also investigated and the obtained results are reported in Fig. S4 and Table S2. The results show that the reduction process makes the water desorption slower, while preserving the diffusion modality of the process (i.e., Supercase II).

3.5. Cu^{2+} -release and mechanical properties

ICP-OES provided useful information about the effects of the reduction treatment on the Cu^{2+} -release properties in water. The obtained data, reported in Table 7, clearly highlight that the amount of copper released by the fibers in 24 h is particularly low: assuming that the copper content estimated by TGA for CuAlg (see Table 5) is representative for all the samples, the percentage of Cu^{2+} released by the fiber ranges between (0.43 % and 2.02 %). Ascorbic acid-treated samples possess a higher tendency to release Cu^{2+} ions with respect to CuAlg, suggesting that the coordination with carboxylate groups reduces the accessibility of Cu^{2+} . The slightly different behavior of CuAlg30 and CuAlg90 can be explained considering that the lower dimension (i.e., higher specific surface) of the copper-based nanostructures in CuAlg30 (see Section 3.2) plays a role. The low and easily tunable Cu^{2+} -release suggests promising perspectives for the application of the fibers in wound healing and water purification. For example, hypothesizing to treat 1 L of water with CuAlg, CuAlg30 and CuAlg90 for 24 h, it would be necessary to add kilograms of material (i.e., 4.65 kg, 0.98 kg, and 1.08 kg respectively) to reach the copper-content upper limit for drinking water (1.3 mg/L) set by US-EPA (United States - Environmental Protection Agency). However, copper concentrations well below this limit (e.g. around 177 ppb) proved to be already effective against a wide range of bacteria [34]. With a view to a possible application in the aforementioned sectors, we investigated the effect of the reducing treatment on the mechanical properties of the fibers (see Fig. S5 for the description of the experimental procedure). As highlighted in Table 7 (see stress vs strain curves in Fig. S6), increasing the duration of the reduction decreases both the Young's modulus and the ultimate tensile strength of the fibers (due to an increase in the rigidity). Again the properties of the fibers proved to be tunable as a function of the preparation.

4. Conclusions

We have developed a facile and reliable method for the preparation of Cu^{2+} -crosslinked alginate fibers, containing copper nanoparticles. The polymeric scaffolds were obtained by continuous extrusion of the polysaccharide aqueous solution into a crosslinking bath. The nanoparticles were then synthesized *in situ* using ascorbic acid to reduce the copper ions present in the polymeric network for variable times.

Our strategy satisfies many of the 12 Principles of Green Chemistry: in fact, the process fully prevents the generation of waste and entirely adheres to the atom economy principle, as the preparation minimizes the number of steps and it is designed to maximize the incorporation of all materials used in the process. The substances used for the process display no toxicity to human health, as well as to the environment, are cheap, and most of them are produced from renewable sources. Finally, the preparation process is characterized by low energy consumption and avoids safety hazards.

The optimization of the preparation parameters allowed to maximize

the copper content and to obtain samples with peculiar physico-chemical properties. The fibers morphology was characterized by means of SEM in order to determine the presence of copper nanostructures and their distribution: the technique revealed that the reduction process generates nanoparticles homogeneously distributed in the polymeric network, together with micrometric clusters of the same nanoparticles, as confirmed by EDX spectroscopy. FT-IR spectroscopy proved to be useful for determining a *pseudo*-bridging monodentate coordination mode for the copper-alginate complex, consistent with the well-known *egg box* coordination model. TGA and DSC also made it possible to determine the thermal stability of the fibers and the molecular order of the polymer within them, providing useful hints about their interaction with environmental humidity. It was found that the cross-linking and the subsequent treatment with ascorbic acid contribute to reducing the thermal stability of the fibers. These latter also showed to be responsive to variations in environmental humidity: the investigation of the swelling properties of the aforementioned fibers highlighted not only the maximum water absorption capacities, but also the kinetics of this phenomenon. The amount of copper released in water was determined as a function of reduction time using ICP, showing that the released amount could be tuned by using either Cu^{2+} -crosslinked fibers or reduced fibers to reach effective antimicrobial values, well within safety regulations. Also the mechanical properties of the fibers were assessed, highlighting their dependence on the duration of the reduction. Results suggest that the prepared fibers have a huge application potential in (antimicrobial) water/air purification systems.

CRediT authorship contribution statement

Pietro Tordini. Investigation, Formal analysis, Writing - Original Draft. **Francesca Ridi.** Conceptualization, Supervision, Writing - Review & Editing. **Massimo Bonini.** Conceptualization, Supervision, Writing - Review & Editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Supplementary material available

The following material is available free of charge in the [Supplementary material file](#): full FT-IR spectra assignments, additional SEM morphological analysis, EDX elemental distribution maps, DSC freezable water evaluation, water retention properties, mechanical properties, video of the extrusion and cross-linking process.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.colsurfa.2023.132396](https://doi.org/10.1016/j.colsurfa.2023.132396).

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A bioinspired and sustainable route for the preparation of Ag-crosslinked alginate fibers decorated with silver nanoparticles

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ABSTRACT

Functional materials obtained through green and sustainable routes are attracting particular attention due to the need to reduce the environmental impact of the chemical industry. In this work we propose a bioinspired approach for the preparation of alginate fibers containing silver nanoparticles (AgNPs), to be used for antimicrobial purposes. We demonstrate that filiform polymeric structures with length of a few meters can be easily obtained by extruding an alginate solution in an aqueous Ag⁺-containing bath (i.e. wet spinning) and that treating the fibers with freshly-squeezed lemon juice leads to the formation of AgNPs homogeneously distributed within the polymeric network. Using mixtures of ascorbic and citric acid to mimic lemon juice composition we highlight the influence of the aforementioned molecules on the nanoparticles formation process as well as on the properties of the fibers. Varying the amount of citric and ascorbic acid used for the treatment allows to finely tune the thermal, morphological and water absorption properties of the fibers. This evidence, along with the possibility to easily monitor the preparation through FT-IR spectroscopy, endows the fibers with a high application potential in several fields such as wound healing, water/air purification and agriculture.

1. Introduction

Alginate is an anionic polysaccharide discovered by E.C.C. Stanford in 1881 (Stanford, 1881). It is commonly obtained through alkaline extraction from brown algae belonging to the *Phaeophyceae* class (Yoon et al., 2009), but its occurrence in some bacteria is also reported (Skjåk-Bræk et al., 1986). Alginate is considered safe by the Food and Drug Administration (FDA), which classifies it as a food additive. This characteristic, combined with its biodegradability and biocompatibility, makes alginate suitable to be used in the medical, cosmetic, agricultural and food sectors. The structure of this polymer consists of (1,4) linked β-D-Mannuronate (M) and α-L-Guluronate (G) residues and can be elucidated through both ¹H and ¹³C NMR analyses (Grasdalen, 1983; Grasdalen et al., 1979, 1981; Salomonsen et al., 2009). The extraction source directly influences the M/G ratio (Aarstad et al., 2013; Huang & Larsen, 1962; Haug et al., 1967; Grasdalen et al., 1981) and the sequence of the residues. Homogeneous (GG or MM) and heterogeneous (GM or MG) blocks can coexist in the same polymeric chain (Grasdalen et al.,

1981). The carboxylate moieties of the residues can strongly interact with cationic species to form complexes with various geometries: this phenomenon is commonly called crosslinking and is a simple approach to obtain hydrogels. It is interesting to note that the nature of the complex is strongly influenced by the nature of the ion in terms of charge and dimensions and by the sequence of the M and G residues. Alginate is reportedly able to crosslink with specific monovalent (Lengert et al., 2017), divalent (Haug & Smidsrød, 1965), trivalent (Singh et al., 2014; Zhou et al., 2014) and tetravalent cations (Elhoudi et al., 2022; Qing et al., 2022) to form hydrogel structures, whose properties depend on both the ion and the complex characteristics.

Among the ions able to crosslink with alginate, silver is particularly attractive for its antimicrobial properties both in nanoparticle (NP) and cationic form (Durán et al., 2016). The high specific surface allows the NPs to cap and disrupt bacterial membranes, releasing at the same time silver cations. The cytotoxicity of AgNPs, largely attributable to the generation of reactive oxygen species (ROS), increases as the NP dimension decreases (Durán et al., 2016). The chemical reduction of

Abbreviations: Alg, Alginate; Ag, Silver; NPs, Nanoparticles; CA, Citric acid; AA, Ascorbic acid; MW, Molecular weight; RH, Relative humidity; RT, Room temperature; TGA, Thermogravimetric analysis; FT-IR, Fourier transform-infrared; SR, Swelling ratio; FE-SEM, Field emission scanning electron microscopy; FIB, Fraction of ionic bonding; DSC, Differential scanning calorimetry; SD, Standard deviation.

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silver salts is the most common strategy to obtain AgNPs, although the toxic and polluting character of most of the chemicals commonly used is a remarkable drawback to this approach. In order to overcome this limitation, bioinspired strategies involving microorganisms (El-Naggar et al., 2017; Sivasankar et al., 2018) and plant extracts (Mane Gavade et al., 2015; Ravichandran et al., 2019) were developed in the last decades. In this context, AgNPs with predictable particle size were successfully synthesized using *Citrus lemon* extracts (Prathna et al., 2011). The reducing agents present in lemon juice which are responsible for the formation of AgNPs are reported to be citric acid (CA) and ascorbic acid (AA) (Ortega et al., 2021). However, there is no consensus on the role of the two components, some studies indicating the reducing role being mainly due to the CA (Prathna et al., 2011). Although alginate composite materials containing AgNPs were already reported in the literature (Ambroggi et al., 2020; Lin et al., 2013; Porter et al., 2021), alginate crosslinking with silver cations has been scarcely investigated so far. The high ionic radius of Ag^+ (1.15 Å) (Shannon, 1976) and the consequent soft character of this ion reduce both the number of binding sites and the interaction strength with the polymeric chains, hampering the preparation of complex-shaped hydrogel structures (e.g. fibers).

The aim of this paper is the design, preparation and characterization of alginate fibers crosslinked with silver ions and containing AgNPs. We want to demonstrate that a wet spinning approach can be used to easily produce filiform hydrogel structures with lengths up to some meters, due to the possibility of varying multiple preparation parameters. To obtain AgNPs formation on the alginate fibers, bioinspired solutions of CA and AA are used, mimicking the composition of the lemon juice (Prathna et al., 2011). Our work aims to unravel the effect of different CA/AA ratios on the features of both the fibers and the obtained Ag nanostructures, to prepare products attractive for the development of antimicrobial materials useful in wound healing, agriculture and water/air purification.

2. Materials and methods

2.1. Materials

Alginic acid sodium salt was purchased from Sigma Aldrich (Product number 180947. Mannuronate/Guluronate = 1.50 ± 0.04 , determined through FT-IR spectroscopy (Gómez-Ordóñez & Rupérez, 2011; Sakugawa et al., 2004; Vetrano et al., 2022) (see Fig. S1 and Table S1 in the Supplementary Material). Molecular weight ≈ 132 kDa, determined through viscosimetric analysis (Masuelli & Illanes, 2014; Vetrano et al., 2022) (see Table S2 in the Supplementary Material). Silver nitrate (AgNO_3 , Assay >99.8 %) was obtained from Carlo Erba. AA (Assay ≥ 99.0 %) was provided by Fluka, while CA monohydrate (min. 99.8 %) was purchased by J. T. Baker. Alginic acid from brown algae was provided by Sigma Aldrich (product number 1003449856). Controlled 95 % relative humidity (RH95) conditions were obtained using KNO_3 (Merck, Gehalt min. 99 %) supersaturated solutions in deionized water. Deionized water was used to prepare the sodium alginate, silver nitrate and CA-AA solutions. All reagents were used without any further purification.

2.2. Preparation of crosslinked alginate fibers containing silver nanostructures

2.2.1. Ag^+ -crosslinked alginate fibers preparation

A 4 % (w/v) sodium alginate (MW Mannuronate/Guluronate unit = $193.12 \text{ g mol}^{-1}$) water solution was prepared by dissolving the polymer at room temperature under stirring for about 40 min. The solution was used to fill a 10 mL syringe and extruded through a needle (0.9 mm of internal diameter) in 50 mL of AgNO_3 0.5 M. The extrusion process was carried out using a HYREL 3D Engine SR injection 3D printer equipped with an SDS-10 print head provided with an electric motor (model LDO-28STH51-0674 A). The extrusion flux was equal to 5.76 mL/min: 4.8 mL

of polymeric solution were extruded for each batch, leading to a Ag-alginate fiber with a length of ~ 2.5 m. The instantaneously formed fiber was kept immersed in the silver nitrate solution for 1.5 h. The hydrogel was then washed with deionized water (5 mL/cm of fiber) for 1 h, to remove the excess of uptaken silver. Both the crosslinking and the washing steps were carried out in the dark to avoid any potential effect of light towards Ag^+ reduction. The samples' preparation is schematized in Fig. 1.

2.2.2. Ag^+ ions reduction

The washed Ag^+ -crosslinked fibers were treated for 0.5 h in solutions containing different amounts of CA and AA (see Table 1), taking a cue from the lemon juice composition. For each sample, 30 cm of fiber was treated in 30 mL of solution. During the reduction, the solutions were periodically shaken to homogenize the treatment. The fibers were then washed for 1 h in deionized water (5 mL/cm of fiber). Both the reduction and the washing steps were carried out in the dark. Samples were either dried under the fume hood overnight or lyophilized. As a proof of concept, a portion of Ag-alginate fiber was reduced using fresh lemon juice, obtained by squeezing and filtering commercial lemons.

2.3. Characterization techniques

2.3.1. Evaluation of the color during the reduction

To monitor the color change during the reduction, 2 cm of Ag-alginate fibers were put in contact with 2 mL of the reducing solutions (see the composition in Table 1) in plastic cuvettes, and photos were taken at regular intervals for 30 min. A white-balance operation was carried out on the images using a graphic editor software, according to a white reference present in all photos. The color variation in time was quantified by converting the photos in 8-bit (i.e., conversion in grayscale), and applying an auto-contrast operation using the software *ImageJ*. The gray values of the fibers at half of their height were sampled, and plotted for each sample as a function of time.

