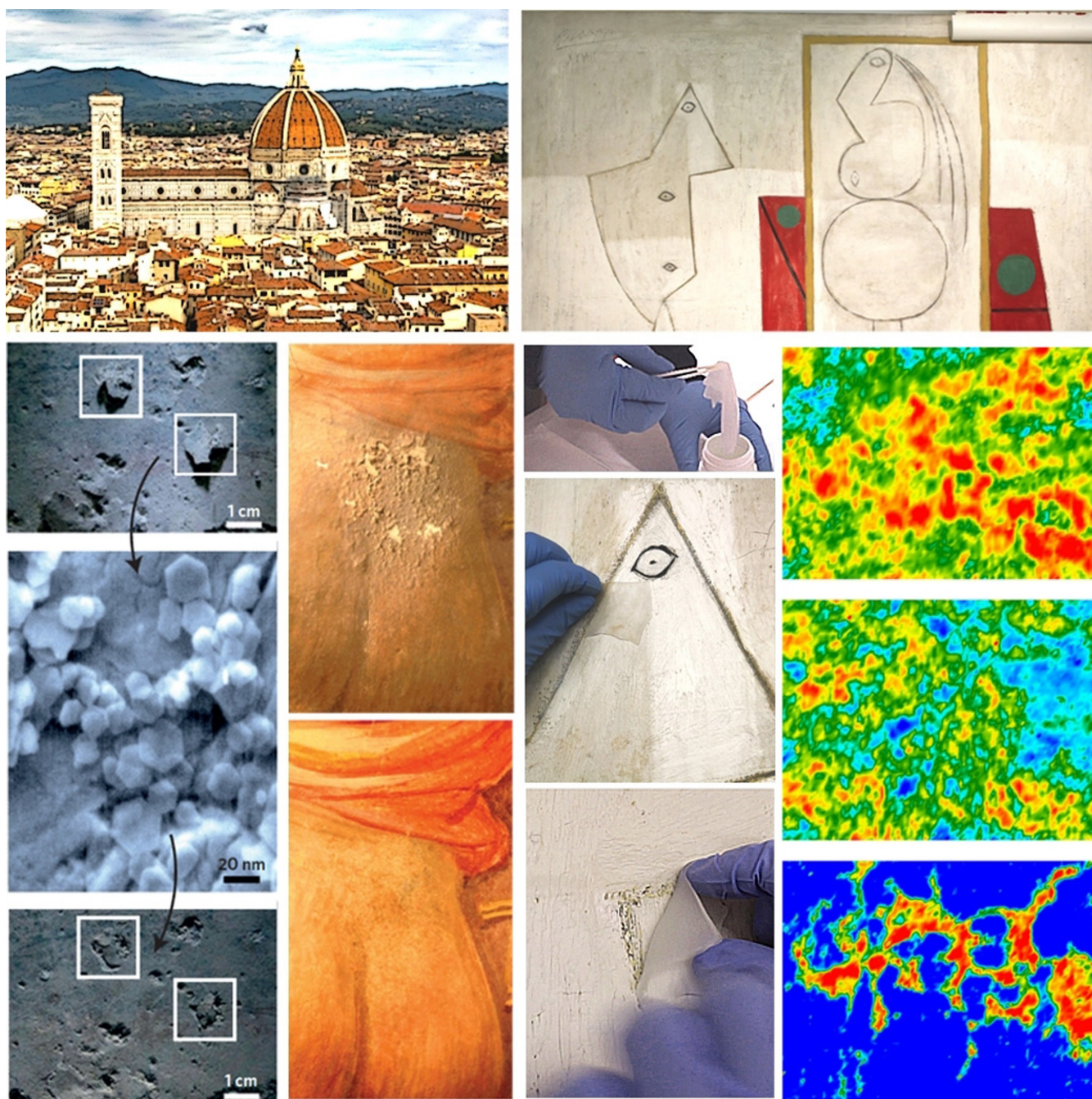


How Science Can Contribute to the Remedial Conservation of Cultural Heritage

Piero Baglioni^{†*}[a, b] and David Chelazzi^{*[c]}



Abstract: Colloid science is contributing solutions to counteract the degradation of artifacts, favoring their transfer to future generations. Advanced materials such as nanoparticles, coatings, gels and microemulsions have been assessed in conservation, spanning from archeological sites to modern and contemporary art. We give an overview of the fundamen-

tal milestones and latest innovations in conservation science, targeting solutions and tools for remedial conservation based on green nanomaterials and hybrid systems. Future perspectives and outstanding challenges in this exciting field are then outlined.

1. The Role of Science in Preserving Cultural Heritage

Resilience has come to be a key concept in today's economics and societal issues, and art is a crucial resource in this sense. Cultural Heritage (CH), when properly preserved and transferred, is a fundamental economic and social welfare driver.^[1–3]

Unfortunately, CH objects are in turn subjected to degradation by environmental factors (light, temperature, relative humidity, pollutants), biocontamination, natural or anthropogenic disasters (fires, flood), and wrong restoration interventions. Conservation measures are made even more difficult by the large number of objects potentially affected by degradation in storages and deposits, and by the use of art materials derived from industry, which are often prone to fast or autocatalytic degradation paths. In this framework, science has great possibilities to counteract degradation processes and put CH in its best position to boost social welfare. In a parallel to medicine, science can act preventively to minimize environmental threats to CH (preventive conservation), provide techniques to analyze works of art (diagnostics), or develop materials and methodologies to remedy damaged artifacts (remedial conservation).

Diagnostics is one of the first fields where science contributed to CH preservation, and has been widely explored for decades now. The artifacts are typically analyzed to study degradation processes or gain anthropological, historical and artistic information.^[4] Current challenges involve the development of newer non-invasive techniques^[5] with high spatial resolution,^[6] and portable instruments to allow feasible analysis of precious works.^[7] Analytical tools can gain great support from modeling and theoretical chemistry, which can be employed to construct mechanisms for the degradative reactivity of art materials.^[8] Diagnosis also links to preventive

conservation when enhanced sensors^[9] are used to monitor the presence of pollutants in museum environments and art storages. In principle, the citizens themselves could contribute to analysis campaigns of CH through smartphone diagnostics.^[10]

However, while diagnosis and preventive conservation are preliminary steps to the preservation of artifacts, remedial conservation has the fundamental task to provide materials and methodologies to restore the physical integrity of the works. Information and communication technologies (ICT) can favor the fruition and management of CH assets, but cannot replace the direct enjoyment of the artifacts by citizens and tourists.^[11] Having the actual CH objects in good shape and accessible is what enhances their shared fruition, effectively triggering economic and social benefits.

