Chemical functionalization: a valuable tool for the smart surface engineering of heterogeneous catalysts

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NEW CHEMISTRY FROM YOUNG ITALIAN CHEMISTS

Chemical functionalization: a valuable tool for the smart surface engineering of heterogeneous catalysts

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Abstract Heterogeneous catalysis plays a pivotal role in many key chemical transformations engaged in industrial productions of commodities and fine chemicals, environmental protection and renewable energy technologies. With the aim at overcoming limits dealing with the use of benchmark precious metal-based catalytic materials, metal-free carbon-based systems (eventually doped with light hetero-elements) and 2D transition metals dichalcogenides (TMDCs) have gained increasing interest among the scientific community as effective, cheap and sustainable catalysts for several challenging transformations. However, their complex structural/chemical composition poses often serious limits to the identification of the active sites engaged in the processes hence hampering any rational optimization of their performance. On this ground, chemical functionalization with well-defined moieties holds the potential to tackle these issues through a controlled engineering of surface chemico-physical/structural properties of either organic or inorganic materials. In this work, achievements in (electro)catalytic processes promoted by covalently grafted materials will be described, highlighting at the same time the key role of this *top-down* synthetic strategy in the comprehension of key structure/reactivity relationships as well as the underlying reaction mechanisms.

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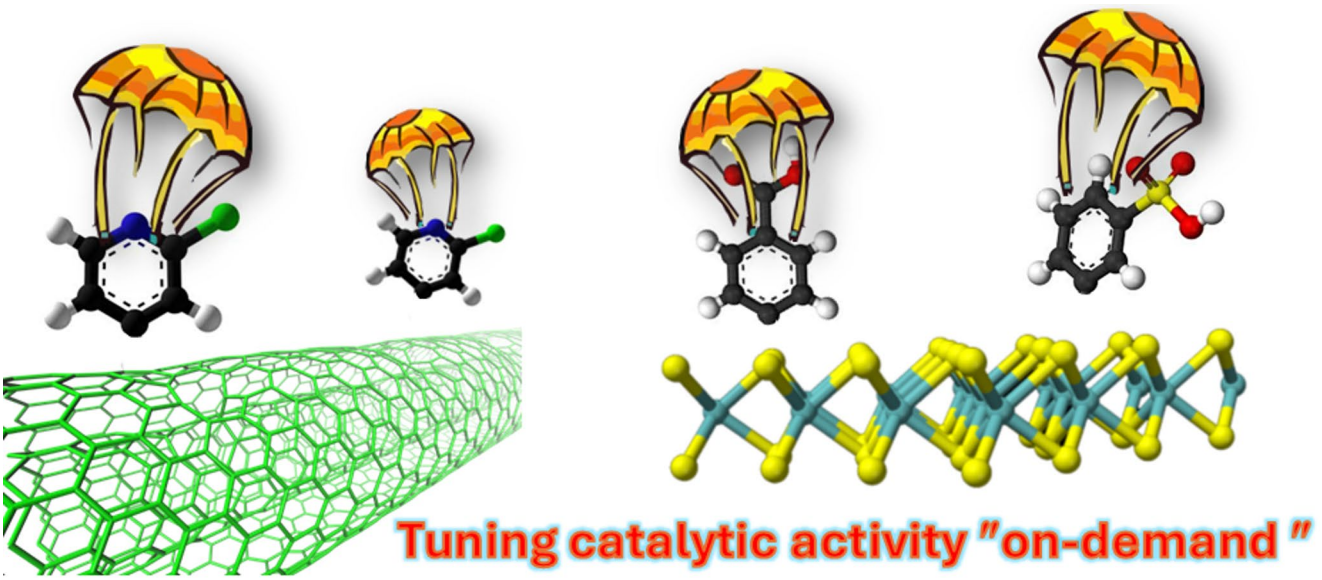
Graphical abstract



Keywords Chemical functionalization · Surface engineering · Carbon nanomaterials · Transition metals dichalcogenides · Heterogeneous catalysis