2.3.2. Evaluation of the fibers diameter

The diameter of the fibers immediately after preparation and when dried was measured with a digital microscope from Park Systems. For each image, 10 measurements of the diameter were collected along the fiber, and the results are expressed as average $\pm$ standard deviation (SD). *ImageJ* software was used to analyze the data.

2.3.3. Swelling tests

To evaluate the swelling properties of the samples, 20 cm of dry fiber were weighted and then placed in 200 mL of deionized H_2O . Mass measurements were then acquired at regular intervals, extracting the samples from the fluid and removing the excess water by means of paper towel. The experiments were interrupted when a stable weight was attained for each sample. The swelling ratio (SR) was calculated according to Eq. (1):

$$SR = \frac{m_t - m_0}{m_0} \quad (1)$$

where m_t is the mass of the swollen sample at time t and m_0 is the initial (i.e., dry) mass of the sample. For the determination of the SR at the equilibrium, measurements were performed in triplicate.

2.3.4. Field emission-scanning electron microscopy (FE-SEM)

Field emission-scanning electron microscopy (FE-SEM) analysis was conducted using a Zeiss Σ GMA FE-SEM (Carl Zeiss Microscopy GmbH). The fibers, either lyophilized or air dried, were placed over aluminum stubs by means of conductive tape. The micrographs were acquired with an accelerating voltage of 2 kV, sample-detector distance 2–4 mm, aperture 10 μm and using the In-Lens detector. Energy dispersive X-ray spectroscopy (EDX) analysis was carried out with an X-act Silicon Drift

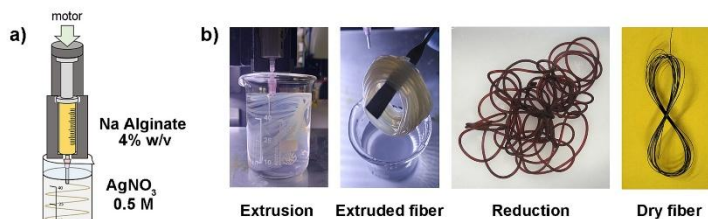


Fig. 1. a) Sketch of the extrusion process with the 3D printer. b) Photos of the different stages of fiber preparation.

Table 1

Nomenclature and composition of the solutions for the Ag-alginate fibers reduction. The pH of the AA solution is 3.73 ± 0.01 , while that of all the CA-containing solutions is 1.99 ± 0.01 (experimental error of the pH-meter).

Sample	CA/AA (mol)	Citric acid (mg/ml)	Ascorbic acid (mg/ml)
AgAlg	—	—	—
AgAlg AA	0	0	0.42
AgAlg CA/AA = 5	5	48.18	8.83
AgAlg CA/AA = 25	25	48.18	1.77
AgAlg CA/AA = 50	50	48.18	0.88
AgAlg CA/AA = 105	105	48.18	0.42
AgAlg CA/AA = 150	150	48.18	0.29
AgAlg CA/AA = ∞	∞	48.18	0

Detector (Oxford Instruments), using an accelerating voltage of 10 kV, a working distance of about 8 mm and an aperture of 60 μm . For each sample, three different sites were analyzed, and the average $\pm$ SD is reported.

2.3.5. X-ray diffraction (XRD)

XRD patterns were collected with a D8 Advance with DAVINCI design (Bruker), using as X-ray source the Cu K α radiation (wavelength $\lambda = 1.542 \text{ \AA}$) operating at 40 kV and 40 mA. The 2θ range was $30\text{--}80^\circ$, the step size 0.03° and the time/step 0.3 s. Before the analysis, the lyophilized fibers were cut into small pieces, grinded and flattened on a Si zero-background sample holder.

2.3.6. Fourier transform - infrared spectroscopy (FT-IR)

FT-IR spectra were collected using a Nexus 870 FT-IR spectrophotometer equipped with an ATR (Attenuated Total Reflectance) Golden Gate accessory. All the spectra were recorded at room temperature within the wavenumber range of $4000\text{--}650 \text{ cm}^{-1}$ with a spectral resolution of 2 cm^{-1} and recording 128 scans for measurement.

2.3.7. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using Discovery SDT650 (TA Instruments). A heating ramp from room temperature (RT) to 1000°C , with a rate of $10^\circ\text{C}/\text{min}$, was applied to all the samples previously equilibrated at RH95. For the water content determination in the air dried samples, a heating ramp from RT to 200°C (rate of $10^\circ\text{C}/\text{min}$) was applied. Measurements were performed under N_2 flux (100 mL/min), using alumina pan. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments). To determine the silver content of the fibers, a heating ramp from RT to 1000°C , with a rate of $20^\circ\text{C}/\text{min}$, was applied to all the samples under air flux (100 mL/min). Measurements were performed in duplicate. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments).

2.3.8. Differential scanning calorimetry (DSC)

DSC analysis was carried out by means of Discovery DSC 2500 (TA Instruments). Tzero Aluminum Hermetic pan (TA Instruments) were used for all the measurements. Samples were analyzed by applying a heating ramp from 0°C to 120°C , with an heating rate of $20^\circ\text{C}/\text{min}$. Measurements were performed in duplicate. Data were analyzed with Trios v5.1.1.46572 software (TA Instruments).

2.3.9. Inductively coupled plasma-atomic emission spectrometry (ICP-OES)

The amount of released silver was determined using an Agilent 720-ES Inductively coupled plasma-atomic emission spectrometer (ICP-OES) equipped with a pneumatic nebulizer and a cyclonic spray chamber. The calibration lines were obtained by preparing the standard solutions starting from commercial standards certified at 1000 ppm. Silver absorbance was evaluated at 328.068 nm. After each measurement, the system was washed with a 2 % HNO_3 solution. Measurements were performed in triplicate, and the results are expressed as μg of Ag^+ released per mg of fiber.

2.3.10. Mechanical tests

A Discovery DHR-3 rheometer (TA Instruments) was used to evaluate the mechanical properties of the fibers. The latter were fixed to a paper support using bicomponent glue and clamped (Alves Fidelis et al., 2013; Tordì et al., 2023), applying a force equal to 30 cN-m (see Fig. S2 for details). The traction test was performed with a $10 \mu\text{m}/\text{s}$ rate. Measurements were performed in quadruplicate and the data were analyzed using Trios v5.1.1.46572 software (TA Instruments).

2.4. Ag release experiment

The release of Ag from the fibers upon incubation in water was performed by placing about 10 cm of each sample (dry fibers) in a glass vial filled with 10 mL of MilliQ water. The vials were kept at room temperature in an orbital shaker for 24 h. Afterwards, the incubating solutions were collected and analyzed to determine the amount of released Ag (see Section 2.3.9). The fibers were dried under the fume hood and imaged by means of FE-SEM to check for the presence of AgNPs. The experiment was carried out in triplicate.

2.5. Stability against dissolution

The stability against dissolution of the AgAlg sample was tested by immersing about 4 cm of dry fiber in 8 mL of MilliQ water. The samples were kept at room temperature in the orbital shaker and collected after 1, 3, 7, 10 and 14 days of incubation. The fibers were recovered from the solution and dried under the fume hood. When a constant weight was attained, their mass was recorded and compared with the mass before incubation, to obtain the weight % as a function of time. The test was performed in triplicate, and the average weight % $\pm$ SD was reported.

3. Results and discussion

3.1. In situ AgNPs synthesis

Phase separation, diffusion and rheological phenomena strongly influence the characteristics of polymeric fibers obtained through wet spinning (Rohani Shirvan et al., 2022). Mastering these aspects, especially in the crucial coagulation step, allowed us to obtain alginate fibers with a length of some meters with captivating properties despite the relatively weak interaction between alginate and Ag^+ ions (see Fig. 1b) (Qin, 2005, 2008). These fibers were treated with lemon juice to reduce Ag^+ to metallic silver by directly immersing the extruded and washed alginate fibers into a filtered solution of freshly-squeezed commercial lemons. The reduction was monitored for 30 min by observing the color of the fibers during the process (see Fig. 2a). In a few minutes, the fiber color changes from pale yellow to orange, then it goes brown (~ 10 min) and eventually black. This evolution reasonably indicates the successful formation of AgNPs within the alginate fiber, due to the reduction of the Ag^+ ions that crosslink the polymeric chain. The progressive color change suggests that the process occurs gradually. The dried fiber reduced for 30 min with the lemon juice was imaged by means of FE-SEM: the micrographs shown in Fig. 2b confirm the formation of AgNPs, both isolated and agglomerated into small clusters, on the fiber surface.

Aiming at understanding how the use of different CA/AA ratios in the reducing solution of the AgAlg fibers affects the Ag nanostructures formed on the fibers and their properties, we prepared a series of solutions with different content of CA and AA. The composition of the solutions, given in Table 1, was inspired by the average composition of lemon juice, which corresponds to sample AgAlg_CA/AA = 105 (Haytowitz et al., 2019). The color evolution of the AgAlg fibers reduced in the different solutions is displayed in Fig. 3a. AgAlg, which is shown as a reference, does not change its color during the experiment, confirming that the color variations observed in the other samples are solely due to the chemical reduction driven by AA and CA and not to uncontrolled photoreduction of Ag^+ . The color evolution of the other samples dramatically depends on the reducing solution used. AgAlg_AA turns light brown in a few minutes, suggesting that AA alone at the same concentration found in lemon juice (see Table 1) is able to form Ag nanostructures on the fibers. AgAlg_CA/AA = 5, which is prepared in the reducing solution with the highest amount of AA, immediately turns black. Samples AgAlg_CA/AA = 25 and AgAlg_CA/AA = 50 also become black, but the color progression is more gradual, and a transition from yellow, to orange, to brown is observed. A progressive color evolution is also observed for AgAlg_CA/AA = 105 and AgAlg_CA/AA = 150 which, after 30 min of reduction, retain a brown and reddish color, respectively. Interestingly, AgAlg reduced in the solution containing only CA becomes pale yellow at the end of the process. This simple test suggests that with the increase of CA/AA ratio, the reduction is slower, and the different

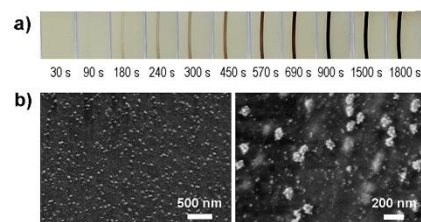


Fig. 2. a) Photos in time (from left to right) of the AgAlg fiber immersed in lemon juice. b) FE-SEM micrograph of the surface of AgAlg fibers reduced using lemon juice.

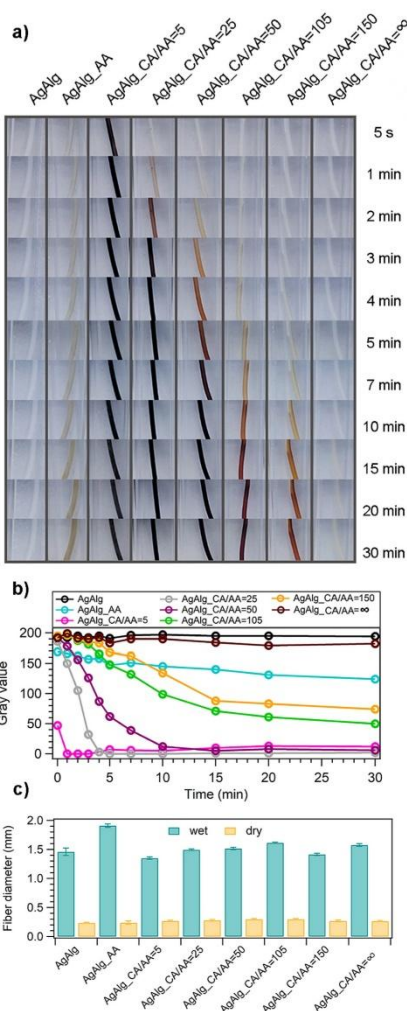


Fig. 3. a) Photos of the evolution in time of AgAlg fibers in the CA/AA solutions. b) Plot of the gray value sampled at half height of each specimen as a function of time (see Section 2.3.1). c) Diameter of the wet and dry fibers obtained from the optical microscopy images in Fig. S3. The error bar refers to the average $\pm$ SD of 10 measurements. The diameters of the wet fibers are the ones at the end of the preparation.

color obtained at the end of the reduction indicates a difference in the size/morphology/aggregation of the Ag nanostructures on the fibers. The color evolution in time could be quantified by converting the images in grayscale, and plotting the gray value in the middle of the fiber as a function of time (see the details in Section 2.3.1). The results reported in Fig. 3b corroborate the previous observations: the color of AgAlg is constant all over the experiment, showing a gray value compatible with a light gray color (about 200), slightly above AgAlg_CA/AA = ∞ . AgAlg_CA/AA = 5 is also constant, but with a gray value close to 0 (black). All the other samples gradually decrease their gray value, in agreement with a slow color variation which depends on CA/AA ratio.

The diameter of the fibers at the end of the process was measured, and the results are given in Fig. 3c and Fig. S3. All samples except AgAlg_AA have a diameter around 1.5 mm, while that of AgAlg_AA is around 1.9 mm. Considering that the internal diameter of the needle used during the extrusion is 0.9 mm, a significant swelling of the fiber occurs during the crosslinking, reduction and washing steps. The measured maximum diameter of the wet AgAlg sample (i.e. 1.53 mm resulting from $1.46 \text{ mm} \pm 0.07 \text{ mm}$, see Fig. 3c), considerably higher than the one of the needle, is due to formation of the insoluble hydrogel structure that hampers the flow of the polymeric solution. Taking into account the amount of alginate solution extruded, the theoretical length of the extruded fiber is 2.62 m. The result is not far from the experimental value obtained (i.e. $\sim 2.5 \text{ m}$): the mismatch can be attributed to the amount of polymer that diffuses into the Ag^+ solution during the crosslinking. Upon drying, the diameter of the fibers decreases up to about 0.3 mm, therefore a size reduction of about five times occurs.