Because the degradation of works of art often occurs in meso- and nano-scale domains at the interface of the artifacts, it follows that materials in the same dimensional scales can prove highly beneficial to counteract the detrimental processes. Indeed, colloid and materials science have gradually provided valuable solutions since the beginning of the 2000s, and a commentary on the full potential of nanomaterials in art conservation was given only few years ago in *Nature Nanotechnology*.^[12] Besides, important applications have been reported in dedicated textbooks.^[13] Materials such as nanoparticles, hybrid composites (e.g., inorganic particles in polymer matrices), functionalized coatings, swollen micelles, microemulsions and gels have been formulated and proposed as consolidants, protectives, and cleaning tools for the conservation of works of art. The physicochemical compatibility of these materials to the original artifacts, their durability and sustainability based on “green” chemistry, and their responsiveness to degradation processes, all have been used as guidelines in the synthetic processes and applicative protocols, overcoming the traditional limitations of the restoration practice, which is typically based on classic solvents and polymers chemistry. The importance of the new approach is testified by several recent and current European projects funded in this area (FP7, H2020), and in the successful application of products to masterpieces such as works by Pablo Picasso, Jackson Pollock and Roy Lichtenstein, among others. The most effective formulations developed so far have been brought to the market and are currently available to conservators worldwide.

This is an exciting field in materials science, and despite the successful results obtained it is far from being concluded. In the following paragraphs some of the most relevant contributions

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are presented, along with conclusive remarks and future challenges.

2. Consolidation and Protection of Works of Art

Regardless the type of artistic substrate, one of the main effects of artifacts' degradation is the worsening of their mechanical properties. Mechanical failure can then occur as flaking/powdering pictorial layers, weakening and tearing of natural fibers, embrittlement of plastics, and blistering or delamination of mortars and stone, just to mention some of the most recurring cases.

The consolidation of flaking murals' surfaces is one of the applications that originated the development of colloids and advanced materials specifically tailored for CH preservation. In the aftermath of the 1966 Florence flood, a large portion of the art capital's heritage was endangered by contamination with salts and detrimental organic compounds. The physical chemist Enzo Ferroni developed a methodology, based on ammonium carbonate and barium hydroxide aqueous solutions, to extract sulfates and re-create lime ($\text{Ca}(\text{OH})_2$) in the pores of weakened fresco paintings.^[14] Working on the principle of ion-exchange reactions, the idea to re-create in situ the original binder of the frescoes (the newly formed hydroxide, which sets into calcium carbonate by reaction with atmospheric CO_2) proved not only highly beneficial, but a real turning point in the restoration practice that had until then employed polymeric adhesives to reattach flaking parts. Because the Ferroni method uses materials that are physicochemically compatible with the

original substrates, medium- and long-term drawbacks during the aging of the treated artifacts are avoided as opposed to covering the frescoes with layers of synthetic polymers that are prone to degradation and enhance the detrimental action of salts by blocking the natural porosity of mortars.^[14]

Starting from the late 1990s, the principle of the method was translated into the formulation of $\text{Ca}(\text{OH})_2$ nanoparticles, mostly in the form of hexagonal platelets (roughly 100–200 nm wide and few nm thick), which can be stably dispersed in short-chain alcohols and applied directly onto murals, mortars and stone^[15,16] After solvent evaporation, the hydroxide particles carbonate inside the artifact's pores, building a network of cohered and adhered crystalline CaCO_3 that provides mechanical reinforcement and fixes flaking parts (Figure 1). Nanoparticles improved the Ferroni method in two ways: the amount of consolidant delivered directly is larger, hence consolidation effects are enhanced; the hydroxide ions are packed in solid particles, rather than being freely mobile ions in solutions, which avoids issues on alkaline-sensitive pigments and binders. Over the years, particles synthesis has ranged from bottom-up reactions in homogeneous phase to top-down grinding of micron-sized lime in solvents and solvothermal processes: this allows tuning the particle' size distribution and the synthesis yield, and eventually the refined products reached the market after extensive testing in relevant case studies.^[17] Besides, it was found that colloidal earth-alkaline hydroxides are optimal to adjust the pH of cellulose- and collagen-based artifacts (paper, wood, parchment and leather), counteracting the acid-catalyzed hydrolysis that produces severe degradation of these natural polymers.^[16,18]

Stemming from these pioneering applications, colloidal materials of different kinds have been formulated and functionalized, or combined in hybrid systems for the consolidation of different types of artistic substrates. For instance, poly(ethylene glycol) (PEG, a traditional consolidant for waterlogged and archaeological wood or leather) can be mixed with functionalized halloysite nanotubes filled with $\text{Ca}(\text{OH})_2$; the tubes release the hydroxide at controlled rate, extending the neutralization of acidity in the wood over time. Besides, the halloysite– $\text{Ca}(\text{OH})_2$ /PEG nanohybrid acts as a consolidant, penetrating the wooden matrix and increasing its flexural strength and rigidity.^[19]

Two recent and exciting applications regard the consolidation of canvases and silk. In the first case, polyelectrolyte-treated silica nanoparticles (SNPs) and cellulose nanofibrils (CNF) have been combined to treat the backside of canvases, which are the support to classic and modern paintings.^[20] The cellulose nanofibrils film at the canvas surface, increasing its ductility, SNPs penetrate deeper and reinforce at the fiber scale, increasing stiffness; the two effects are balanced varying the SNP/CNF ratio, in an elegant approach alternative to the traditional relining of canvases with synthetic adhesives, which are prone to yellowing and acidity development.^[21] In the case of silk, dispersions of self-regenerated silk fibroin (SRSF) have been recently used to improve the mechanical behavior of aged silk fibers through a robust approach where SRSF is obtained from waste silk and adhered onto weak fibers.^[22] By varying the concentration of the dispersions, films at different

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Figure 1. Left: Application of $\text{Ca}(\text{OH})_2$ nanoparticles for the consolidation of Renaissance wall paintings in Florence Cathedral. Top: before and bottom: after restoration. Reproduced with permission from ref. [15]. Copyright: 2001, American Chemical Society. Center and right: Mayan wall paintings in the United Nations Educational, Scientific and Cultural Organization world heritage site of Calakmul (Mexico). a) Photograph of the wall paintings after restoration with $\text{Ca}(\text{OH})_2$ nanoparticle dispersions. b) Grazing visible light image showing the detaching paint flakes before the application of nanoparticles. c) Scanning electron microscopy micrograph of the $\text{Ca}(\text{OH})_2$ nanoparticles (hexagonal platelets) that were applied to the degraded painted surface. d) Grazing visible light image showing re-attached and re-adhered paint flakes after the application of nanoparticles. Panels a, b, and d reproduced with permission from ref. [13c]. Copyright: 2014, The Royal Society of Chemistry. Panel c reproduced with permission from ref. [12]. Copyright: 2015, Macmillan Publishers Limited.

degrees of fibroin amorphousness or crystallinity are obtained, which provide different mechanical properties upon adhesion to the silk fibers: crystalline layers produce brittle materials, while amorphous ones increase ductility.