1 Introduction

Catalysis is the engine that moves our modern society. It holds a central role in many fundamental industrial processes from the bulk production of fine chemicals up to the abatement of pollution/toxic emissions as well as in many processes at the heart of renewable energy technologies (Friend and Xu 2017; Melchionna and Fornasiero 2025; Mürtz and Palkovits 2024). The development of non-critical and cheap heterogeneous catalysts represents therefore the pillar for a sustainable future. On this ground, the stringent need of moving beyond precious metal-based catalysts has boosted the development of different classes of alternative materials to be engaged in catalytic transformations with comparable or even better performance compared to classical systems of the *state-of-the-art*. Among them, metal-free carbon-based materials as such or doped with light hetero-elements (i.e., N, O, B, P, S mainly) (Sanoja-López and Luque 2025; Zhai et al. 2024) and 2D transition metals dichalcogenides (TMDCs)(Roy et al. 2024; Suman Srivastava and Khatri 2025) have emerged in the last decades for their low cost, high abundance and promising catalytic activity in many key transformations.

On carbon nanomaterials side, despite several research efforts and remarkable catalytic outcomes, one main limit is still represented by the lack of a clear-cut comprehension of their complex mechanism of action. Indeed, the nature of active sites and their ultimate role in selected catalytic processes often remain on a merely speculative ground and represent matter of controversial debates within the scientific community. As a matter of fact, classical *bottom-up* synthetic approaches used for their large-scale production (*i.e.* Chemical Vapour Deposition (CVD) or post-synthetic thermo-chemical treatments of pre-formed C-networks with heteroatom-containing precursors) are not suitable to achieve a satisfactory control on both nature and degree of the hetero-elements doping (Liu et al. 2019). Consequently, any unambiguous identification of the active sites engaged in a specific catalytic transformation is hard to be accomplished. To address this controversial matter, exohedral chemical functionalization of carbon networks offers a valuable tool for the fine tuning and full control on the final catalysts' composition other than a unique model for shedding light on the reaction mechanism at work. The comprehension of the latter is a fundamental prerequisite to the rational design and synthesis of more efficient heterogeneous catalytic materials, hence making chemical functionalization a precious tool for the future development of enabling technologies.

As for TMDCs, their atomic-scale thickness with abundance of surface/edge atoms, their rich chemical compositions featuring diverse metals/chalcogens combinations as well as their remarkable tunability have proven to be interesting properties for applications in many catalytic processes (Suman Srivastava and Khatri 2025; Zhao et al. 2022). In addition, their intrinsic polytype nature allows to

choose the most appropriate structural/electronic properties as a function of the downstream application: the thermodynamically stable, semiconductive 2 H phase (trigonal prismatic) is particularly suitable for photo- and photoelectrocatalytic applications, while the metastable, metallic 1T phase (octahedral) is featured by outstanding electronic conductivity and finds large utilization in electrocatalytic processes. TMDCs performance can be greatly boosted by their judicious structural and chemical modulation through phase, size, composition, defects, dopants, topological and heterostructure engineering. The challenge is to rationally design and control such engineering levers to maximize performance outcomes for targeted applications. In this regard, chemical functionalization of TMDCs surface with organic species has emerged as a *top-down*, tailored approach for the fine tuning and control of the surface properties of TMDCs and in turn their catalytic behavior. The highly controlled synthetic strategy provides unambiguous materials structure/reactivity relationships and a unique viewpoint on the underlying mechanism of the catalytic transformations under study with the possibility to rationally design TMDCs-based catalysts with improved performance.

This review gives an insight into the most relevant achievements in the field of heterogeneous (electro) catalysis promoted by either metal-free exohedrally grafted carbon-based materials or TMDCs hybrids covalently decorated with discrete organic moieties. The main advantages of the adopted synthetic protocols and related findings on the nature of the active species at work in targeted catalytic transformations will be analyzed and discussed.