3.2. Water absorption properties

The amount of water that the dried fibers are able to absorb when immersed in water was estimated with a swelling experiment, described in Section 2.3.3. The results reported in Fig. 4a show the swelling ratio (SR) as a function of time; in Eq. 1, the m_0 values (dried mass of the samples at the beginning of the experiment) were normalized for the different amount of water present in the dry fibers, estimated by means of TGA (see Fig. S4 and Table S3). The results show that different samples display a remarkably different swelling behavior. The non-reduced AgAlg fiber, when immersed in water, undergoes a negligible swelling (SR ~ 0.1). The fiber reduced only with AA has a modest SR at equilibrium (SR ~ 4). This phenomenon is due to the dishomogeneous distribution of reduced silver in that sample: regions with high silver content irreversibly collapse during dehydration and are not able to swell anymore. Interestingly enough, the fibers reduced in solution containing CA and AA are characterized by a SR at equilibrium between ~ 28 and ~ 47 , its value being directly proportional to the CA/AA ratio in the range 5–105 (see Fig. 4b). This linear relationship makes it possible to obtain Ag-alginate fibers with predictable swelling ability in this CA/AA range. The reason for the different behavior of the samples in terms of swelling might be due to differences in the structure of the polymeric network induced by Ag^+ reduction: we can imagine that in AgAlg, all silver ions interact with the carboxylate groups of alginate, tightening the polymeric chains and hampering their interaction with water. When Ag^+ is reduced to metallic Ag, part of it is no longer able to crosslink alginate chains: as a consequence, the polymeric network is loosened and it is easier for water to penetrate the structure and swell it.

3.3. Morphological and elemental characterization

The morphology of the Ag nanostructures formed on the fibers was assessed with FE-SEM. The micrographs showing the outer surface of the samples are given in Fig. 5. While AgAlg displays the smooth surface typical of polymers, all other samples are covered by small inorganic structures with a size from tens to hundreds of nm, which reasonably consist of the AgNPs produced during the reduction. AgAlg_AA is covered by NPs with a size of tens of nm together with larger aggregated

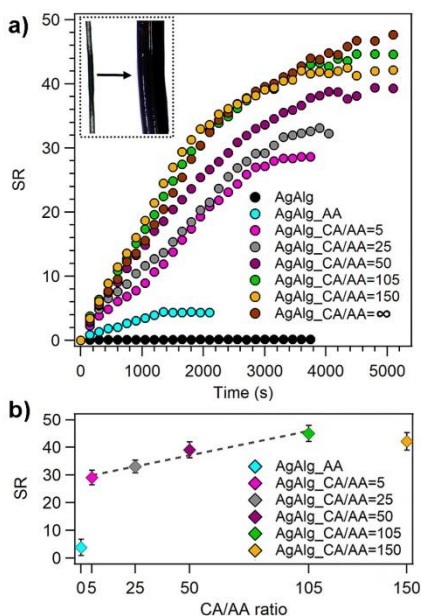


Fig. 4. a) Swelling curves of the samples. The inset shows the image of a fiber at the beginning (left) and at the end (right) of the experiment. Representative curves are reported for each sample. b) Plot of the SR at equilibrium as a function of the CA/AA ratio of the samples (SD was used as error bar). The equation of the line that interpolates the data between CA/AA = 5–105 is $y = 0.16x + 29.0$, $r^2: 0.98$.

clusters with an irregular shape. AgAlg_CA/AA = 5 (Fig. 5c) is characterized by irregular objects with a size of hundreds of nm: we can hypothesize that the very fast reduction of Ag^+ occurring in this sample (see the photos in Fig. 3a) leads to an uncontrolled formation of Ag nanostructures, in which the growth step is favored with respect to the nucleation. In the other samples, in which the reduction is more gradual given the higher CA/AA ratio, a higher amount of Ag nuclei forms, resulting in a decrease of the size of the object with decreasing AA amount in the reducing solution. Out of note, samples from CA/AA = 50 to CA/AA = 150 are characterized by AgNPs both spherical and cubic (the latter are more abundant in AgAlg_CA/AA = 50 sample, see Fig. 5e). It is also worth mentioning that despite AgAlg_AA and AgAlg_CA/AA = 105 were prepared with the same amount of AA in the reducing solution, the AgNPs morphology and distribution is markedly different (see Fig. 5b and f): the presence of CA might therefore contribute to the stabilization and dispersion of the small NPs on the alginate fiber, preventing the formation of large clusters. The observation of the fiber external surface also suggests that samples with a low CA/AA have the polymeric surface completely covered by Ag nanostructures, whereas in samples reduced in solutions with a low amount of AA the smaller NPs are not able to entirely cover the polymeric surface of the sample. This evidence might be related to the different swelling behavior of the samples previously discussed: the progressive increase in the SR with the increase of CA/AA (see Fig. 4) might indicate an easier access for water

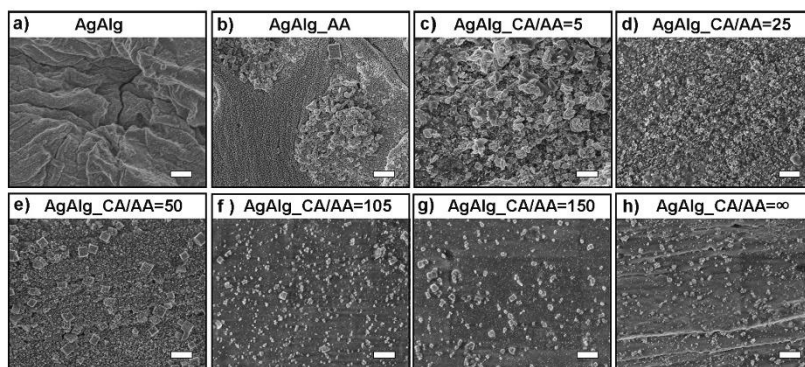


Fig. 5. FE-SEM micrographs of the surface of the dried fibers. The scale bar is 500 nm.

molecules to the hydrophilic polymeric chains in samples with low AA amount, thus resulting in a high swelling ability. In contrast, for samples with low CA/AA the fiber surface is entirely covered by metallic Ag, which hampers water interaction with the polymeric chains resulting in a lower swelling ability.

To understand if the specific morphology of the samples was induced by the drying process, we also imaged samples which were freeze-dried immediately after the last washing step of the preparation. The FE-SEM micrographs, reported in Fig. S5, reveal that all the samples have a morphology similar to the dried one. With the freeze-dried samples it was also possible to image the internal portion of the fibers, which is shown in Fig. S6. All samples are characterized by a porous network, with pore size of hundreds of nm. Qualitatively, the size of the pores appears to increase with the decrease in AA amount in the reducing solution. In order to understand if the formation of AgNPs also occurs within the fibers or if it is restricted to their surface, the cross-sections of each sample were imaged with SEM, and the results are shown in Fig. S7. For sample AgAlg_AA and AgAlg_CA/AA = 5 it was possible to detect Ag nanostructures also in the inner portion of the fiber, whereas for all the other samples no nanoparticles could be observed in the internal regions, suggesting that AgNPs formation mainly occurs on the fibers' surface.

The elemental composition of the fiber samples was investigated by coupling EDX analysis with SEM imaging. The results obtained from the EDX analysis of the samples in Fig. 5 are reported in Table S4 and confirm the presence of Ag in all the prepared fibers, together with C and O constituting the polymeric network. Out of note, the amount of Ag % decreases with the increase in CA/AA, in agreement with the amount of Ag nanostructures observed in SEM micrographs (see Fig. 5). <1 % of Na and Cl is found in all samples (Na likely comes from the residual ions of the sodium alginate that were not washed away or replaced by Ag⁺ during the crosslinking). This very small amount of NaCl could also be responsible for a small portion of the cubic structures observed in the SEM images, as both Ag and NaCl are known to crystallize into cubic lattice structures. It has to be though remarked that considering the relative abundance of the two materials, NaCl cannot account for all the cubic structures observed on the fibers surfaces, which are therefore largely due to AgNPs.

Considering that Ag is present in our samples both as the crosslinking cation and as the constituent of the Ag nanostructures observed on the fibers (except for AgAlg sample), we aimed at further characterizing their crystallinity through XRD analysis. The patterns are reported in

Fig. S8 and confirm that all the reduced samples but AgAlg_CA/AA = ∞ show the distinctive peaks of AgNPs (Fateme et al., 2017). On a qualitative basis, we can observe that the peak related to the (111) reflection ($2\theta = 38^\circ$) broadens as the CA/AA increases, in agreement with the average smaller size of the AgNPs pointed out in SEM micrographs (see Fig. 5). The pattern of AgAlg_CA/AA = ∞ does not show the peaks typical of Ag, likely due to the low amount evidenced by EDX. Interestingly, this sample shows two low intensity peaks at $2\theta = 32.3^\circ$ and 46.3° , which are compatible with both Ag₂O (Fowsiya & Madhumitha, 2019) and NaCl (Qin et al., 2017).

3.4. Alginate-Ag⁺ interaction through FT-IR spectroscopy

The FT-IR spectra of all the prepared fibers are reported in Fig. 6 together with those of Sodium alginate and Alginic acid samples as references.

The full assignment of the spectra, based on literature data (Filipiuk et al., 2005; Papageorgiou et al., 2010), is reported in Table S7, while the assignment of the bands related to the -COO vibrations is reported in Table 2. The analysis of the FT-IR spectra of both AA (Yohannan Panicker et al., 2006) and CA (Bichara et al., 2011) (Fig. S9, Tables S5 and S6 in the Supplementary Material) testifies that the washing procedure completely removes these substances from the polymeric matrix of the fibers. The region between 1750 cm^{-1} and 1350 cm^{-1} provides useful information on the influence of both the crosslinking and the reducing treatment on the properties of the starting polymer backbone. The coordination of Ag⁺ by the carboxylate groups shifts the absorption band related to the asymmetric stretching of -COO⁻ groups [$\nu(\text{COO}_{\text{asym}})$] to lower energies. The coordination does not alter the symmetric -COO⁻ stretching band [$\nu(\text{COO}_{\text{sym}})$] and no other peaks appear/shift in this area. Treating AgAlg with AA alone partially protonates the carboxylate groups as testified by the absorption band at 1726 cm^{-1} in the spectrum of AgAlg_AA. This band is present in the Alginic acid spectrum and becomes more intense when also CA is used for the Ag⁺ reduction (i.e., AgAlg_CA/AA = X samples), reasonably due to the lower pH of the reducing formulations (see Section 2.2.2). The work of Nakamoto allows one to determine the geometry of metal-carboxylate complexes simply by evaluating the difference in energy between the -COO⁻ stretching bands (both the symmetric and the asymmetric) (Nakamoto, 1986). Metal-carboxylate complexes can assume the three different geometries reported in Fig. 6: monodentate, bidentate chelating and bidentate bridging. By using Eq. (2), the values of $\Delta\nu_{\text{Ag}}$ and $\Delta\nu_{\text{Na}}$ were determined

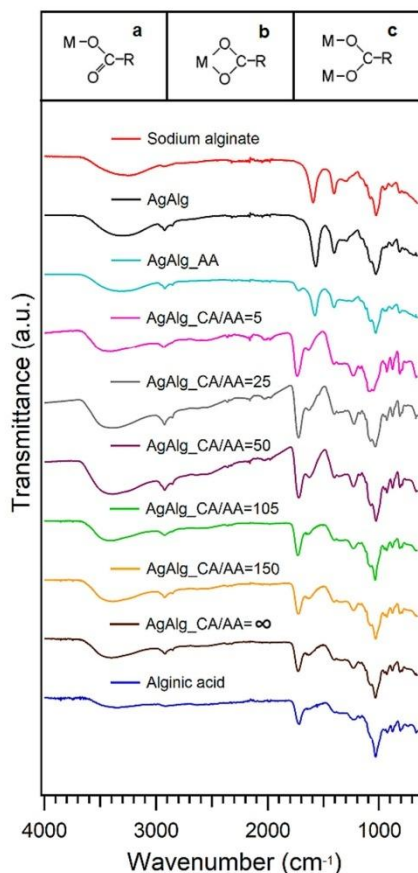


Fig. 6. FT-IR spectra of Sodium alginate (red), AgAlg (black), AgAlg_AA (light blue), AgAlg_CA/AA = 5 (pink), AgAlg_CA/AA = 25 (gray), AgAlg_CA/AA = 50 (purple), AgAlg_CA/AA = 105 (green), AgAlg_CA/AA = 150 (yellow), AgAlg_CA/AA = ∞ (brown) and Alginic acid (blue). The spectra were offset along the y axis for display purposes. In the a, b and c panels on top, the different coordination geometries of the metal-carboxylate complexes: monodentate (a), bidentate chelating (b) and bidentate bridging (c). All the spectra were normalized to the $\nu(\text{CO}) + \delta(\text{CCO}) + \delta(\text{CC})$ band, except for AgAlg_CA/AA = 5 that was normalized to the $\nu(\text{OCO})$ ring band (see Table S7). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and compared. $\Delta\nu_{\text{Ag}}$ values higher, equal or lower than $\Delta\nu_{\text{Na}}$ can be attributed to monodentate, bidentate bridging or bidentate chelating coordination modes, respectively (Nakamoto, 1986).

$$\Delta\nu = \nu_{\text{COO}_{\text{asym}}} - \nu_{\text{COO}_{\text{sym}}} \quad (2)$$

Table 2

Assignment of the FT-IR spectra reported in Fig. 6, in the 1750–1350 cm^{-1} region (Error: $\pm 2 \text{ cm}^{-1}$, instrumental resolution). The complete assignment of the spectra is reported in Table S7.