Another promising application with high potential socio-economic impact involves the consolidation of earthen masonry. As widespread as earthen materials are in both archaeological and current daily life housing, finding feasible and robust formulations for their consolidation would be key to heritage valorization and sustainable architecture. Yet, earthen masonry is susceptible to degradation by weathering and erosion. An approach has been recently proposed to consolidate adobe bricks, one of the most common earthen building materials: mimicking the setting of Portland cement, $\text{Ca}(\text{OH})_2$ and silica nanoparticles have been mixed in a composite formulation along with a cellulose ether, and applied to crumbling adobe; the hydroxide and silica react together forming calcium silicate hydrate (CSH), which consolidates the powdering earth substrate against peeling, abrasion and wet-dry cycles (Figure 2).^[23] Nanoparticles enhance the formation of CSH due to the large surface to volume ratio and the extended total surface of particles per unit of material. With the possibility of using the colloidal blend also as an additive in adobe formulations, this update might open new scenarios for sustainable construction, alternative to cement, in underdeveloped countries. Because cement is a substantial source of global CO_2 emission, using a valid alternative for building materials would help target the issues of greenhouse gases and climate change (e.g., global warming).

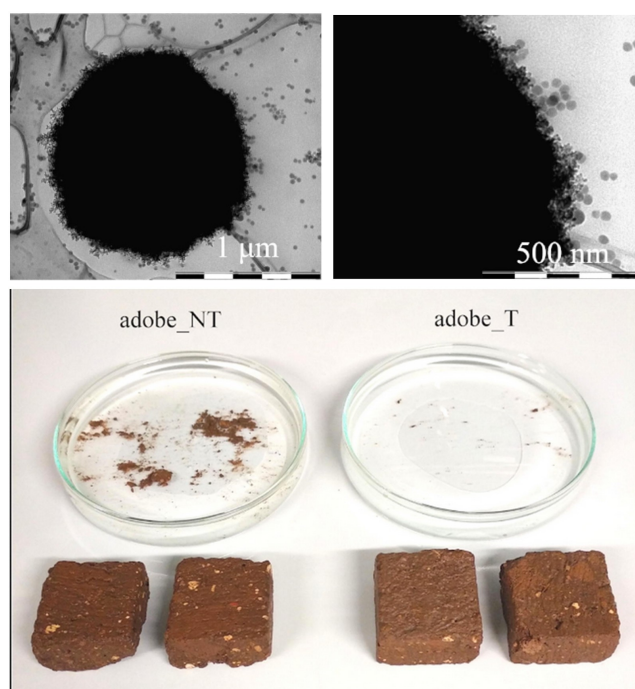


Figure 2. Top: Transmission electron microscope (TEM) images of a ternary hybrid system composed of silica nanoparticles (spherical), $\text{Ca}(\text{OH})_2$ nanoparticles, and hydroxypropyl cellulose, formulated for the consolidation of earthen masonry. The micron-sized agglomerate is formed by the interaction of nanoparticles and cellulose fibrous structures. Bottom: Adobe bricks that underwent wet/dry aging cycles, either without (left) or with prior treatment with the hybrid system (right). The untreated brick lost significant portions, whereas the treated brick stood the accelerated aging without relevant significant damage. Reproduced with permission from ref. [23]. Copyright: 2018, Elsevier Inc.

The same type of reaction has been employed to have silica oligomers react with portlandite crystalline $\text{Ca}(\text{OH})_2$ found in cement: the oligomers can penetrate cement, polymerize by sol-gel process, and form in situ a CSH gel that is incorporated in the existing CSH of cement, opening the way for simple repairs of contemporary concrete monuments.^[24]

Protection of artistic surfaces against recurring soiling and degradation is another type of remedial intervention where relevant contributions have been derived from colloids and materials science. Halloysite and other nanoclays can be incorporated into a polymer matrix (e.g., fluorinated or biopolymers) able to form protective films on stone and metals against atmospheric pollutants, corrosive agents, entomological attacks, and even graffiti vandalism.^[25] Silane/siloxane emulsions can be combined with chitosan, a “green” and renewable biopolymer, and silver nitrate as biocides, or with polyurethane dispersion (to produce hydrophobic fabrics) while mesoporous silica nanoparticles have been used as controlled releasers of antimicrobials for stone preservation.^[26] Coatings can be tailored to act as self-cleaning surfaces to avoid dust and particulate deposition on buildings: gold nanoparticles (AuNPs) boost the photoactivity of TiO_2 under solar radiation by promoting absorption in the visible range; thus, by varying the content of AuNPs in Au– $\text{TiO}_2/\text{SiO}_2$ coatings, obtained by a simple sol-gel route, soot deposition on stone can be prevented.^[27] TiO_2 can also be formulated as nanorods (NRs) and added to hybrid methacrylic–siloxane or commercial resins to impart self-cleaning properties to treated stone surfaces.^[28]

With regards to metal surfaces, chitosan-based coatings have been recently explored as green, renewable matrices to confine and release anti-corrosion molecules at controlled rate; for instance, imidazolium salts can be efficiently confined in this way to protect bronze surfaces against corrosive processes.^[29] Besides, novel corrosion inhibitors have been formulated to decrease the toxicity of benzotriazole derivatives, one example being triazole thiones that showed good inhibiting efficiency.^[30] Polyurethane protective coatings can be improved by adding silsesquioxane nanoparticles, as they cause an increase of water contact angle and enhance the plasticity and the abrasion resistance of the coating, as well as an improvement of protective ability, as indicated by impedance spectroscopy measurements.^[31]

Finally, it is important to recall that advanced colloidal materials can improve diagnostic methodologies; a representative example is that of surface-enhanced Raman scattering (SERS), where colloidal pastes and metal nano-inks can be employed as probes to obtain enhanced spectra with highly diagnostic features, which is particularly useful in the non-invasive analysis of dyes that can be present in complex mixtures on works of art.^[32]