2 Carbon-based materials

2.1 Thermic processes

2.1.1 Esters hydrolysis/synthesis, transesterification and etherification reactions

One of the first applications of carbon nanomaterials as heterogeneous catalysts involved their basic and/or acidic surface properties. On this ground, Feng's group developed already in 2007 sulfonic acid-decorated ordered mesoporous carbons (OMCs) to be exploited as efficient and reusable catalysts for condensation reactions as well as esterification of model compounds and biodiesel production (Liu et al. 2008; Wang et al. 2007). Following this pioneering work, sulfonic acids were then successively anchored on different C-networks [*i.e.*, OMCs, reduced graphene oxide (rGO) or carbon nanofibers (CNFs)] *via* classical diazonium salts chemistry and employed for esters hydrolysis and transesterification processes. Independent research groups demonstrated the superior activity and stability of such covalently grafted materials with respect to those classically prepared by indiscriminate sulfonation with concentrated sulfuric acid (Gao et al. 2015; Geng et al. 2012; Ji et al. 2011; Nongbe et al. 2017; Stellwagen et al. 2013). Milder synthetic conditions preserve indeed the porous structure of nanocarbons, hence facilitating the diffusion of long chain hydrophobic molecules such as those involved in biodiesel production. In addition, the higher accessibility of surface sulfonic groups allows to outperform benchmark systems such as Amberlyst-15 and previously reported sulfonated carbons.

More recently, Malaika and co-workers demonstrated the effectiveness of sulfonic acid decorated carbon fibers (CFs) also in glycerol etherification with tert-butyl alcohol to obtain mono-, di- and tri-substituted products (namely MTBGE, DTBGE and TTBGE, respectively) that are of potentially high interest in the sustainable fuels sector (Ptaszyńska et al. 2023). Interestingly, authors prepared two sets of catalysts obtained either with classical CFs treatment with concentrated sulfuric acid or by means of covalent functionalization with aryldiazonium salts derivatives. As shown on Fig. 1, the latter showed highly enhanced catalytic activity in glycerol conversion as well as the higher amount of di-substituted products that these authors attributed to the higher loading of sulfonic groups available at the material surface.

Beyond acidic functionalities, transesterification reactions have successfully been conducted also with nanocarbons grafted with basic surface groups. In particular, Su and Tessonnier developed a series of CNTs decorated with tertiary aliphatic amines to be exploited as catalysts for biodiesel production (Tessonnier et al. 2009; Villa et al. 2009, 2010). Their functionalization approach demonstrated to be highly efficient and avoid side-reactions at CNTs surface. At odds to what observed with less selective functionalization approaches from the literature (*i.e.*, CNTs oxidation followed by activation of carboxylic acid and amine nucleophilic substitution) known to introduce side-functional groups responsible for the reduction of catalyst selectivity, their elegant and clean decoration protocol allowed a fine control on the grafted amine groups, hence achieving optimal catalytic outcomes.

2.1.2 C-C bond formation

Carbon-carbon bond formation represents a fundamental process in organic synthesis and both acid and base decorated carbon nanomaterials have been successfully exploited as durable and reusable catalytic systems for the process. Already in 2010, poly(styrene sulfonic acid)-grafted carbon nanotubes have been employed in hydroquinone