Sample	$\nu(\text{COOH})$	$\nu(\text{COO})_{\text{asym}}$	$\nu(\text{COO})_{\text{sym}}$
Sodium alginate	/	1594	1405
AgAlg	/	1571	1405
AgAlg_AA	1726	1579	1407
AgAlg_CA/AA = 5	1737	1633	1407
AgAlg_CA/AA = 25	1725	1635	1403
AgAlg_CA/AA = 50	1722	1629	1403
AgAlg_CA/AA = 105	1730	1635	1405
AgAlg_CA/AA = 150	1726	1635	1405
AgAlg_CA/AA = ∞	1728	1635	1405
Alginic acid	1718	1635	1397

In this case, since $\Delta\nu_{\text{Na}} - \Delta\nu_{\text{Ag}} = (23 \pm 4) \text{ cm}^{-1}$, it is possible to assess that alginate coordination of Ag^+ is bidentate chelating. This information is coherent with the inter- and intramolecular coordination geometries proposed by Hassan (Hassan, 1991). In the first case alginate can interact with either two carboxylate groups or one carboxylate and one hydroxyl group of two different alginate chains, forming a planar complex perpendicular to the plain of the polymeric chains. In the second case, silver coordinates the carboxylate groups of two adjacent glycosidic units (Hassan, 1991). Both options imply that a high quantity of silver can be loaded in the alginate matrix in the AgAlg sample. Analogous considerations cannot be drawn for the samples containing reduced silver, in which the shift of the asymmetric -COO^- stretching band to higher energies is probably due to the protonation (see Alginic acid spectrum assignment in Table 2). For the determination of the binding character (in terms of Fraction of Ionic Bonding, FIB) in the Ag-alginate complex of the AgAlg samples, we used Eq. (3), proposed by Chen (Chen et al., 2002):

$$\text{FIB} = \frac{\nu(\text{COOH}) - \nu(\text{COOAg})}{\nu(\text{COOH}) - \nu(\text{COONa})} \quad (3)$$

where $\nu(\text{COOH})$ is the IR absorption frequency of Alginic acid -COOH stretching (classic covalent bond), while $\nu(\text{COOAg})$ and $\nu(\text{COONa})$ are the asymmetric -COO^- stretching frequencies of the Ag^+ -crosslinked samples and Sodium alginate (classic ionic bond), respectively. The obtained FIB value for AgAlg (1.19 ± 0.04) exceeds unity, as a consequence of the lower frequency of the asymmetric stretching in the -COOAg complex with respect to the -COONa one. This phenomenon is attributable to electronic delocalization on the carboxylate groups, due to polarization and electronic retro-donation phenomena that stabilize the complex (Chen et al., 2002). Except for the AgAlg_AA sample (FIB = 1.12 ± 0.04), which is the less protonated sample, all the other reduced AgAlg fibers are characterized by FIB values close to zero, as a consequence of the shift to higher energy experienced by the $\nu(\text{COO}_{\text{asym}})$.

3.5. Thermal properties

The TGA analysis allowed us to rationalize the evidence from the previously discussed techniques, providing precious quantitative insights relatable to both elemental composition and molecular structuration. The TGA curves of the prepared fibers are reported in Fig. 7a, together with the ones of Sodium alginate and Alginic acid reference samples. As clearly shown in Fig. 7a, the weight losses of the samples were compared in 4 significant regions (denoted as Region I, II, III, and IV in Table 3). The equilibration of the samples at the same humidity level (i.e., RH 95 %) allows one to exclude that variations in the degradative profiles might be due to different environmental factors.

The evaluation of the TGA curves up to 130°C provides information on the water amount taken up by the samples due to humidity. The introduction of Ag^+ ions in the alginate matrix clearly hampers its ability to absorb water from the environment: in fact Sodium alginate

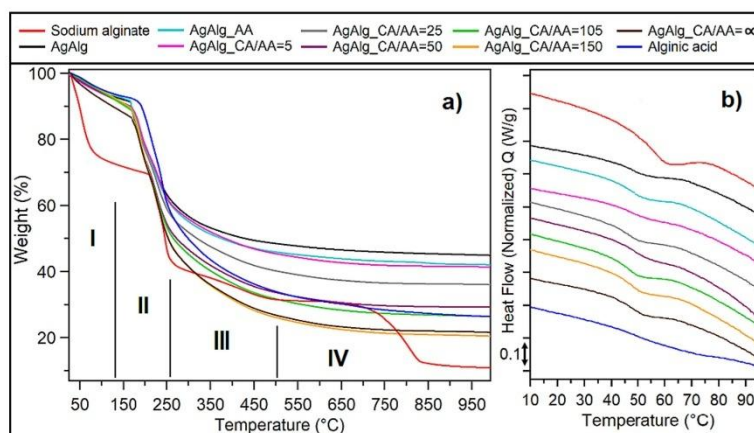


Fig. 7. TGA (a) and DSC (b) thermograms of Sodium alginate (red), AgAlg (black), AgAlg_AA (light blue), AgAlg_CA/AA = 5 (pink), AgAlg_CA/AA = 25 (gray), AgAlg_CA/AA = 50 (purple), AgAlg_CA/AA = 105 (green), AgAlg_CA/AA = 150 (yellow), AgAlg_CA/AA = ∞ (brown) and Alginic acid (blue). TGA thermograms (a): I (RT - 130 °C), II (130 °C - 260 °C), III (RT 260 °C - 505 °C), IV (505 °C - 1000 °C). DSC thermograms are offset for clearness. * TGA samples were equilibrated at RH 95 %, while the DSC ones were dried overnight in a ventilated environment (RH ~ 39 %, room temperature). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

contains about 20 % more water than AgAlg. The reducing treatment does not seem to have a strong impact on the water absorption properties of the Ag⁺-crosslinked samples. This phenomenon can be attributed to the protonation of the polymer chains (highlighted with FT-IR spectroscopy): the acidic reducing agents protonate the carboxylate groups progressively released by Ag⁺ during the formation of the AgNPs, making the samples more similar to Alginic acid, which shows a reduced tendency to interact with environmental humidity with respect to Sodium alginate. Another reason for the poor water vapor absorption properties of the AgNPs-containing samples is the huge amount of silver nanoparticles on the surface (see SEM section) that can act as a barrier towards the uptake of humidity. Probably the two hypotheses co-exist, as suggested by the analysis of the AgAlg_CA/AA = ∞ TGA curve. The latter contains the highest amount of water among all the reduced samples, probably due to the lack of a compact AgNPs coverage (no AA in the reducing formulation, see Table 1) and to the simultaneous protonation of the polymeric network. It is important to clarify that the first degradative event of the polymeric chains occurs in Region II (130 °C - 260 °C) (Ross et al., 2011). The onset of this phenomenon significantly varies as a function of the sample, as clearly shown in Table 3. The introduction of Ag⁺ in the polymeric network strongly reduces thermal stability: the temperature onset of the first degradation event in the AgAlg sample is approximately 45 °C lower than Sodium alginate. This evidence suggests that replacing of Na⁺ with the larger Ag⁺ in the polymeric network increases the distance between the polymer chains, making them more susceptible to decarboxylation. Furthermore, the study of the conductivity of silver-alginate gels suggests that the coordination of silver can decarboxylate alginate in order to reduce Ag⁺ ions, resulting in the production of free radicals (Hassan, 1991). The reduction with the sole AA does not influence the onset, while CA and mixtures of CA and AA produce samples with relatively higher thermal stability than that of AgAlg and AgAlg_AA samples. A homogeneous AgNPs distribution in a polymeric backbone is reportedly capable of stabilizing composites towards thermal degradation (Dash et al., 2021; Vodnik et al., 2009). Qualitatively, the degradation onset of the highly

protonated fibers is smoother and resembles the one of the Alginic acid curve. In Table 3 the characteristic weight losses in specific temperature intervals are reported for each analyzed sample. Above 130 °C, it is useful to evaluate the weight losses normalized for the water content of the samples (Table 3). The weight loss in the 130 °C - 260 °C range is associated with the loss of the carboxylate groups in the form of CO and CO₂ from the polymer backbone (Ross et al., 2011). Fibers experience increasing weight losses (%) as the amount of AA used for the reduction decreases. This trend in the weight losses results in decreasing residues at the end of the thermal ramp (1000 °C, see Table 4) and can be attributed to the progressively reduced amount of silver in the samples highlighted performing TGA measurements in air on the same samples (see Fig. S10 and Table S8). Due to the absence of residue in the Alginic acid sample, it is possible to state that the residue at the end of the heating ramp is only due to the silver present in the samples. AgAlg is, as expected, the sample with the highest silver content (36.2 w/w % of the dried sample, Table 4). This result is particularly relevant since it indicates that the fiber obtained through the wet spinning approach contains 1 Ag⁺ ion per monomeric unit of the alginate backbone, suggesting that only the bidentate chelating interaction between Ag⁺ and carboxylate groups (elucidated by FT-IR Spectroscopy) is strong enough to maintain the inorganic species in the hydrogel through the washing cycles. This aspect is particularly interesting since it enables us to predict the amount of Ag⁺ ions that can be loaded in the fibers as a function of the monomeric units present. It is interesting to note that an increasing amount of AA in the reducing formulation leads to an increase in the amount of silver in the fibers. The metal content is negligible in the case of AgAlg_CA/AA = 105, AgAlg_CA/AA = 150 and AgAlg_CA/AA = ∞ samples: this evidence suggests that a faster reduction implies a more efficient trapping of silver (in the form of AgNPs) in the polymeric network. AgAlg_AA is not coherent with the highlighted trend: this is probably due to the huge amount of silver quickly formed on the surface, which can easily be lost during the washing steps. The results also confirm that the protonation (highlighted through FT-IR Spectroscopy and forming the water insoluble alginic acid) is useful to preserve the

Table 3

TGA weight losses for the samples illustrated in Fig. 7a. Region I (RT - 130 °C), Region II (130 °C - 260 °C), Region III (RT 260 °C - 505 °C), Region IV (505 °C - 1000 °C). Data normalized for the water content of the samples are also reported (Norm. weight loss (%)). The error on the Weight loss associated with each sample never exceeds 1.0 %.

Sample	Region	Weight loss (%)	Norm. weight loss (%)	Onset I polymeric degradation
Sodium alginate	I	27.5	0	
	II	29.2	40.3	212.1 °C
	III	11.9	16.4	
	IV	20.5	28.3	
AgAlg	I	7.2	0	
	II	31.3	33.7	166.4 °C
	III	13.1	14.1	
	IV	3.5	3.7	
AgAlg AA	I	6.6	0	
	II	33.3	35.7	166.0 °C
	III	14.3	15.3	
	IV	3.8	4.1	
AgAlg CA/AA = 5	I	7.9	0	
	II	31.7	34.4	170.4 °C
	III	15.1	16.4	
	IV	3.9	4.2	
AgAlg CA/AA = 25	I	7.9	0	
	II	35.3	38.3	169.5 °C
	III	16.8	18.2	
	IV	4.0	4.3	
AgAlg CA/AA = 50	I	8.1	0	
	II	39.8	43.3	169.3 °C
	III	18.6	20.2	
	IV	4.3	4.7	
AgAlg CA/AA = 105	I	8.1	0	
	II	40.9	44.5	171.8 °C
	III	19.5	21.2	
	IV	5.2	5.7	
AgAlg CA/AA = 150	I	7.6	0	
	II	44.2	47.8	169.0 °C
	III	22.3	24.1	
	IV	5.4	5.8	
AgAlg CA/AA = ∞	I	10.5	0	
	II	41.4	46.3	168.7 °C
	III	21.5	24.0	
	IV	5.0	5.6	
Alginate acid	I	6.4	0	
	II	36.2	38.7	187.5 °C
	III	23.7	25.3	
	IV	7.3	7.8	

filiform structure when Ag^+ abandons the coordination sites. The weight losses in the 260 °C - 1000 °C range (i.e. Region III and IV in Table 3, mainly connected to the degradation of the polymeric component) are similar for all the samples, except for Sodium alginate. In this case heating the sample produces Na_2CO_3 that decomposes to NaO and CO_2 around 700 °C (Soares et al., 2004).

The DSC thermograms of the analyzed samples are illustrated in Fig. 7b, while the evaluated glass transition temperatures (T_g) are reported in Table 4. All the samples were dried overnight in a ventilated environment (RH ~ 39 %, room temperature). The analysis on the AgAlg sample highlighted that the crosslinking process induces a shift (from 53.6 °C to 47.6 °C) of the T_g to lower temperatures. The higher dimension of Ag^+ with respect to Na^+ likely reduces the organization of the polymer chains, increasing their mobility. The different reducing treatments do not influence the glass transition temperature which remains comparable to the AgAlg sample, although the Alginate acid reference sample shows a T_g at higher temperature (50.2 °C). This phenomenon, considering the amount of silver in the samples, suggests that only the Ag^+ -mediated crosslinking step alters the polymer chains mobility.

Table 4

Silver content (TGA under air flux, Fig. S10 and Table S8), degradative highlights (TGA under nitrogen flux, Fig. 7a and Table 3) and DSC (Fig. 7b) evaluation for the investigated samples. The error associated with each TGA value reported never exceeds 1.0 %.

Sample	Ag (w/w %)	Norm. Residue at 1000 °C (TGA)	T_g (DSC)
Sodium alginate	/	15.0 %	(53.6 ± 0.5) °C
AgAlg	36.2	48.5 %	(47.6 ± 0.8) °C
AgAlg AA	24.7	44.9 %	(46.2 ± 0.5) °C
AgAlg CA/AA = 5	27.3	45.0 %	(47.2 ± 0.4) °C
AgAlg CA/AA = 25	21.3	39.2 %	(46.8 ± 0.4) °C
AgAlg CA/AA = 50	13.3	31.8 %	(47.4 ± 0.5) °C
AgAlg CA/AA = 105	~ 0	28.6 %	(46.3 ± 1.0) °C
AgAlg CA/AA = 150	~ 0	22.3 %	(47.6 ± 0.6) °C
AgAlg CA/AA = ∞	~ 0	24.1 %	(47.2 ± 0.4) °C
Alginate acid	/	26.4 %	(50.2 ± 0.6) °C

3.6. Silver release and mechanical properties evaluation

In the view of a possible application of the fibers in water purification systems, silver release experiments were performed (see Section 2.4 for details). The results of the ICP-OES analysis reported in Table 5 highlighted that AgAlg is the sample with the highest silver release over 24 h (i.e. ~ 9 μg of Ag^+ / mg of fiber). The reduction strongly reduces the amount of silver released in water by the samples (especially when both CA and AA are used), suggesting that this property can be tailored as a function of the preparation. It is interesting to note that, irrespectively of the total amount of silver in the samples (see Table 4), samples from CA/AA = 25 to CA/AA = ∞ show similar values of released Ag^+ : this evidence suggests that the release of cations is mostly attributable to the silver-based structures present on the surface. The latter are still present on the surface after 24 h in water, as illustrated from the FE-SEM micrographs in Fig. S11. It is worth mentioning that the effectiveness of Ag^+ against bacteria was already proved for low silver concentrations (~ 0.08 mg/mL (Nawaz et al., 2012)), while the upper limit for the silver

Table 5

Silver release and mechanical properties (see Fig. S14) of the fibers. The release experiment was carried out in triplicate (mean ± SD), whereas the mechanical properties results are the average ± SD resulting from four replicated experiments. The Young's modulus (GPa) was evaluated for strain values between 0 and 0.01 for all the samples.