3. Cleaning of Works of Art

Soiling and contamination do not just alter the aesthetic looks of works of art, they also participate in degradative processes; not surprisingly, in fact, cleaning is one of the most recurring

and common operations in cultural heritage preservation. However, traditional cleaning operations can pose risks to the safety of the artifacts, as they typically rely on classic solvent chemistry that is neither completely selective nor controlled. Essentially, solubility parameters, or more recently solvatochromic polarity and equilibrium swelling capacity,^[33] are used to match solvents with unwanted layers (grime, aged coatings/adhesives, etc.), and the solvents are applied either as non-confined (e.g., using cotton swabs) or poorly confined in viscous polymer dispersions (cellulose ethers or polyacrylic acid being two common choices),^[34] the fundamental issues of this traditional approach are the scarce spatial and temporal control of the solvent action, and the presence of residues from polymer dispersions calling for invasive rinsing processes. Besides, some of the traditional solvents have toxicity issues. Soaps and surfactants have also been used since a long time for cleaning art, with little awareness and mostly through serendipity or in-house formulations, before some guidelines were provided towards the end of the 1980s.^[34]

Moving on from these limitations, colloids and materials science have provided effective and systematic methodologies in the last decades.^[35,36] Oil-in-water (o/w) microemulsions marked a turning point in cleaning formulations back in 1986, when they were employed for the first time to remove wax contaminants from Italian Renaissance frescos.^[14] By properly selecting surfactant and co-surfactant molecules, it is possible to stably disperse the solvents as nano-sized droplets, confined by surfactant and co-surfactant micelles in a continuous aqueous phase. The nano-dimensions of the droplets ensures a huge surface area, orders of magnitude larger than the same mass of bulk solvent, boosting the interaction of the droplets with layers of grime and soil. The first formulations featured non-ionic surfactants (e.g., sodium dodecyl sulfate, SDS) and fully non-polar solvents (alkanes), with the purpose of dissolving wax and transporting it inside the micelles in the aqueous phase; when the latter is taken up in sorbents, such as cellulose poultices, the contaminants are effectively removed from the fresco surface. The nanostructured cleaning fluid is largely aqueous (> 80% w/w), which greatly decreases the environmental impact of the o/w microemulsions as opposed to solvent blends.^[14]

Several crucial aspects regarding the structure of these systems and their interaction with surfaces have been clarified. The inclusion of molecules inside the micelles, and detergency mechanisms, drive the removal of low molecular weight compounds (fatty acids and triglycerides found in grime), while other complex mechanisms are involved when the microemulsions interact with polymer layers, such as poly-(acrylate) and poly(vinyl acetate), found in synthetic coatings applied on the surface of murals since the 1960s.^[35] One of the most intriguing aspects involve the dewetting of the polymer layers induced by the interaction with the cleaning fluids: while the selection of a good solvent for the polymer facilitates the swelling and mobility of polymer chains, it is the co-presence of surfactants that boosts the kinetics of the dewetting process. The amphiphilic molecules, in fact, favor the formation of new solid-liquid and liquid-liquid interfaces, lowering the dewetting

energy barrier, which also depends on the polymer thickness. In this sense, highly surface-active non-ionic surfactants (e.g., alcohol ethoxylates) proved to be more efficient than SDS.^[37] Once initiated, dewetting can proceed by evolution of the detachment areas via nucleation and growth of holes, which eventually coalesce until the polymer film is disrupted and detaches from the substrate as swollen droplets, resulting in effective removal (Figure 3).

The advantages in this approach are evident as opposed to traditional solution chemistry, where the polymer are dissolved, when possible, by solvent blends and at least partially transported deeper in the murals' pores, rather than completely removed.

Over the last decades, o/w nanostructured fluids (NSFs) have been assessed in a vast number of case studies, spanning from Renaissance art to Mesoamerican archaeological sites, where the main target has been the removal of detrimental polymeric coatings applied in past conservation interventions (Figure 3).^[14,35,36] Such coatings block the natural porosities of stone and wall paintings, enhancing the damage caused by saline solutions to the artifacts; besides, the polymers themselves eventually undergo degradation, jeopardizing the surface of the works. Thanks to the dynamic exchange of solvents and surfactants by the nanodroplets, the NSFs proved to be highly effective in safely and selectively removing the coatings, bringing back the original painted layers.^[14,35,36] Several formulations have been proposed over the years, using "green" solvents such as alkyl carbonates, and biodegradable or self-cleavable surfactants (e.g., alcohol ethoxylates or amine oxides). Some of the employed solvents are partially water-miscible, and are thus partitioned between the confined phase (micelles) and the continuous water phase; this feature can further boost the efficacy of polymer removal.^[14,35,36] The biodegradable/self-

cleavable surfactants further decrease the environmental impact of the NSF, and reduce the need for rinsing steps after the cleaning intervention to remove non-volatile components of the formulation.^[38]

It is also possible to use reversed water-in-oil (w/o) microemulsions, where water is dispersed in a continuous solvent phase. The rationale for employing these systems in art cleaning relies in the possibility to control the accessibility of aqueous solutions to water-sensitive surfaces by dispersing them in a low-polar solvent (hydrocarbons); the water droplets can be loaded with chelating agents and surfactants, and have cleaning power towards hydrophilic dirt, while the solvents are selected to be inert to water-sensitive painted layers (e.g., modern oil or acrylic paints).^[39] While some promising applications have been reported, possible drawbacks of this approach are due to the use of high amounts of surfactants, which can leave residues whose effects have yet to be explored.

Complementarily to NSFs, an efficient strategy to control the action of fluids on water- and solvent-sensitive surfaces is to confine them in retentive matrices such as gels and highly viscous polymeric dispersions (HVPDs).^[34,35] There is a virtually infinite plethora of polymers and synthetic approaches to choose from in order to formulate confining networks, but there are precise criteria to comply with to produce systems that can be successfully adopted in the restoration practice. Gels or gel-like networks have to exhibit high viscoelasticity to favor handling, homogeneous adhesion, and easy removal in one piece without the necessity of rinsing steps. They also need to have the capacity of uploading large amounts of water or solvents and release them at controlled rate on well-delimited areas without excessive wetting of surfaces. Traditional materials employed in the restoration practice include either thickeners (e.g., polyacrylic acid or cellulose ethers HVPDs) or