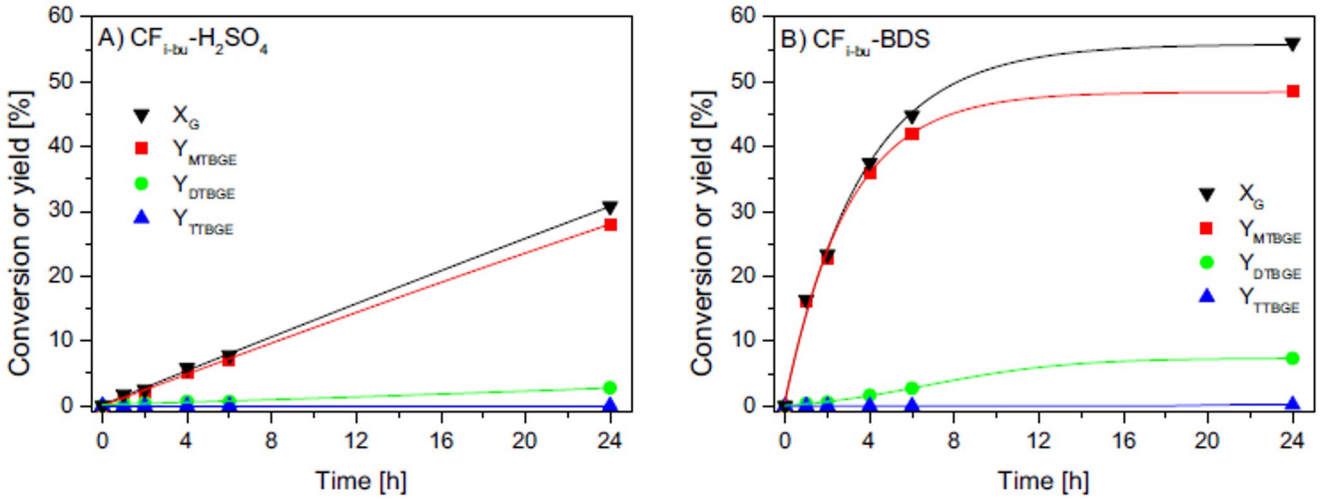


Fig. 1 Conversion of glycerol (X_G) and yields (Y) of individual products in the glycerol etherification performed with tert-butyl alcohol over (**A**) CF_{i-bu}-H_2SO_4, (**B**) CFi-bu-BDS. Reproduced from (Ptaszyńska et al. 2023) with permission from Springer Nature

alkylation with tert-butanol (Liu et al. 2010). Authors demonstrated the effectiveness of their catalytic material that shows higher activity and selectivity with respect to classical CNTs systems where sulfonic moieties are introduced by an indiscriminate acidic treatment. In the same period, surface hydroxyl groups present at the fullerene surface (C_{60}-fullerenol) were shown to promote a series of C-C bond formation processes due to the ability of -OH groups to fruitfully interact with reactants throughout hydrogen bonds (Niu et al. 2011). In particular, C_{60}-fullerenol exhibited high catalytic activity in Henry reaction and aldol condensation with complete selectivity for nitro alcohols and β-hydroxyl ketones, respectively. Finally, hydrogen bond interactions allowed to obtain optimal catalytic results also in Michael addition and Friedel-Craft reaction making C_{60}-fullerenol a highly versatile catalytic system. A few years later, the same group reported a series of amino-decorated fullerenes to be scrutinized in Knoevenagel condensation (Sun et al. 2015). The basic surface character of their materials promoted the process with several substrates ensuring high catalytic activity and functional groups tolerance. In 2016, we reported enhanced catalytic performance in the same process by means of highly basic aziridine groups covalently anchored to CNTs (MW@N^{Az}) (Tuci et al. 2016a). A two-step synthetic procedure where *tert*-butyl azidoformate was first anchored on multi-walled carbon nanotubes (MWCNTs) surface by a [2 + 1] cycloaddition followed by a controlled thermal decomposition of the carbamate moiety, allowed us to obtain aziridine decorated CNTs with relatively high -NH groups loading. The as-prepared catalysts exhibited excellent activity and stability in Knoevenagel condensation of several substrates with performance exceeding that reported for classical N-doped carbon nanomaterials prepared by *bottom-up* approaches (Fig. 2).

Finally, Tagmatarchis and co-workers succeeded in the anchoring of proline groups either on fullerene (Chronopoulos et al. 2014) or oxidized MWCNTs (Chronopoulos et al. 2015) and their exploitation in enantioselective aldol condensation between acetone and 4-nitrobenzaldehyde. Exohedral functionalization ensured a complete control on the chemical nature of grafted N-moieties directly engaged on the ultimate materials catalytic performance. For instance, authors obtained the desired chiral aldol product with high enantioselectivity when the active proline unit was connected to fullerene throughout a flexible chain. The latter was indeed necessary for proline to adopt the ideal orientation for maximizing enantioselective aldol condensation. Remarkably, the nature of carbon support allowed authors to perform the process also in aqueous media with higher activity with respect to benchmark organocatalysts such as L-proline and L-4-hydroxyproline even if with lower enantiomeric excess.