Sample	Ag^+ rel. / mg of fiber (μg)	Young's modulus (GPa)	Ultimate tensile strength (MPa)
AgAlg	9.05 ± 0.28	5.60 ± 0.36	108.9 ± 0.6
AgAlg AA	1.47 ± 0.02	3.57 ± 0.47	61.2 ± 3.4
AgAlg CA/AA = 5	0.39 ± 0.01	3.77 ± 0.19	86.5 ± 3.6
AgAlg CA/AA = 25	0.82 ± 0.01	3.36 ± 0.51	82.4 ± 2.5
AgAlg CA/AA = 50	0.73 ± 0.01	2.96 ± 0.05	68.5 ± 2.0
AgAlg CA/AA = 105	0.77 ± 0.01	3.01 ± 0.33	64.4 ± 3.5
AgAlg CA/AA = 150	0.71 ± 0.01	2.17 ± 0.38	72.1 ± 3.4
AgAlg CA/AA = ∞	0.61 ± 0.01	3.42 ± 0.24	80.1 ± 1.1

content in drinking water set by US-EPA is equal to 0.1 mg/mL): the ability to control the release of silver from the composite matrix is crucial to satisfy law requirements without losing functionality. It is also important to remark that at the end of the release experiment all the fibers preserved their integrity (see Fig. S12). To further inspect the stability against dissolution of the AgAlg sample, we carried out an experiment to monitor its weight loss as a function of the incubation time. This test, which is useful in view of an application of AgAlg fibers in which the materials should be maintained in contact with aqueous media, can also give insights into the stability of the Ag⁺-alginate complex. As described in Section 2.5, the weight change of the fiber was monitored in time up to 14 days (see Fig. S13), demonstrating an excellent stability against dissolution of the material (weight loss after 14 days: ~1 %).

Traction tests were also performed to characterize the mechanical properties of the fibers and the collected stress vs strain curves are reported in Fig. S14. AgAlg possesses the highest Young's modulus (*i.e.* ~5.60 GPa) and Ultimate tensile strength (*i.e.* ~108.9 MPa) among the analyzed samples (see Table 5), suggesting that the reduction increases the rigidity of the fibers, making them more brittle. All the reduced fibers are similar in terms of both Young's modulus and Ultimate tensile strength (see Table 5). It is interesting to note that AgAlg-AA is characterized by the shortest plastic deformation region that extends up to a maximum strain value of about 0.04. The protonation of the network experienced by the other reduced samples (highlighted through FT-IR spectroscopy, see Section 3.4), might be beneficial to maintain a certain plasticity after the Ag⁺ removal from the silver-carboxylate complex.

4. Conclusions

In this work we demonstrated that the interaction between alginate and Ag⁺ cations can be profitably exploited for the production of complex-shaped hydrogel structures such as fibers. The Ag⁺-alginate interaction is commonly neglected by the scientific community, due to the poor bibliography regarding this topic and to the large variety of multivalent cations that can be chosen for the preparation of multi shaped hydrogels. Nevertheless, silver possesses unique antimicrobial properties that make it particularly attractive. The wet spinning approach for the preparation of Ag⁺-crosslinked alginate fibers here reported, although simple and capable of maximizing the quantity of loaded silver, is unprecedented in the literature due to the “weak” interaction between Ag⁺ and alginate that strongly reduces the chances of success. However, we proved that the optimization of a few experimental parameters enabled us to reach our goal.

We took advantage of the “weak” Ag⁺-alginate interaction to decorate the polymeric fibers with AgNPs, which were obtained from the reduction of Ag⁺ ions with a mild reducing agent, *i.e.* lemon juice-mimicking AA and CA solutions. We demonstrated that both the aforementioned molecules act as reducing agents and that peculiar properties can be imparted to the fibers varying the CA/AA ratio. Specifically, SEM analysis highlighted that increasing amounts of AA lead to an increase in the silver nanostructure density on the fibers surface. The observation of the color variation during the process also highlighted that higher amounts of AA lead to a faster reduction of the Ag⁺ ions. FT-IR spectroscopy allowed us to determine a bidentate chelating coordination mode for the carboxylate group in the Ag⁺-crosslinked fibers and to follow the impact of preparation steps on the polymeric structure. The use of CA clearly promotes the protonation of the polymeric chains, strongly influencing the properties of the fibers. Thermogravimetric analysis highlighted that the introduction of silver in the network reduces the thermal stability, while the reduction leads to a slight increase of the latter. Furthermore this characterization unraveled the amount of silver contained in each sample, proving that it can be easily varied as a function of the amount of AA used. Also water absorption properties proved to be tunable as a function of the CA/AA ratio: the obtained

swelling curves for AgNPs-containing samples indicate that the obtained fibers can be classified as super absorbents. It is worth mentioning that our preparation minimizes the number of steps required for the obtainment of the composite material. The latter is one of the many *Principles of Green Chemistry* respected by our preparation. Among them the use of reagents from renewable sources (alginate from algae, AA and CA from fruit) and the low energy consumption (only the extrusion step requires electricity) are undoubtedly fulfilled. These aspects, added to the biocompatibility and biodegradability of the used materials, suggest a promising future of such fibers in many fields, such as wound healing or in water/air purification processes.

CRedit authorship contribution statement

Pietro Tordini: Investigation, Formal analysis, Writing – original draft. **Rita Gelli:** Investigation, Formal analysis, Writing – original draft. **Francesca Ridi:** Conceptualization, Supervision, Writing – review & editing. **Massimo Bonini:** Conceptualization, Supervision, Writing – review & editing, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbpol.2023.121586>.

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Alginate crosslinking beyond calcium: Unlocking the potential of a range of divalent cations for fiber formation

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ABSTRACT

Alginate is a promising biopolymer for functional materials' preparation due to its biocompatibility, biodegradability, and high reactivity with metal cations. This study aims to advance the understanding of the crosslinking dynamics of alginate hydrogels, with the hypothesis of developing a reliable wet spinning method for preparing tunable alginate fibers crosslinked not only with Ca^{2+} , but also with Sr^{2+} , Ba^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} . We optimized multiple parameters to successfully produce fibers with consistent cross-sections and lengths of up to several meters. Our findings show that the type of crosslinker significantly affects the fibers' morphology, water absorption, and mechanical properties. Notably, fibers exhibited high Young's Modulus and ultimate tensile strength. Small angle X-ray scattering analysis revealed correlations between the polymer chain organization and the metal ion affinity, impacting swelling capacity and thermal stability. This comprehensive comparison of M^{2+} -crosslinked alginate fibers, ensured by consistent preparation conditions, fills a gap in the literature. Our results highlight the tunability of these fibers' properties, making them suitable for applications such as wound healing, water purification, and flame retardancy.

1. Introduction

The shift towards sustainable industrial practices is driving innovation in the use of biopolymers for functional materials. Among biopolymers, polysaccharides stand out due to their abundance, cost-effectiveness, and adaptability for applications in medicine, food, and environmental remediation. Alginate, discovered by E.C.C. Stanford in 1881 [1,2], is a highly versatile anionic polysaccharide due to its biocompatibility, biodegradability, and ability to interact with various metal cations. The unique structure of (1,4)-linked β -D-Mannuronate (M) and α -L-Guluronate (G) blocks [3–6], allows alginate to selectively coordinate metal cations across multiple oxidation states [7–10], with both hydroxyl and carboxylate groups on its backbone playing key roles in the formation of crosslinked hydrogel structures with distinct porosities and mechanical properties.

In particular, the G blocks are considered the preferential binding sites for metal cations [11,12], making the M/G ratio and residue sequence critical to the final product's properties. Among the various divalent cations that interact with alginate, those from both alkaline earth and transition metal families are the most extensively studied for their role in forming crosslinked structures [13]. Alginate's polymeric

chains have a unique ability to bind divalent cations, forming intricate complexes that can be either intermolecular or intramolecular. Brus et al.'s NMR (Nuclear Magnetic Resonance) studies revealed that the structure of these complexes can adapt according to the size of the ion, becoming progressively less regular as ion size decreases [14]. Additionally, kinetic and equilibrium studies on ionic exchange reveal a hierarchy in ion affinity, ranked from highest to lowest as follows [15–17]: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Co}^{2+} \approx \text{Ni}^{2+} \approx \text{Zn}^{2+} > \text{Mn}^{2+}$. This selective binding behavior underscores alginate's versatility in coordinating with a broad spectrum of metal ions, each imparting distinct structural and functional characteristics. Such diversity enables the creation of functional materials tailored for applications in fields like environmental remediation, biomedicine, and sensing technologies where specific ion interactions are crucial [18–20].

Calcium ions have been studied in depth for their strong affinity to guluronate residues, forming structures stabilized by ionic interactions or egg box junctions [21], a concept first introduced by Grant et al. for Ca^{2+} -crosslinking [22]. Larger ions like strontium and barium further expand the binding landscape by creating more interaction sites [23,24], with barium producing some of the most stable hydrogels among the alkaline-earth metals due to its ability to crosslink both

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gulonate and mannuronate sections [24]. Notably, Mn^{2+} also displays similar behavior: as Enmerichs et al. showed, the ribbon-like structure of poly-mannuronate sections interacts with C-6 and C-5 carbons, while poly-gulonate sections bind Mn^{2+} ions at C-6, C-5, and C-1, resulting in deeper integration of the cation [25]. Zinc and copper, by contrast, show low selectivity in binding sites, forming networks with dense crosslinking [26,27]. Copper binding, however, adds a fascinating complexity: absorption studies indicate that the classic egg box model holds at low Cu^{2+} concentrations, whereas at higher concentrations binding sites on the alginate backbone reduce to one or two [28]. Furthermore, small angle X-ray scattering (SAXS) analysis of copper-induced sol-gel transitions reveals that copper ions prefer a less selective binding pattern than the traditional egg box structure [29]. Each metal ion brings unique properties to the table; for instance, Cu^{2+} and Zn^{2+} enable applications like antimicrobial and flame-retardant materials, respectively [30,31], showcasing alginate's potential for customized applications across diverse fields.

Despite the expanding interest in biopolymers for sustainable solutions, most studies on alginate crosslinking have focused predominantly on calcium, often overlooking the potential of other metal ions. Additionally, while shaping alginate into fibers offers numerous application possibilities, a thorough examination of these fibers' physicochemical properties as a function of the different crosslinking cations remains limited. In this study, we aimed to fill this gap by systematically investigating how divalent cations (Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+}) influence the structural, thermal, mechanical, and water absorption properties of alginate fibers.

We hypothesized that the choice of divalent cation used for crosslinking significantly affects these properties due to varying ionic affinities and binding mechanisms. By correlating macroscopic properties with molecular interactions using techniques such as SAXS, FT-IR (Fourier Transform – Infrared Spectroscopy), and thermal analysis, we demonstrate the tunability of alginate fibers. These findings offer valuable insights into M^{2+} -alginate interactions, using a preparation method that ensures radially symmetric crosslinking and homogeneity across the length of hydrogel specimens. The choice of alginate fibers provides a dual advantage: they are ideal for applications due to their aspect-ratio, high surface area, and versatility, while also serving as a unique model system. Radial symmetry enables precise investigation of the dynamics and spatial evolution of crosslinking, making fibers a platform for advancing the understanding of crosslinking processes in material science. Ultimately, this study simplifies and expands the design of alginate-based fibers with potential applications in wound healing, water purification, and flame retardancy.

2. Materials and methods

2.1. Materials

Alginic acid sodium salt (product number 180947; Mannuronate/Gulonate = 1.50 ± 0.04 , determined through FT-IR spectroscopy, Molecular weight ≈ 132 kDa, determined through viscosimetric analysis, as previously characterized by our group [32]) and Alginic acid (HAlg) from brown algae (product number 1003449856) were provided by Sigma Aldrich. $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (purity $>99\%$) was obtained from Riedel-de Haën, while CaCl_2 (purity $\geq 98\%$) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (purity $\geq 99\%$) were purchased from Sigma Aldrich. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (purity $\geq 99\%$) was provided by Fluka, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (purity $\geq 99\%$) by Carlo Erba and ZnCl_2 (purity $>98\%$) by Merck. Sodium alginate and MCl_2 solutions ($\text{M} = \text{cation}$) were prepared with deionized water. Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA, purity $>99\%$), Sodium hydroxide (NaOH, purity $\geq 98\%$) and Rhodamine 6G (purity $>99\%$) were purchased from Sigma Aldrich. All reagents were used without any further purification.

2.2. Preparation of crosslinked alginate fibers

A 4 % w/v sodium alginate aqueous solution was prepared by dissolving the polymer under magnetic stirring for approximately 40 min at room temperature. The solution was transferred into a 10 mL plastic syringe and extruded through a needle (inner diameter: 0.9 mm) in 50 mL of a 0.5 M aqueous solution of MCl_2 ($\text{M} = \text{Ca, Sr, Ba, Mn, Cu, Zn}$, see Fig. 1a). The extrusion process was carried out by means of a HYREL 3D Engine SR injection 3D printer (Norcross, GA, United States), equipped with a SDS-10 print head with an electric motor (model LDO-28STH51-0674A). The extrusion flux was set to 5.76 mL/min. For each batch, about 4.8 mL of polymeric solution were extruded, resulting in a M^{2+} -alginate fiber ~ 2.5 m long. The hydrogel fiber was kept in the crosslinking bath for 1.5 h and then washed with deionized water (5 mL/cm of fiber) during 1.5 h, to remove the loosely bound metal cation. The appearance of the fibers in the wet state is shown in Fig. 1b. To obtain dry fibers and prevent curling, samples were laid down on a polycarbonate support and kept overnight at a constant relative humidity (RH 39%). The fibers' ends were fixed to the support using weights of 20 g. The humidity level was carefully monitored with a hygrometer, and the drying process was carried out until the fibers reached a constant weight, indicating equilibrium moisture content under the controlled conditions. In the rest of the paper these fibers will be referred to as dry fibers.