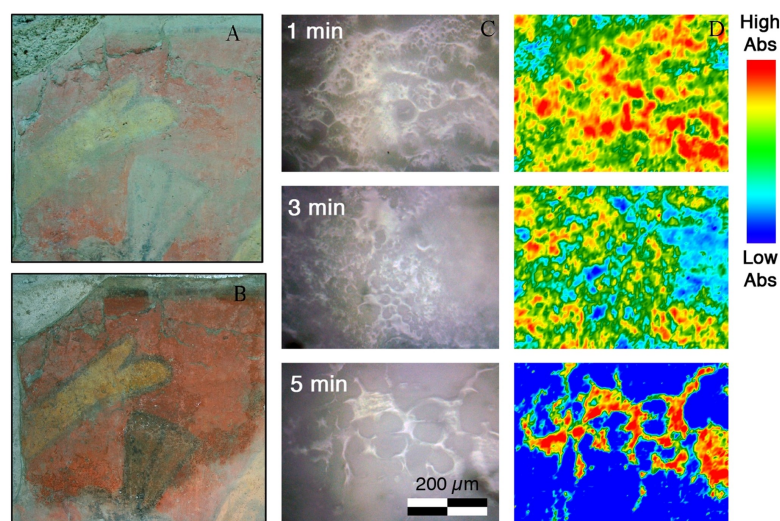


Figure 3. Removal of aged, detrimental organic coatings from a Mesoamerican mural painting in Cholula. A) The presence of the organic coating significantly alters the readability of the painting. B) The same area partially cleaned after the application of a microemulsion (courtesy of Piero Baglioni). Reproduced with permission from ref. [14]. Copyright: 2013, American Chemical Society. C) and D) Visible light and FTIR 2D imaging of mortar tiles coated with Paraloid B72 and immersed in an o/w nanostructured cleaning fluid for different times. C) The surfaces under visible light and D) FTIR chemical maps of the polymer peak at 1735 cm^{-1} (C=O stretching; right). The spatial resolution of the chemical maps is $5.5\text{ }\mu\text{m}$. Reproduced with permission from ref. [37]. Copyright: 2018, Wiley-VCH.

rigid sheets (gellan),^[34] which are, respectively, scarcely retentive and prone to leave residues, or too rigid to homogeneously adapt to the rough painted surfaces frequently found in modern/contemporary paintings.^[40–42]

Alternatively, advanced confining systems based on chemical (held by covalent bonds) or physical networks (held by secondary bonds) have been specifically designed to cope with the requirements of art cleaning.^[14,35] The key-concept to select a synthetic path over the other is the possibility to systematically tune parameters such as pore size distribution, polymer mesh size, elastic and viscous moduli, free water index, diffusivity of fluids inside the network, and water release rate. One of the most successful class of chemical gels comprises chemical networks of poly(hydroxyethyl methacrylate) semi-interpenetrated with linear chains of polyvinylpyrrolidone (pHEMA/PVP semi-IPNs), highly retentive and viscoelastic hydrogels that can be loaded with aqueous solutions or o/w fluids to selectively remove unwanted layers from water-sensitive surfaces.^[41] These semi-IPNs are typically made as gel sheets, easy to handle and remove, and their successful applications have comprised the cleaning of fragile canvas paintings, murals and paper artworks.^[14,35,41,43]

Another promising class of confining matrices for art cleaning includes dispersions and gels based on polyvinyl alcohol (PVA), a green, biocompatible and sustainable polymer able to form networks through different synthetic routes such as cast-drying, freeze-thawing and chemical manipulation.^[42,44–46] PVA-based systems are well known in tissue engineering, food chemistry and drug delivery; however they were firstly introduced in conservation science in the first

decade of the 2000s, when PVA was crosslinked with borate to yield viscoelastic HVPDs able to confine water and hydro-alcoholic blends; the rheological properties of these dispersions are such that they are easily “peeled” off the surface after the application, which is a big improvement over traditional thickeners.^[44] These HVPDs were positively assessed in several case studies, but other formulations have been eventually developed where borate, which has some toxicity to humans, was avoided, and other properties improved. Namely, freeze-thawing (FT) was adopted to create physical networks where PVA crystallites hold together polymer chains, acting as joints, without the need for crosslinkers. The main properties of the network have been modified by blending in, before the FT process, either PVP or a PVA with different molecular weight and hydrolysis degree.^[42,45] Recently, a new class of gels, PVA/PVA “twin-chain” networks, have been synthesized and employed to remove surface dirt or aged coatings from Pablo Picasso, Jackson Pollock and Roy Lichtenstein’s masterpieces, among others (Figure 4).^[42,47,48] The presence of the lower-molecular-weight PVA (L-PVA) produces, after the FT process, a final network with a sponge-like interconnected porosity that differs from the tightly packed channel-like pores of the single-PVA analogue. The difference could play a fundamental role when it comes to absorb detached dirt from surfaces, with interconnected pores favoring the capture of dirt and its migration through the gel network. L-PVA is also partially included in, and protruding from, the gel walls, which overall makes the “twin-chain” networks compliant and able to adapt homogeneously to the rough painted surfaces commonly exhibited by modern and contemporary paintings.^[42] These gels

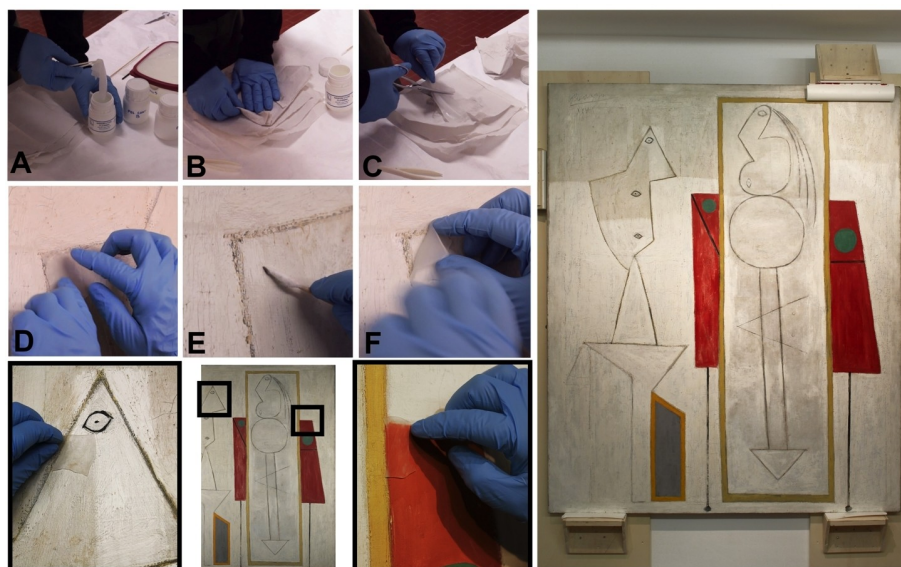


Figure 4. The cleaning of Pablo Picasso’s *The Studio*, 1928, oil and black crayon on canvas, 161.6 × 129.9 cm, Peggy Guggenheim Collection, Venice (The Solomon R. Guggenheim Foundation, New York). A) A PVA/PVA “twin-chain” hydrogel is loaded with the o/w NSF (24 h immersion). B) Gel sheets loaded with the NSF are gently squeezed with blotting paper to remove the fluid excess from their surface, and C) cut to the desired shape and size. D) The gel is applied to the painted surface. E) Gentle mechanical action with a dry cotton swab allows the removal of the swollen/softened varnish and wax. F) Rinsing step: a water-loaded gel is briefly applied to the same spot to remove possible residues of the NSF. Bottom center: the cleaning of white and red areas; the sections in black boxes are shown in detail either side. Right: The painting during cleaning. The lighter cleaned areas can easily be distinguished from the darker uncleaned areas at the top. Reproduced with permission from ref. [47]. Copyright: Succession Picasso, by SIAE 2020.

constitute the most advanced cleaning system currently available.