2.1.3 CO_2 valorization processes

Carbon dioxide (CO_2) is nowadays considered not only a waste but rather a useful, inexpensive and abundant C_1 synthon for the production of added-value products with the assistance of a proper catalyst (El-Gendy et al. 2025; Hu et al. 2025). One of the first approaches developed for CO_2 valorization is represented by its addition to epoxide derivatives to produce cyclic carbonates, a class of widely used compounds employed as polar aprotic solvents and raw materials for plastics engineering (Yan et al. 2023). On this ground, since hydrogen bonding between catalyst and epoxide was found to be a key factor for promoting CO_2 cycloaddition, Cao and Song's group exploited the aforementioned hydroxyl groups-rich C_{60}-fullerenol (see Sect.

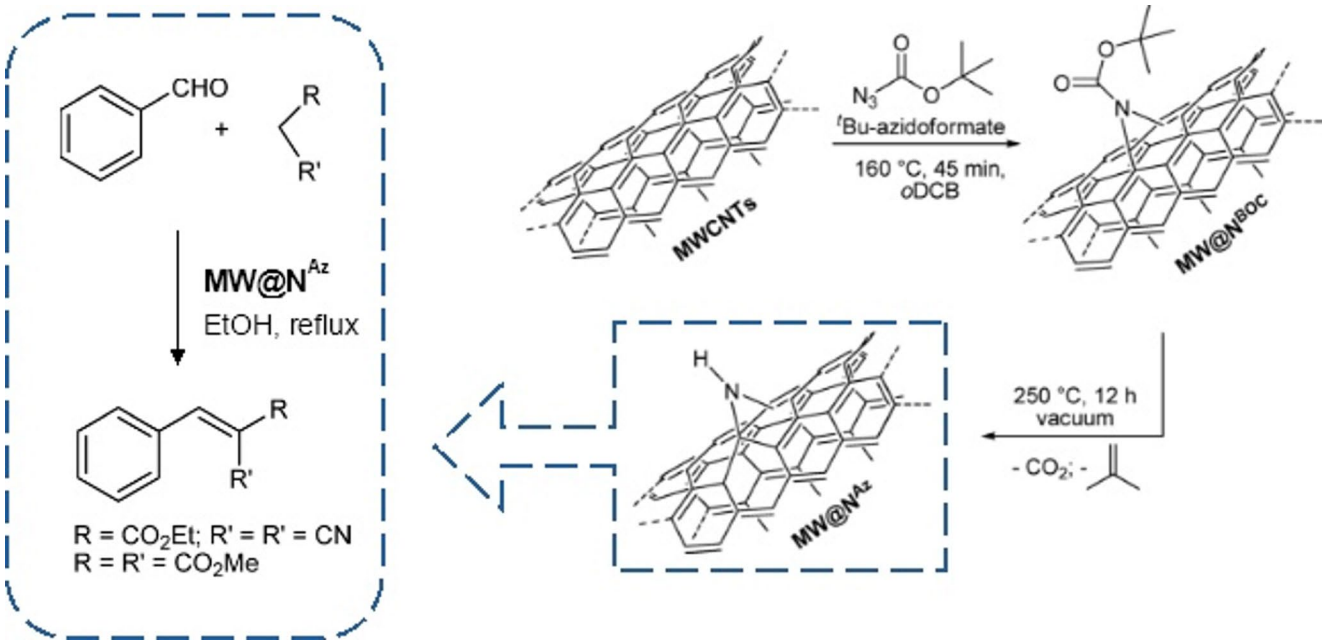


Fig. 2 Sidewall functionalization of MWCNTs by [2+1] cycloaddition followed by controlled thermal decomposition of **MW@N^{BOC}** to give **MW@N^{Az}** and its exploitation in Knoevenagel condensation. Reprinted (adapted) with permission from (Tuci et al. 2016a, b). Copyright 2016 American Chemical Society.