2.3. Characterization techniques

2.3.1. Measurement of the fibers diameter

The diameter of the dry fibers was measured taking images of the samples by means of a USB digital microscope (Park Systems, Suwon, South Korea). For each image, 20 measurements of the diameter were collected along the fiber, and the results are given as average $\pm$ standard deviation.

2.3.2. Field emission-scanning electron microscopy (FE-SEM)

Field Emission-Scanning Electron Microscopy (FE-SEM) was carried out with a Zeiss Σ IGMA FE-SEM (Oberkochen, Germany). Samples prepared as described in 2.2 were freeze-dried when in the wet state, immediately after the washing step. In order to expose the cross-section of the freeze-dried fibers, the samples were immersed in liquid nitrogen for 10 s and fractured. The fibers were placed over aluminum stubs by means of conductive tape and the imaging was conducted by tilting the sample stage at 90° , in order to image the fracture surface of the fiber. The micrographs were collected at an accelerating voltage of 2 kV, a sample-detector distance 4–6 mm, an aperture of 10 μm and using the secondary electron detector.

2.3.3. Small angle X-ray scattering (SAXS)

All small-angle X-ray scattering measurements were performed using a Xeuss 3HR system (Xenocs, Grenoble, France) equipped with a hybrid detector (Eiger 1 M, Dectris, Baden-Dättwil, Switzerland) comprising 1028×1062 pixels which are $75 \times 75 \mu\text{m}^2$ in size. Co K α radiation with a wavelength (λ) of 1.542 Å at a power of 30 W was obtained using an ultra-bright point microfocus X-ray source (GENIX-Fox 3D, Xenocs, Grenoble, France). Two sample-to-detector distances (370 mm and 1800 mm, calibrated using silver behenate) provided a measurable q -range between 0.0006 Å^{-1} and 0.5 Å^{-1} (where q , the scattering vector, is given by $q = 4\pi/\lambda \sin\theta$, and 2θ is the scattering angle). Data analysis was performed using SasView software (<http://www.sasview.org/>).

2.3.4. Inductively coupled plasma-atomic emission spectrometry (ICP-AES)

The amount of Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} in the M^{2+} -crosslinked alginate fibers (CaAlg , SrAlg , BaAlg , MnAlg , CuAlg and ZnAlg respectively) was determined by means of an Agilent 720-ES Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Santa Clara, CA, United States) equipped with a pneumatic nebulizer

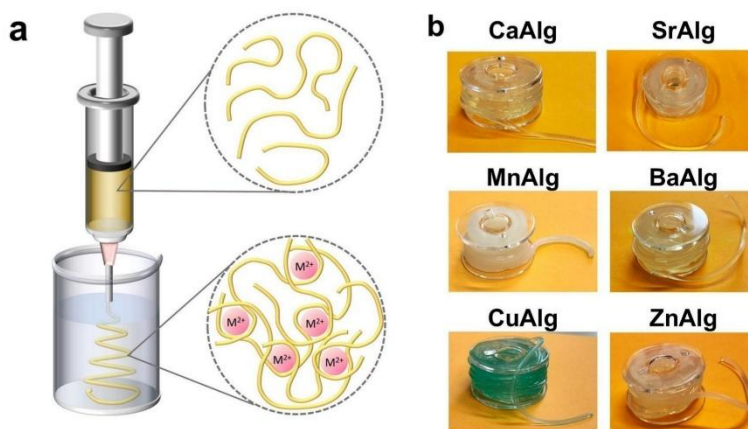


Fig. 1. a) Sketch of the extrusion process: the solution in the syringe is alginate 4 % w/v in water, while the beaker contains MCl_2 0.5 M aqueous solution ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Mn}, \text{Cu}, \text{Zn}$). b) Photos of the samples in the wet state curled around bobbin coils.

and a cyclonic spray chamber. Approximately 10 mg of each sample was kept in 2 mL of a Na_2EDTA 0.05 M + NaOH 10 % (w/v) water solution (20 mL and 1.5 mL respectively) for 1 h at 100 °C, under magnetic stirring. After dissolution, 10 mL of MilliQ water was added in each sample. The calibration lines were obtained by preparing the standard solutions starting from commercial standards certified at 1000 ppm. Calcium, strontium, barium, manganese, copper and zinc absorbance were evaluated at 396.847 nm, 421.552 nm, 455.403 nm, 257.610 nm, 324.754 nm and 202.548 nm respectively. After each measurement, the system was washed with a 2 % HNO_3 solution.

2.3.5. Fourier transform - infrared spectroscopy (FT-IR)

FT-IR spectra were acquired in ATR (Attenuated Total Reflectance) mode with a Thermo Nicolet Nexus 870 FT-IR spectrophotometer (Thermo Fisher Scientific, Waltham, MA, United States) equipped with a Golden Gate accessory. The dried fibers were cut in small pieces and placed on the sample holder. All the spectra were recorded with a resolution of 2 cm^{-1} , averaging 128 scans for measurement, in the range $4000\text{--}650 \text{ cm}^{-1}$.

2.3.6. Thermogravimetric analysis (TGA)

TGA was carried out with a Discovery SDT650 from TA Instruments (New Castle, DE, United States). Dried fibers were cut and placed in alumina pans and the weight and heat flux were measured during a heating ramp ($10^\circ\text{C}/\text{min}$) from room temperature (RT) to 950°C , under N_2 flux (100 mL/min). Data were analyzed with Trios v5.1.1.46572 software (TA Instruments, New Castle, DE, United States). Samples were equilibrated at RH = 95 % prior to the measurement.

2.3.7. Differential scanning calorimetry (DSC)

DSC analysis was carried out by means of Discovery DSC 2500 (TA Instruments, New Castle, DE, United States). Tzero Aluminum Hermetic pan (TA Instruments, New Castle, DE, United States) were used for all the measurements. Samples were analyzed by applying a heating ramp from -10°C to 120°C , with a heating rate of $20^\circ\text{C}/\text{min}$. Two heating cycles were performed, separated by a cooling cycle from 120°C to -10°C at the same rate. Data were analyzed with Trios v5.1.1.46572

software (TA Instruments, New Castle, DE, United States). Samples were equilibrated at RH = 95 % prior to the measurement.

2.3.8. Mechanical properties

The tensile properties of the dried fibers were determined by means of a Discovery DHR-3 rheometer (TA Instruments). The fibers were fixed to a paper support using bicomponent glue and then clamped [33,34], applying a clamping force equal to 30 cN·m. Traction tests were performed at $10 \mu\text{m}/\text{s}$ extension rate. Measurements were carried out in triplicate and the data were analyzed using Trios v5.1.1.46572 software (TA Instruments). Young's Modulus and Ultimate tensile strength were extracted from the curves, and the average $\pm$ standard deviations for each sample are reported.

2.3.9. Swelling experiments

The swelling properties of the fibers were assessed by immersing 20 cm of a pre-weighed dry fiber in 200 mL of deionized H_2O . The sample was weighed at regular time intervals by taking it out from the fluid and removing the excess water by placing it on a paper towel. The experiments were interrupted when a constant weight was achieved.

2.4. Rhodamine 6G uptake

To assess the potential of our alginate fibers in the field of water remediation, the rhodamine 6G (one of the most commonly used dyes in the textile, plastic, and cosmetic industries [35]) uptake from the fibers was evaluated by incubating 15 cm of dry fiber in 3 mL of a $5 \mu\text{M}$ aqueous solution of rhodamine 6G, at room temperature. After 10 h (with the maximum swelling capacity already reached) the sample was removed from the medium, which was analyzed by means of UV-vis spectroscopy to quantify the rhodamine 6G left in the solution. The spectra were collected using an Agilent Cary 3500 spectrophotometer (Santa Clara, CA, United States) in the $300\text{--}800 \text{ nm}$ range, using plastic cuvettes with 1 cm path length. The calibration curve for rhodamine 6G in water is reported in Fig. S1.

3. Results and discussion

3.1. Morphological analysis of the fibers

The extrusion of sodium alginate in aqueous solutions of all the investigated metal cations (Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+}) readily forms long hydrogel fibers, as shown in the photos in Fig. 1b. The diameter of these fibers, as measured by optical microscopy, ranges from 0.96 ± 0.01 mm for CuAlg to 1.5 ± 0.1 mm for MnAlg (see Fig. 2, Fig. S2 and Table S1 in the Supplementary Material). These results indicate significant differences in how cations influence the extrusion process: in fact, the diameter of the hydrogel fibers (*i.e.*, wet samples in Fig. 2) is the result of the counterbalance between the size of the needle (which represents the starting diameter in the extrusion process, *i.e.*, 900 μm), the swelling tendency of alginate in water (pushing towards an increase in the diameter of the fiber) and the counter-effect resulting from the crosslinking produced by the cation (confining alginate through the formation of an insoluble fiber). Among the tested cations, Cu^{2+} produces the smallest and most regular fibers, with an average diameter fairly close to the size of the needle and a very small standard deviation. In contrast, Ca^{2+} , Sr^{2+} , and Ba^{2+} produce somewhat larger fibers, slightly exceeding 1 mm in size. A greater effect is observed with Zn^{2+} and, even more pronouncedly, with Mn^{2+} (fibers diameter about 1.3 and 1.5 mm, respectively).

In the dry state, all the fibers but MnAlg maintain a cylindrical shape and decrease their diameter by a factor of 4 to 5. MnAlg behaves differently, resembling a 2D stripe rather than a 1D cylinder, with a width of 1.0 ± 0.1 mm and a thickness of 0.09 ± 0.01 mm. To compare these values with the other fibers, one could consider the equivalent diameter of a cylinder with the same cross-section area of the stripe, which would correspond to 0.167 ± 0.015 mm.

The dramatic decrease of the fibers size upon drying, as well as the different starting diameters of the hydrogel fibers, suggests a highly porous inner structure of the fibers, with significant differences as a function of the cation. To investigate this porosity and internal morphology, FE-SEM imaging was conducted. The use of a field emission source allows for direct imaging of the cross-sectional fracture surfaces of freeze-dried fibers without the need of a metallization step, providing detailed visualization of the hydrogel internal structure by imaging the corresponding xerogel [36,37]. The results (see Fig. 3 and Fig. S3) reveal a layered structure in all samples, except for MnAlg, which exhibits a three-dimensional network with polygonal voids. This

difference clearly explains the distinct behavior of MnAlg compared to the other cations; moreover, FE-SEM results suggest that different cations correspond to different crosslinking mechanisms, leading to variations in morphology and functional properties. To further understand these alginate-cation interactions and the crosslinking mechanisms, the fibers were characterized using a multi-technique and multi-scale approach.

3.2. M^{2+} -alginate interaction

ICP-AES provides valuable insights for interpreting and modeling the data obtained from the various characterizations in this study. Due to the high concentration of the crosslinking bath, it is assumed that each fiber contains the maximum possible amount of M^{2+} ions relative to the used 4 % w/v concentration. As shown in Table 1, ICP-AES revealed that approximately one M^{2+} ion per two glycosidic units is incorporated into the polymeric network. In general, the amount of ions retained in a polymer matrix is expected to result from an interplay between the ion's size and its affinity for the polymer backbone. In our case, Cu^{2+} and Zn^{2+} ions, which have different affinities but similar sizes, are present in equal amounts in the CuAlg and ZnAlg samples. This observation suggests that size is the dominant factor in determining the maximum loadable amount of M^{2+} species (see Table 1). This trend is also observed with the alkaline earth metals (*i.e.*, Ca^{2+} , Sr^{2+} , and Ba^{2+}), where the loaded cation amount decreases as ion size increases. Notably, MnAlg contains the lowest amount of M^{2+} ions, despite manganese's moderate ionic radius. This may account for the poor structural integrity of MnAlg and is likely due to the poor affinity for alginate chains.

Leveraging SAXS, we identified the role of the different crosslinking ions in the polymer chains' assembly at the nanoscale. The scattering curves of the MAlg samples are illustrated in Fig. 4a. Given the similar ion content across all samples, the results obtained from SAXS are only ascribable to the ionic distribution in the hydrogel network.

Among the examined hydrogels, MnAlg exhibits the strongest scattering intensity, resulting in its curve reaching the lowest q value. Most samples show two relative maxima in the scattering profile, indicative of multiple characteristic lengths in the polymer chains distribution. To fit the data - keeping into account this multiscale assembly - we used the following double Lorentzian function:

$$I(q) = A/[1 + (q\xi_1)^n] + B/[1 + (q\xi_2)^m] + bkg \quad (1)$$

in which B is the background, A and C are the two Lorentzian scale factors (LSF1 and LSF2 in Table S2), ξ_1 and ξ_2 are the respective correlation lengths, and n and m are the corresponding power law exponents (PLE1 and PLE2 in Table S2). The extracted "long distance" (ξ_1) and "short distance" (ξ_2) correlation lengths are reported in Table 1.

This model is visualized in Fig. 4b, depicting two levels of organization. The short distance correlation lengths (ξ_2) can be ordered as follows, ranging from 2.6 to 6.1 nm: $\text{ZnAlg} > \text{CaAlg} \approx \text{SrAlg} > \text{CuAlg} \approx \text{BaAlg} > \text{MnAlg}$. Interestingly, cations that strongly interact with alginate (*i.e.*, Cu^{2+} and Ba^{2+}) produce the shortest ξ_2 values (~ 2.6 nm). Ca^{2+} and Zn^{2+} show intermediate values around 4.0 nm, while for Mn^{2+} it is not even possible to define ξ_2 . The weak nature of the Mn^{2+} -alginate interaction is clearly responsible for the lack of organization at shorter length scales. The "long distance" correlation (ξ_1) of MnAlg, on the other hand, is the largest among the examined MAlg samples (~ 58 nm) indicating poor interconnection between polymer chains and resulting in a particularly soft hydrogel matrix. All the other samples show correlation lengths in the 24–48 nm range, with the transition metal ions showing larger ξ_1 values with respect to alkaline earth cations.