Notably, both pHEMA/PVP and the PVA-based hydrogels can be uploaded with o/w microemulsions, and the micelles are able to diffuse through the gel network without detrimental alteration of either their structure or the gel's.^[43,47,49] This is an appealing solution when the cleaning power of aqueous nanostructured fluids is needed on a water-sensitive surface, making the coupled system one of the most sophisticated tools currently available to conservators.

PVA dispersions, opportunely formulated, can also be cast directly on the surface of artworks, let film, and then peeled off the surface removing engrained dirt or other unwanted materials. This approach has been employed, for instance, in the removal of corrosion layers from historical bronze, using chelators to upload in the PVA filming dispersion.^[50] The main advantage is to have close adhesion to surfaces whose cavities and crests have such a scale that a viscous dispersion is needed to reach all the hidden spots.

4. Conclusions and Perspectives

The contribution of science has proven fundamental to help the preservation of Cultural Heritage over the last decades, and the call to scientists remains so as to transfer this inheritance to future generations. While improvements in diagnostics are focusing on portable and non-invasive techniques with increasingly higher spatial resolution and sensitivity, materials and colloid science have opened a vast range of possibilities for effective formulations to be used in remedial conservation. Many successful products have been developed, and some of them are now available to conservators and curators, but there is still broad space for improvements, implementation and the exploration of new solutions. Currently, the challenge is to develop materials and methodologies based on the principles outlined by the President of the EU Commission, that is, the development of a sustainable and circular economy, the use of green chemistry and “safe by design”, and enhancing the resilience of cultural assets, coping with the advancing threats of climate change. Life-cycle assessment (LCA), materials modeling, and the use of data platforms are crucial to help decrease the environmental impact of new materials directly from the design stage. According to these criteria, renewable materials derived from nature are being progressively introduced in restoration; examples include chitosan, fibroin, nanocellulose, and castor oil.^[22,51–53] Inspiration for the formulation of new solutions might also come from our ancient past: archaeological and paleontological materials that have survived to recent times are a magnificent example of *a posteriori* extreme resilience to alteration; moreover, many such materials were synthesized in soft chemical ways with low energy resources.^[54] Mimicking either these processes or natural biosynthesis with current awareness of materials science would represent an ideal case of a circular economy and resilience in art conservation.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: advanced materials · art preservation · conservation science · colloids · nanomaterials

- [1] a) F. Mucci, N. Mucci, F. Diolaiuti, *Clin. Neuropsychiatry* **2020**, *17*, 63–64; b) M. Choi, H. Tessler, G. Cao, *Int. Rev. Educ.* **2020**, *66*, 715–735; c) A. Cabedo-Mas, C. Arriaga-Sanz, L. Moliner-Miravet, *Front. Psychol.* **2021**, *11*, 606180.
- [2] Paris Declaration: Heritage, Sciences and Technologies: an Opportunity for our Societies and the Global Economy, 15 February 2019, Institut de France, Paris, France. http://tiny.cc/paris_declaration; <https://www.reach-culture.eu/wpcontent/uploads/2019/05/Horizons-for-Heritage-Research-Towards-a-Cluster-on-Cultural-Heritage-Symposium-Report.pdf>.
- [3] Creating growth. Measuring cultural and creative markets in the EU. EY, 2014. <http://www.creatingeurope.eu/en/wp-content/uploads/2014/11/study-full-en.pdf>.
- [4] a) L. de Viguierie, P. Walter, E. Laval, B. Mottin, V. Armando Solé, *Angew. Chem. Int. Ed.* **2010**, *49*, 6125–6128; *Angew. Chem.* **2010**, *122*, 6261–6264; b) L. Monico, K. Janssens, E. Hendriks, F. Vanmeert, G. Van der Snickt, M. Cotte, G. Falkenberg, B. G. Brunetti, C. Miliani, *Angew. Chem. Int. Ed.* **2015**, *54*, 13923–13927; *Angew. Chem.* **2015**, *127*, 14129–14133.
- [5] a) J. E. Fernandez, F. Taccetti, J. M. Kenny, R. Amendola, *Rend. Fis. Acc. Lincei* **2020**, *31*, 819–820; b) L. Randazzo, G. Paladini, V. Venuti, V. Crupi, F. Ott, G. Montana, M. Ricca, N. Rovella, M. F. La Russa, D. Majolino, *Appl. Sci.* **2020**, *10*, 6745.
- [6] a) D. Badillo-Sanchez, D. Chelazzi, R. Giorgi, A. Cincinelli, P. Baglioni, *Polym. Degrad. Stab.* **2018**, *157*, 53–62; b) D. Badillo-Sanchez, D. Chelazzi, R. Giorgi, A. Cincinelli, P. Baglioni, *Sci. Rep.* **2019**, *9*, 17239.
- [7] a) C. Rehorn, B. Blümich, *Angew. Chem. Int. Ed.* **2018**, *57*, 7304–7312; *Angew. Chem.* **2018**, *130*, 7426–7434; b) G. Senesi, R. S. Harmon, R. R. Hark, *Spectrochim. Acta Part B* **2021**, *175*, 106013.
- [8] L. H. Oakley, F. Casadio, K. R. Shull, L. J. Broadbelt, *Angew. Chem. Int. Ed.* **2018**, *57*, 7413–7417; *Angew. Chem.* **2018**, *130*, 7535–7539.
- [9] M. S. Zalaffi, N. Karimian, P. Ugo, *J. Electrochem. Soc.* **2020**, *167*, 037548.
- [10] a) R. Brigham, J. Rau-Bové, A. Rudnicka, M. Cassar, M. Strlic, *Angew. Chem. Int. Ed.* **2018**, *57*, 7423–7427; *Angew. Chem.* **2018**, *130*, 7545–7549; b) C. Daffara, G. Marchioro, D. Ambrosini, *Opt. Arts Archit. Archaeol.* **2019**, *VII*, 110581 K.
- [11] a) J. Tribe, M. Mkono, *Ann. Tour. Res.* **2017**, *66*, 105–115; b) G. Ritzer, A. Liska in *Touring Cultures: Transformations of Travel and Theory* (Eds.: C. Rojek, J. Urry), London: Routledge, **1997**, pp. 96–109.
- [12] P. Baglioni, E. Carretti, D. Chelazzi, *Nat. Nanotechnol.* **2015**, *10*, 287–290.
- [13] a) *Nanotechnologies and Nanomaterials for Diagnostic, Conservation and Restoration of Cultural Heritage* (Eds.: G. Lazzara, R. F. Fakhruddin), Elsevier, **2018**; b) *Nanoscience for the Conservation of Works of Art* (Eds.: P. Baglioni, D. Chelazzi), The Royal Society of Chemistry, **2013**; c) P. Baglioni, R. Carrasco Vargas, M. Cordeiro Baqueiro, D. Chelazzi in *Science and Art: The Painted Surface* (Eds.: A. Sgamellotti, B. G. Giovanni, C. Miliani), Royal Society of Chemistry, **2014**, pp. 68–93.
- [14] P. Baglioni, D. Chelazzi, R. Giorgi, G. Poggi, *Langmuir* **2013**, *29*, 5110–5122.
- [15] a) M. Ambrosi, L. Dei, R. Giorgi, C. Neto, P. Baglioni, *Langmuir* **2001**, *17*, 4251–4255; b) L. Randazzo, V. Venuti, G. Paladini, V. Crupi, D. Majolino, F. Ott, M. Ricca, N. Rovella, M. F. La Russa, *J. Cult. Herit.* **2020**, *46*, 31–41.

- [16] a) D. Chelazzi, G. Poggi, Y. Jaidar, N. Toccafondi, R. Giorgi, P. Baglioni, *J. Colloid Interface Sci.* **2013**, *392*, 42–49; b) R. Camerini, G. Poggi, D. Chelazzi, F. Ridi, R. Giorgi, P. Baglioni, *J. Colloid Interface Sci.* **2019**, *547*, 370–381; c) S. Bastone, D. F. Chillura Martino, V. Renda, M. L. Saladino, G. Poggi, E. Caponetti, *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *513*, 241–249.
- [17] a) C. Rodriguez-Navarro, E. Ruiz-Agudo, *Pure Appl. Chem.* **2018**, *90*, 523–550; b) E. Ciliberto, G. G. Condorelli, S. La Delfa, E. Viscuso, *Appl. Phys. A* **2008**, *92*, 137–141; c) I. Natali, M. L. Saladino, F. Andriulo, D. Chillura Martino, E. Caponetti, E. Carretti, L. Dei, *J. Cult. Herit.* **2014**, *15*, 151–158.
- [18] a) M. Baglioni, A. Bartoletti, L. Bozec, D. Chelazzi, R. Giorgi, M. Odlyha, D. Pianorsi, G. Poggi, P. Baglioni, *Appl. Phys. A* **2016**, *122*, 114; b) R. Giorgi, D. Chelazzi, P. Baglioni, *Appl. Phys. A* **2006**, *83*, 567–571; c) R. Giorgi, D. Chelazzi, E. Fratini, D. Langer, A. Niklasson, M. Rådemar, J. E. Svensson, P. Baglioni, *J. Cult. Herit.* **2009**, *10*, 206–213.
- [19] G. Cavallaro, S. Milioto, F. Parisi, G. Lazzara, *ACS Appl. Mater. Interfaces* **2018**, *10*, 27355–27364.
- [20] a) K. Kolman, O. Nechyporchuk, M. Persson, K. Holmberg, R. Bordes, *ACS Appl. Mater. Interfaces* **2018**, *1*, 2036–2040; b) K. Kolman, O. Nechyporchuk, M. Persson, K. Holmberg, R. Bordes, *Colloids Surf. A* **2017**, *532*, 420–427.
- [21] D. Chelazzi, A. Chevalier, G. Pizzorusso, R. Giorgi, M. Menu, P. Baglioni, *Polym. Degrad. Stab.* **2014**, *107*, 314–320.
- [22] D. Chelazzi, D. Badillo-Sanchez, R. Giorgi, A. Cincinelli, P. Baglioni, *J. Colloid Interface Sci.* **2020**, *576*, 230–240.
- [23] R. Camerini, D. Chelazzi, R. Giorgi, P. Baglioni, *J. Colloid Interface Sci.* **2019**, *539*, 504–515.
- [24] R. Zarzuela, M. Luna, L. M. Carrascosa, M. P. Yeste, I. Garcia-Lodeiro, M. Blanco-Varela, M. A. Cauqui, J. M. Rodriguez-Izquierdo, M. Mosquera, *Cem. Concr. Res.* **2020**, *130*, 106008.
- [25] a) G. Cavallaro, G. Lazzara, F. Parisi, S. Riel, S. Milioto in *Nanotechnologies and Nanomaterials for Diagnostic, Conservation, and Restoration of Cultural Heritage* (Eds.: G. Lazzara, R. Fakhruddin), Elsevier, **2019**, pp. 149–170; b) M. Licchelli, M. Malagodi, M. Weththimuni, C. Zanchi, *Appl. Phys. A* **2014**, *116*, 1525–1539.
- [26] a) S. Eyssautier-Chiune, I. Calandra, N. Vaillant-Gaveau, G. Freonteau, C. Thomachot-Schneider, J. Hubert, J. Pleck, M. Gommeaux, *Prog. Org. Coat.* **2018**, *120*, 132–142; b) A. Presentato, F. Armetta, A. Spinella, D. F. Chillura Martino, R. Alduina, M. L. Saladino, *Front. Chem.* **2020**, *8*, 699; c) C. Dresler, M. L. Saladino, C. Demirbag, E. Caponetti, D. F. Chillura Martino, R. Alduina, *Int. Biodeterior. Biodegrad.* **2017**, *125*, 150–156; d) G. Mazzon, M. Zahid, J. A. Herredia-Guerrero, E. Balliana, E. Zendri, A. Athanassiou, I. S. Bayer, *Appl. Surf. Sci.* **2019**, *490*, 331–342.
- [27] M. Luna, J. J. Delgado, M. L. Almoraima Gil, M. J. Mosquera, *Nanomaterials* **2018**, *8*, 177.
- [28] a) C. Esposito Corcione, C. Ingrassio, F. Petronella, R. Comparelli, M. Striccoli, A. Agostiniano, M. Frigione, M. L. Curri, *Prog. Org. Coat.* **2018**, *50*, 290–301; b) E. Caponetti, V. Ciaramitaro, F. Armetta, V. Renda, L. Ercoli, M. L. Saladino, *Prog. Org. Coat.* **2021**, *151*, 106020; c) V. Renda, M. Alvarez de Buergo, M. L. Saladino, E. Caponetti, *Prog. Org. Coat.* **2020**, *141*, 105515.
- [29] D. K. Silva da Conceição, K. Nunes de Almeida, E. Nhuch, M. G. Raucci, C. Santillo, M. Salzano de Luna, L. Ambrosio, M. Lavorgna, C. Giuliani, G. Di Carlo, M. P. Staccioli, T. Falcade, H. S. Schrekker, *Herit. Sci.* **2020**, *8*, 40.
- [30] A. Dermaj, D. Chebabe, M. Doubi, H. Erramli, N. Hajjaji, M. P. Casaletto, G. M. Ingo, C. Riccucci, T. de Caro, *Corros. Eng.* **2015**, *50*, 128–136.
- [31] M. Mihelčič, M. Gaberšček, G. Di Carlo, C. Giuliani, M. Salzano de Luna, M. Lavorgna, A. K. Surca, *Appl. Surf. Sci.* **2019**, *467–468*, 912–925.