FT-IR spectroscopy is a proven tool for studying the interaction between alginate carboxylate groups and cations [32,34]; in this study, the technique was used to shed light on the relationship between the molecular interactions and the structure of the obtained fibers. The recorded spectra, offset for clarity, are illustrated in Fig. 5. The full

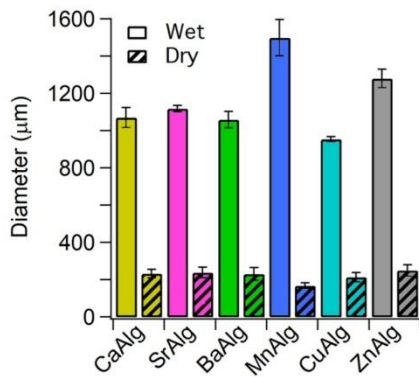


Fig. 2. Size of the alginate fibers prior (wet) and post (dry) dehydration.

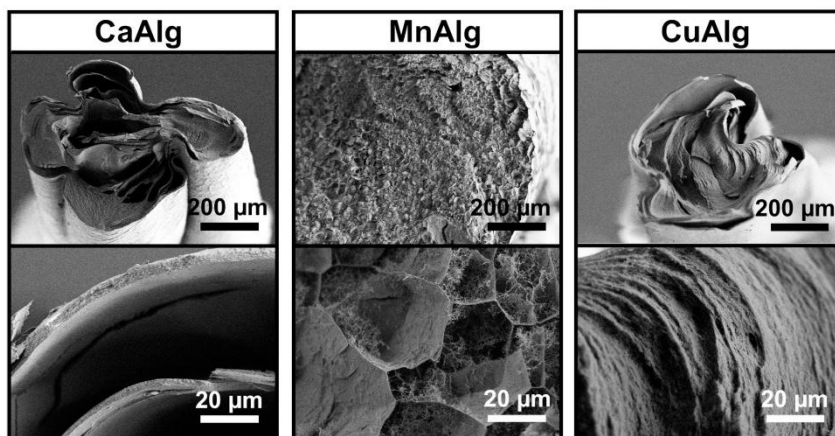


Fig. 3. FE-SEM micrographs of representative freeze-dried samples (cross-sections) at two different magnifications.

Table 1

Results of the ICP-AES analysis of CaAlg, SrAlg, BaAlg, MnAlg, CuAlg and ZnAlg samples, ionic radii of the crosslinking M^{2+} ions (octahedral coordination geometry, literature data [38]) and related correlation lengths (ξ_1 and ξ_2) extracted by SAXS. The full set of parameters obtained from SAXS fitting is reported in Table S2.

Sample	M^{2+} (w/w %)	nAGU ^a / nM ²⁺	M^{2+} ionic radius (Å)	ξ_1 (nm)	ξ_2 (nm)
CaAlg	9.02 ± 0.1	2.09 ± 0.03	1.00	24.8 ± 1.2	4.2 ± 0.2
SrAlg	16.8 ± 0.2	2.25 ± 0.03	1.18	31.8 ± 1.6	3.8 ± 0.2
BaAlg	23.7 ± 0.3	2.30 ± 0.03	1.35	33.0 ± 1.7	2.6 ± 0.2
MnAlg	10.7 ± 0.1	2.37 ± 0.03	0.83	57.8 ± 2.9	–
CuAlg	13.6 ± 0.2	2.09 ± 0.03	0.73	48.1 ± 2.4	2.7 ± 0.2
ZnAlg	13.6 ± 0.2	2.16 ± 0.03	0.74	39.5 ± 2.0	6.1 ± 0.3

^a AGU stands for anhydroglycoside units.

assignment of the peaks, based on literature data [39,40], is reported in Table S3.

The region between 1750 cm^{-1} and 1350 cm^{-1} offers key insights into how crosslinking affects the polymer backbone. The absorption bands related to the asymmetric and symmetric stretching of $-\text{COO}^-$ groups [$\nu(\text{COO}_{\text{sym}}^-)$ and $\nu(\text{COO}_{\text{asym}}^-)$] shift to lower and higher energies, respectively, due to coordination between M^{2+} ions and carboxylate groups, while no other change is noticeable. It is also worth mentioning that the crosslinking does not induce the protonation of the alginate chains, as testified by the absence of the $\nu(\text{COOH})$ around 1720 cm^{-1} (clearly recognizable in the alginic acid spectrum, HAlg sample) in all the analyzed crosslinked samples.

The difference in energy between the $-\text{COO}^-$ stretching bands (both the symmetric and the asymmetric) was used to determine the geometry of the examined metal-carboxylate, as shown by Nakamoto [41]. Three coordination geometries—monodentate, bidentate chelating, and bidentate bridging—are depicted in Fig. 5. Using Eq. 2, the values of $\Delta\nu_M$ and $\Delta\nu_{Na}$ were determined and compared. Monodentate, bidentate

bridging or bidentate chelating coordination modes are related to $\Delta\nu_M$ values higher, equal or lower than $\Delta\nu_{Na}$, respectively [41].

$$\Delta\nu = \nu_{\text{COO}_{\text{sym}}^-} - \nu_{\text{COO}_{\text{asym}}^-} \quad (2)$$

The obtained $\Delta\nu$ values, reported in Table 2, suggest that the coordination between alginate carboxylate groups and M^{2+} ions is predominantly bidentate chelating (Fig. 5b). Eq. 3, proposed by Chen, was used for the determination of the binding character (in terms of Fraction of Ionic Bonding, FIB) in the M^{2+} -alginate complex of the MAlg samples [42]:

$$\text{FIB} = [\nu(\text{COOH}) - \nu(\text{COOM})] / [\nu(\text{COOH}) - \nu(\text{COONa})] \quad (3)$$

In the aforementioned formula $\nu(\text{COOH})$ is the IR absorption frequency of alginic acid $-\text{COOH}$ stretching (classic covalent bond). On the other hand, $\nu(\text{COOM})$ and $\nu(\text{COONa})$ respectively indicate the asymmetric $-\text{COO}^-$ stretching frequencies of the M^{2+} -crosslinked samples and sodium alginate (classic ionic bond). The obtained FIB values for BaAlg, CuAlg and MnAlg (reported in Table 2), always exceed unity as a consequence of the lower frequency of the asymmetric stretching in the $-\text{COOM}$ complex with respect to $-\text{COONa}$. This phenomenon likely reflects electronic delocalization on the carboxylate groups, contributing to complex stabilization via polarization and electronic retro-donation [42]. It is worth mentioning that the ZnAlg, CaAlg and SrAlg FIB is particularly close to the NaAlg one (see Table 2), suggesting that Zn^{2+} , Ca^{2+} and Sr^{2+} interact with $-\text{COO}^-$ mainly through electrostatic forces. M^{2+} cations can be classified as a function on their capability to stabilize the carboxylate groups on the polysaccharide backbone, simply evaluating the $\nu(\text{COO}_{\text{asym}}^-)$ frequency (the higher the frequency, the lower the stability): $\text{Ba}^{2+} \approx \text{Cu}^{2+} \approx \text{Mn}^{2+} > \text{Sr}^{2+} \approx \text{Ca}^{2+} > \text{Zn}^{2+}$. This order is not in agreement with the affinity scale between alginate and M^{2+} ions previously reported [15–17], but it is important to note that the affinity scale reflects interactions not only with carboxylate groups but also with hydroxyl groups, which play a critical role in cation coordination. These contributions are not detectable with the current FT-IR setup.

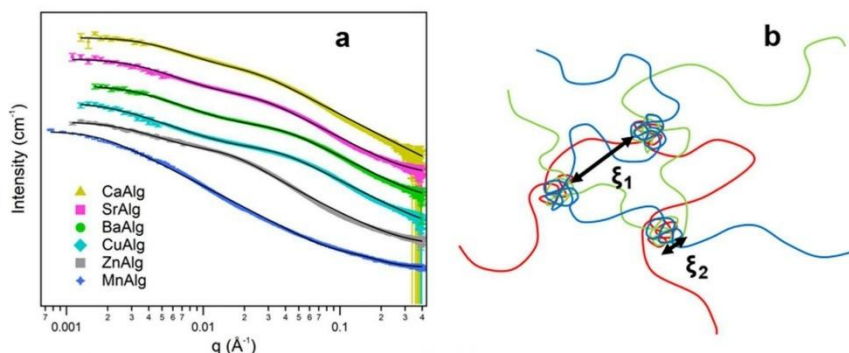


Fig. 4. a) SAXS curves of the MALg samples. The solid black lines represent the fittings of the experimental curves according to Eq. (1). The curves were offset along the y axis for display purposes. b) Sketch of the proposed polymer chains assembly in the MALg gels. ξ_1 and ξ_2 represent the “long distance” and “short distance” correlation lengths obtained from the fitting, respectively.

3.3. Thermal properties

The TGA curves of the prepared fibers are reported in Fig. 6a, together with NaAlg as a reference. Weight losses were analyzed across four distinct regions (denoted as Region I, II, III, and IV in Table S4), since all the curves share common characteristics that allow to easily compare the obtained results.

In Region I (RT–130 °C), weight loss corresponds to water evaporation from the polymer network and is not associated with degradation events. The water content of all the samples is similar, ranging 10–13% wt. Subsequent regions reflect degradative processes, and weight losses were normalized for water content to ensure accurate comparison (Norm. weight loss (%) in Table S4). Region II degradation involves the loss of the carboxylate groups from the polysaccharide and the consequent release of CO and CO₂ [43]. It is interesting to note that the crosslinking always lowers the onset of this degradation, with respect to the NaAlg reference (215.1 °C, Table 3). Crosslinking with alkaline earth metal ions (Ca²⁺, Sr²⁺, Ba²⁺) shifts this event to lower temperature (around 205 °C, Table 3) [44,45]. The introduction of these cationic species might increase the space between the polymer chains, lowering the hydrogen bond-mediated interchains interactions and therefore increasing the polymer backbone susceptibility to thermal variations. Transition metal ions (Mn²⁺, Cu²⁺, Zn²⁺) also lower the onset, but to a larger extent [46–48]. Among all crosslinkers, Cu²⁺ has the strongest catalytic effect, reducing the onset by approximately 55 °C compared to NaAlg. ZnAlg also shows a strong catalytic effect towards polymer degradation (176.0 °C onset), superior to that of MnAlg (193.6 °C onset). The weight losses in Region II and Region III (260 °C–505 °C), related to the decomposition of the glycosidic units with the simultaneous release of CO and CO₂, are comparable for all the samples, except for NaAlg and CuAlg (in this case Region II mass loss > 2× Region III mass loss, see Table S4): this evidence suggests poor char forming capabilities for these two products. NaAlg, CaAlg, SrAlg and BaAlg show peculiar mass losses in Region IV (505 °C–950 °C, see Table S4) related to carbonate salts decomposition: NaCO₃ [49], CaCO₃ [50,51], SrCO₃ [52] and BaCO₃ [53] decompose to Na₂O/CaO/SrO/BaO and CO₂. MnAlg, CuAlg and ZnAlg samples do not show carbonate decompositions in Region IV, since MnCO₃ [54], CuCO₃ [47] and ZnCO₃ [55] are less stable than alkaline and alkaline-earth metal based carbonates, undergoing decomposition below 500 °C. The high residue in the 300 °C–500 °C interval (significantly superior to that of sodium alginate) clearly

indicated that Ba²⁺-crosslinked alginate can find application as flame retardant [13,45,56]. It is interesting to note that ZnAlg shows the highest mass loss in Region IV among the transition metal-crosslinked samples: this is due to the decomposition of ZnO to its elemental components [57].

Differential scanning calorimetry is a powerful tool to elucidate how different cations condition the mobility of the alginate chains. The thermograms related to the first heating cycle (Fig. 6b) show that crosslinking increases the glass transition temperature (T_g) compared to NaAlg ($T_g = 47.1$ °C), reducing polymer chains mobility. It is interesting to note that the M²⁺ ions with the lowest affinity for alginate (*i.e.*, Mn²⁺ and Zn²⁺) lead to MALg samples with the lowest T_g (56.5 °C for MnAlg and 54.6 °C for ZnAlg), testifying a weaker interaction with the polymeric network. All the other M²⁺-crosslinked samples show analogue glass transition temperatures (around 59 °C), suggesting that cations with high affinity impart a similar constraint to the polymer chains when present in huge amounts (see ICP-AES, Table 1). It is worth mentioning that in the second heating cycle (see Fig. S6 in the Supplementary Material) the glass transition is no longer visible, reasonably due to the loss of amorphous domains during the first heating cycle and the subsequent fast cooling that does not allow for the polymeric chains to re-assemble into their previous structure.

3.4. Mechanical properties

We demonstrated that using different cations to crosslink alginate fibers leads to materials with different morphological, structural and thermal properties. These biopolymeric fibers hold potential for applications in various fields, including non-woven textiles, wound dressings, and sorption filters.

Mechanical behavior, particularly tensile properties, is critical when evaluating fibers applications. We recorded stress-strain curves on fiber samples (see Fig. 7) using a rheometer in tensile mode, as described in Section 2.3.8. Table 3 reports, for each sample, the Young's Modulus (extracted from the slope of the linear portion in the elastic region) and the Ultimate tensile strength, *i.e.* the stress value at the fracture point. The shape of the curves suggests that all fibers show a certain degree of ductility, as some elongation occurs in the plastic region before fracture. CuAlg is the most brittle sample, as the deformation in the plastic region is limited. All samples show similar values of ultimate tensile strength except for MnAlg, which breaks at a much lower load value (see

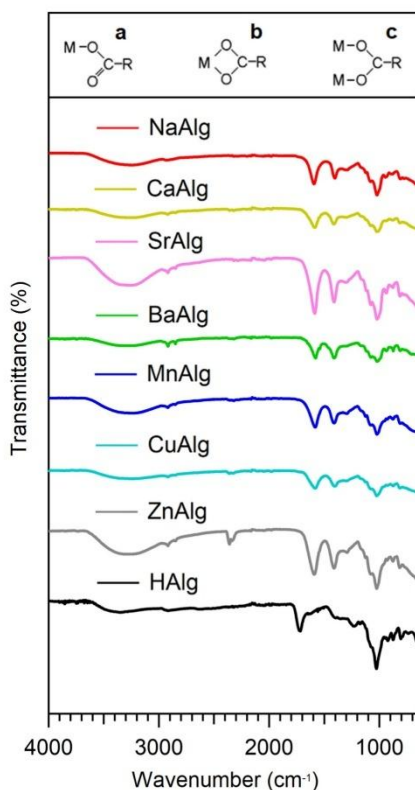


Fig. 5. FT-IR spectra of NaAlg (red), CaAlg (yellow), SrAlg (pink), BaAlg (green), MnAlg (blue), CuAlg (cyan), ZnAlg (gray) and Alginic acid (black). Note that the spectra were offset along the y axis for display purposes. In the a, b and c panels on top, the different coordination geometries of the metal-carboxylate complexes: monodentate (a), bidentate chelating (b) and bidentate bridging (c).