- [32] a) A. Idone, M. Gulmini, A. I. Henry, F. Casadio, L. Chang, L. Appolonia, R. P. Van Duyn, N. Shah, N. C. Silver, *Analyst* **2013**, *138*, 5895–5903; b) A. Alyami, D. Saviello, M. A. P. McAuliffe, A. Mirabile, L. Lewis, D. Iacopino, *Phys. Chem. Chem. Phys.* **2017**, *19*, 14652–14658.
- [33] L. Baij, J. Hermans, B. Ormsby, P. Noble, P. Iedema, K. Keune, *Herit. Sci.* **2020**, *8*, 43.
- [34] a) R. Wolbers, C. Stavroudis in *The Conservation of Easel Paintings* (Eds.: J. Hill Stoner, R. Rushfield), Routledge, New York, **2012**, pp. 500–523; b) R. Wolbers, *Cleaning Painted Surfaces: Aqueous Methods*, Archetype Publications **2020**.
- [35] D. Chelazzi, R. Giorgi, P. Baglioni, *Angew. Chem. Int. Ed.* **2018**, *57*, 7296–7303; *Angew. Chem.* **2018**, *130*, 7417–7425.
- [36] D. Chelazzi, R. Bordes, R. Giorgi, K. Holmberg, P. Baglioni, *Curr. Opin. Colloid Interface Sci.* **2020**, *45*, 108–123.
- [37] M. Baglioni, C. Montis, D. Chelazzi, R. Giorgi, D. Berti, P. Baglioni, *Angew. Chem. Int. Ed.* **2018**, *57*, 7355–7359; *Angew. Chem.* **2018**, *130*, 7477–7481.
- [38] a) M. Stierndahl, D. Lundberg, V. Chauhan, R. Bordes, K. Holmberg, *J. Surf. Deterg.* **2019**, *22*, 1139–1145; b) V. Chauhan, K. Holmberg, R. Bordes, *J. Colloid Interface Sci.* **2018**, *531*, 189–193.
- [39] a) B. Ormsby, J. Lee, I. Bonaduce, A. Lluveras-Tenorio in *Conservation of Modern Oil Paintings* (Eds.: K. J. van den Berg, I. Bonaduce, A. Burnstock, B. Ormsby, M. Scharff, L. Carlyle, G. Heydenreich, K. Keune), Springer Nature, Cham, **2020**, pp. 11–35; b) M. Gillman, J. Lee, B. Ormsby, A. Burnstock in *Conservation of Modern Oil Paintings* (Eds.: K. J. van den Berg, I. Bonaduce, A. Burnstock, B. Ormsby, M. Scharff, L. Carlyle, G. Heydenreich, K. Keune), Springer Nature, Cham, **2020**, pp. 477–494.
- [40] A. Casoli, Z. Di Diego, C. Isca, *Environ. Sci. Pollut. Res. Int.* **2014**, *21*, 13252–13262.
- [41] J. A. L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, *Langmuir* **2013**, *29*, 2746–2755.
- [42] R. Mastrangelo, D. Chelazzi, G. Poggi, E. Fratini, L. Pensabene Buemi, M. L. Petruzzellis, P. Baglioni, *Proc. Natl. Acad. Sci. USA* **2020**, *117*, 7011–7020.
- [43] N. Bonelli, C. Montis, A. Mirabile, D. Berti, P. Baglioni, *Proc. Natl. Acad. Sci. USA* **2018**, *115*, 5932–5937.
- [44] E. Carretti, S. Grassi, M. Cossalter, I. Natali, G. Caminati, R. G. Weiss, P. Baglioni, L. Dei, *Langmuir* **2009**, *25*, 8656–8662.
- [45] N. Bonelli, G. Poggi, D. Chelazzi, R. Giorgi, P. Baglioni, *J. Colloid Interface Sci.* **2019**, *536*, 339–348.
- [46] C. Mazza, L. Severini, F. Domenici, Y. Toumia, F. Mazzotta, L. Micheli, M. Titubante, B. Di Napoli, G. Paradossi, A. Palleschi, *Colloids Surf. B* **2020**, *188*, 11077–348.
- [47] L. Pensabene Buemi, M. L. Petruzzellis, D. Chelazzi, M. Baglioni, R. Mastrangelo, R. Giorgi, P. Baglioni, *Herit. Sci.* **2020**, *8*, 77.
- [48] A. Bartoletti, R. Barker, D. Chelazzi, N. Bonelli, P. Baglioni, J. Lee, L. V. Angelova, B. Ormsby, *Herit. Sci.* **2020**, *8*, 9.
- [49] M. Baglioni, J. A. L. Domingues, E. Carretti, E. Fratini, D. Chelazzi, R. Giorgi, P. Baglioni, *ACS Appl. Mater. Interfaces* **2018**, *10*, 19162–19172.
- [50] T. Guaragnone, A. Casini, D. Chelazzi, R. Giorgi, *Appl. Mater. Res.* **2020**, *19*, 100549.
- [51] a) M. Christensen, E. Larnøy, H. Kutzke, F. K. Hansen, *J. Am. Inst. Conserv.* **2015**, *54*, 3–13; b) E. Bobu, R. Nicu, P. Obrocea, E. Ardelean, S. Dunca, T. Balaes, *Cellulose Chem. Technol.* **2016**, *50*, 689–699.
- [52] Q. Xu, G. Poggi, C. Resta, M. Baglioni, P. Baglioni, *J. Colloid Interface Sci.* **2020**, *15*, 147–157.
- [53] H. D. Santan, C. James, E. Fratini, I. Martínez, C. Valencia, M. C. Sánchez, J. M. Franco, *Ind. Crops Prod.* **2018**, *121*, 90–98.
- [54] L. Bertrand, C. Gervais, A. Masic, L. Robbiola, *Angew. Chem. Int. Ed.* **2018**, *57*, 7288–7295; *Angew. Chem.* **2018**, *130*, 7408–7416.

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