Table 2

Coordination geometry of the analyzed samples. For the calculation of $\Delta\nu$, the data presented in Table S3 were used. The $\Delta\nu$ error is $\pm 4 \text{ cm}^{-1}$, while the error on FTB is 0.05.

Sample	$\Delta\nu \text{ (cm}^{-1}\text{)}$	Coordination geometry	FTB
NaAlg	188	Bidentate bridging	1
CaAlg	172	Bidentate bridging/Bidentate chelating	1.04
SrAlg	175	Bidentate bridging/Bidentate chelating	1.05
BaAlg	168	Bidentate chelating	1.11
MnAlg	170	Bidentate chelating	1.09
CuAlg	176	Bidentate chelating	1.09
ZnAlg	179	Bidentate bridging/Bidentate chelating	1.01

Table 3). The peculiar behavior of MnAlg can be attributed to its characteristic stripe-like shape (see Fig. S2), which results from the previously mentioned substantial structural collapse upon drying (see Fig. S7). This collapse strongly affects the material's mechanical performance.

3.5. Water absorption and remediation potential

In view of their application, the water absorption properties of bi-polymeric fibers are of utmost importance as well. This study investigates how different crosslinking cations affect this property. The results of the swelling experiments are shown in Fig. 8 as plots of the swelling ratio (SR) as a function of time. The SR value was calculated using the following equation:

$$SR = (m_t - m_0) / m_0 \quad (4)$$

where m_t and m_0 are the mass of the swollen fiber at time t and at the beginning of the experiment (i.e., dry), respectively. According to the crosslinking cation, the water absorption properties of alginate fibers are remarkably different. MnAlg exhibits the highest SR (~ 25), absorbing water up to 25 times its dry weight. The other samples have more limited water absorption properties (the SR at the plateau is about 1 for ZnAlg, about 0.7 for CaAlg and SrAlg and about 0.5 for BaAlg and CuAlg). Interestingly, we can observe a trend comparing the SR of the samples and the affinity for alginate of the different cations reported in the literature ($\text{Cu}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$) [15–17]: a higher affinity is related to a more limited swelling ability, likely due to the tightening of the polymeric network driven by the higher affinity of the ions for alginate's carboxylate and hydroxyl groups that hampers water interaction with the polymeric network.

To obtain information about the kinetics of the water sorption properties, a Weibull diffusion model was used to fit the swelling data, according to Eq. 5, in which M_t and M_∞ are the mass of water absorbed at time t and time $t = \infty$ respectively, k is a constant related to the time scale of the diffusion process and n indicates the type of diffusion of a water molecule in the polymeric matrix [58]. The obtained results are reported in Table 4.

$$M_t / M_\infty = 1 - \exp(-kt^n) \quad (5)$$

Given that the higher is the k , the faster is the water uptake, we can conclude that BaAlg displays the fastest water uptake, similar to SrAlg, CuAlg and CaAlg; on the other hand, the process is slower for ZnAlg and, more importantly, MnAlg. The exponent n gives information about the diffusion mode that is related to the nature of the swelling process which, on a general note, results from the interplay of the diffusion rate of water molecules within the hydrogel network (R_{diff}) and the polymer chain relaxation rate (R_{relax}). The swelling kinetic can be described as I . Fickian diffusion (or Case I), when $R_{diff} \ll R_{relax}$ or II . non-fickian diffusion, which is divided in Case II ($R_{diff} > R_{relax}$) or anomalous diffusion ($R_{diff} \sim R_{relax}$) [59]. The n value obtained from the Weibull fitting indicates a Fickian diffusion when $n < 0.75$, a combined mechanism (anomalous transport resulting from Fickian diffusion and Case II transport) when n is in the range 0.75–1.0 and complex mechanisms for $n > 1$ [58]. The n values in Table 3 indicate that SrAlg and ZnAlg follow Fickian diffusion, while CaAlg, BaAlg, and CuAlg exhibit a combination of Fickian diffusion and Case II transport. MnAlg, in contrast, shows a complex swelling mechanism.

To explore potential applications in water purification, the Rhodamine 6G absorption capacity of the fibers was evaluated (details in Table S5) [35,60]. The results in Table 4 prove the high affinity of our fibers for Rhodamine 6G molecules (with absorption ability reaching 0.6 mol/g of fiber). The M_∞ parameter clearly plays a role in the process, being directly proportional to the maximum amount of loadable dye. Overall, CaAlg, SrAlg and ZnAlg (absorption ability $\sim 0.4 \text{ mol/g}$ of fiber) appear as the most promising for water purification purposes, taking

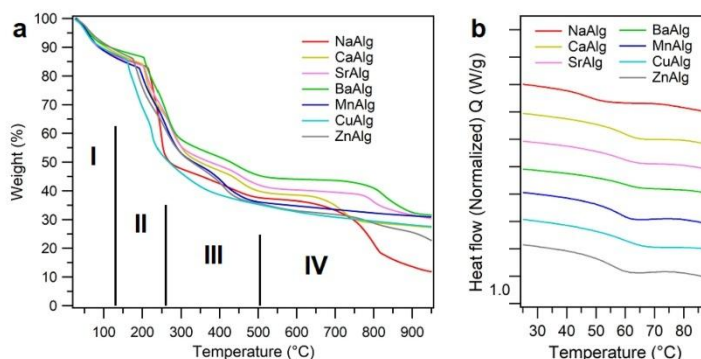


Fig. 6. a) TGA and b) DSC thermograms of NaAlg (red), CaAlg (yellow), SrAlg (pink), BaAlg (green), MnAlg (blue), CuAlg (cyan) and ZnAlg (gray). TGA thermograms (a): I (RT - 130 °C), II (130 °C - 260 °C), III (RT 260 °C - 505 °C), IV (505 °C - 950 °C). The related DTG thermograms are illustrated in Fig. S4, while a zoom of the TGA RT - 260 °C interval is reported in Fig. S5. DSC thermograms are offset along the y axis for clarity.

Table 3

Glass transition temperature (T_g) and onset of the first polymer chains degradation (determined by DSC and TGA, respectively) of the samples. Young's Modulus (GPa) and Ultimate tensile strength (MPa) as extracted from the stress-strain curves in Fig. 7. The error associated with the T_g and Degradation onset determination never exceeds 1.5 °C and 5 °C respectively.

Sample	T_g (°C)	Degradation onset (°C)	Young's Modulus (GPa)	Ultimate tensile strength (MPa)
NaAlg	47.1	215.1	—	—
CaAlg	59.2	202.2	5.3 ± 0.3	135.2 ± 0.9
SrAlg	58.8	205.4	4.2 ± 0.3	121.7 ± 4.0
BaAlg	59.5	204.1	5.1 ± 0.6	147.2 ± 1.9
MnAlg	56.5	193.6	2.5 ± 0.4	57.1 ± 2.4
CuAlg	59.5	161.1	5.2 ± 0.9	140.5 ± 2.5
ZnAlg	54.6	176.0	4.6 ± 0.9	134.2 ± 0.4

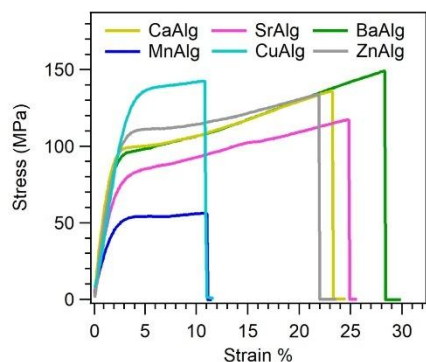


Fig. 7. Stress-strain curves of the MAI samples.

into account the poor mechanical properties of the swollen MnAlg fibers.

When selecting crosslinking ions, it is important to consider both environmental compatibility and functional performance. Ions such as Sr^{2+} and Ca^{2+} are environmentally benign, whereas Zn^{2+} and Cu^{2+} are potentially polluting, but they are also known from the literature to provide antifouling and antibacterial properties [13]. This balance between environmental risks and functional benefits highlights the need to optimize these materials for specific applications. By carefully adjusting parameters such as the amount of water treated and the treatment duration, the controlled use of these ions can guarantee safety while enhancing performance. Additionally, the fibrous structure, with its high surface area, enables efficient contaminant uptake using minimal material quantities, reducing the overall environmental footprint. This approach underscores the importance of tailoring ion selection and application conditions to achieve sustainability while maximizing functionality, making these fibers versatile for water purification and related uses.

4. Conclusion

Our study demonstrates the potential of alginate as a promising material for the preparation of biopolymeric fibers, leveraging its intrinsic biocompatibility, biodegradability, and ability to crosslink with metal cations. Using a wet spinning method, we successfully prepared alginate fibers crosslinked with various divalent cations (i.e., Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+}). Several parameters were optimized to produce fibers with reproducible cross-sections and lengths extending up to several meters.

This study aimed to investigate how divalent cations influence the structural, thermal, mechanical, and water absorption properties of alginate fibers. Our findings demonstrate that both the morphology and the water absorption properties of the fibers (in terms of maximum uptake and kinetics) are significantly influenced by the type of crosslinker used. Mechanical characterization further revealed high Young's Modulus and Ultimate tensile strength (reaching 5.3 GPa and 147 MPa, respectively). These results were profitably correlated with the gel organization at different length scales, through SAXS analysis. The correlation lengths of the polymer chains and the maximum swelling capacity of the fibers exhibit an interesting relationship with the affinity scale between alginate and divalent cations, both increasing as the affinity decreases. Additionally, thermogravimetric analysis proved the

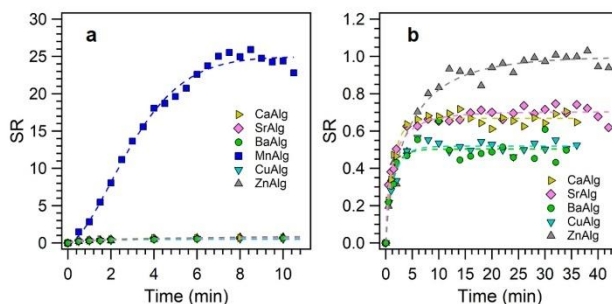


Fig. 8. a) Swelling curves of CaAlg, SrAlg, BaAlg, MnAlg, CuAlg and ZnAlg. b) Zoom of the swelling curves of CaAlg, SrAlg, BaAlg, CuAlg and ZnAlg. SR is defined in Eq. 4. Dashed curves indicate the fittings with a Weibull function.

Table 4

Weibull fitting results for SR curves in Fig. 8 and amount of rhodamine 6G absorbed. The error associated with the fitting is also reported for the swelling results.

Sample	M_{we}	k	n	Diffusion mode	Rhodamine 6G absorbed (mol/g)
CaAlg	0.67 ± 0.01	0.75 ± 0.05	0.92 ± 0.11	Combined	0.35 ± 0.02
SrAlg	0.70 ± 0.01	0.80 ± 0.05	0.58 ± 0.05	Fickian	0.39 ± 0.02
BaAlg	0.50 ± 0.02	0.91 ± 0.16	0.86 ± 0.30	Combined	0.10 ± 0.01
MnAlg	25.0 ± 0.4	0.13 ± 0.02	1.64 ± 0.08	Complex	0.58 ± 0.03
CuAlg	0.52 ± 0.01	0.76 ± 0.07	0.86 ± 0.13	Combined	0.22 ± 0.01
ZnAlg	1.00 ± 0.03	0.33 ± 0.03	0.72 ± 0.05	Fickian	0.41 ± 0.02

high thermal stability of our products (superior to 170 °C), which is also affected by the type of ion employed.

Importantly, the materials and processes employed in this work highlight the practicality and sustainability of our approach. The use of alginate, a renewable biopolymer, and widely available salts such as calcium chloride and manganese chloride ensures cost-effectiveness and scalability for large-scale applications. Furthermore, the limited quantities of salts required for alginate crosslinking, combined with the possibility to recycle the crosslinking baths, significantly reduce concerns related to the depletion of critical raw materials, a challenge often associated with the use of many metals in material science.

All in all, our work successfully demonstrates that the choice of divalent cation plays a pivotal role in defining the structural, thermal, mechanical, and water absorption properties of alginate fibers, validating our starting hypothesis that the ionic affinity and specific binding mechanisms between the cations and alginate significantly influence these properties. By systematically exploring a diverse range of cations under controlled preparation conditions, we provide robust evidence of the tunability of alginate fibers. Moreover, while this study focuses on single cations, future research could explore the use of mixed cation systems to achieve tunable properties, bridging the gap between high mechanical strength and enhanced water absorption capacity. By balancing functionality with sustainability, cation combinations could harness the unique properties of specific ions, such as antimicrobial or antifouling effects, while carefully addressing the environmental impact of potentially polluting ions like Zn^{2+} and Cu^{2+} .

This work not only broadens the understanding of cation-alginate interactions but also establishes a reliable framework for designing next-generation sustainable materials tailored for specific applications, such as wound healing, water purification, and flame retardancy.

CRedit authorship contribution statement

Pietro Tordi: Writing – original draft, Visualization, Investigation,

Formal analysis, Conceptualization. Rita Gelli: Writing – original draft, Visualization, Investigation, Formal analysis, Conceptualization. Simone Tamantini: Investigation, Formal analysis. Massimo Bonini: Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijbiomac.2025.141196>.

Data availability

Data will be made available on request.

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