2.1.2) as a heterogeneous metal-free system for the process with excellent activity in the formation of propylene carbonates starting from propylene oxide (Sun et al. 2014). On the same line, Yin and co-workers developed in 2015 a multi-functional graphene oxide (GO) material bearing silanol groups, quaternary ammonium salts and amines (Lan et al. 2015). The material was straightforwardly obtained by GO silylation with chlorine-terminated silanes followed by nucleophilic attack of tertiary amines. The superior performance of the as-prepared catalyst towards cycloaddition of CO_2 to propylene oxide was attributed to the combined action of amines, performing as adsorption/activation sites for CO_2, and silanol groups able to activate propylene oxide stabilizing the ring-opened oxirane before the intramolecular CO_2 addition/cyclization step. In light of the proven beneficial effect of quaternary ammonium salts on the process, GO and oxidized CNTs were successfully decorated with amino-functionalized imidazole ionic liquid (IL) (Lu et al. 2021) or quaternary ammonium chlorides (Baj et al. 2014), respectively, and successfully exploited in CO_2 cycloaddition to epoxides. In particular, Baj and co-workers found an interesting correlation between catalytic activity and chemical nature of ammonium salts grafted groups (*i.e.*, the length of both alkyl substituents in the quaternary ammonium moieties and the spacer chain) as well as a synergic effect between carboxyl and ammonium moieties anchored on carbon nanotubes. Authors observed the best performance with short (2 carbon atoms) and long (10 atoms) grafted moieties, while middle-sized spacer groups (6 atoms) resulted as not suitable. On the other side, the length of the alkyl chain on the ammonium salt was found to have a minor impact, with ethyl and methyl groups performing slightly better than butyl ones.

Quinazoline-2,4(1 H,3 H)-diones represent an important class of pharmaceutical intermediates that are commonly prepared reacting either anthranilic acid derivatives with urea, anthranilamides with phosgene or anthranilic acid with potassium cyanate/chlorosulfonyl isocyanate with the obvious drawbacks of reagents toxicity (Nikpour and Paibast 2005; Shi et al. 2007; Vorbrüggen and Krolikiewicz 1994; Willis et al. 2006). As an alternative route, they can be synthesized from carbon dioxide and 2-aminobenzonitrile in the presence of a base. On this regard, in 2015 Jain's group prepared carbon nanofibers (CNFs) decorated with 2,6-dimethylpyridine for their exploitation in the synthesis of quinazoline-2,4(1 H,3 H)-diones (Kumar et al. 2015). Authors demonstrated the high efficiency of their system for the synthesis of variably substituted quinazoline-2,4(1 H,3 H)-diones in water medium. Noteworthy, while CO_2 reacted with 2-aminobenzonitrile in 91% yield with functionalized CNFs, a physical mixing of the nanomaterial with the same pyridine derivative gave rise to a moderate yield (39% only) of quinazoline-2,4(1 H,3 H)-dione, hence underlining the importance of the covalent linking of pyridine moieties to CNFs surface.

Catalytic CO_2 conversion into methanol represents a highly desirable process capable of transforming a greenhouse gas into a synthetic fuel that can be exploited as

an alternative energy source (Khalil et al. 2025). On this ground, we presented in 2017 the first example of a robust, heterogeneous catalyst for CO_2 chemical reduction to methanol (Tuci et al. 2017). In particular, pyridine-decorated MWCNTs demonstrated excellent performance in the process, with turnover numbers close to those claimed for other metal and metal-free homogeneous systems of the *state-of-the-art*. Noteworthy, an excess of free pyridine (as a homogeneous catalyst) did not show any appreciable catalytic performance under the optimized reaction conditions, hence unambiguously demonstrating the existence of a synergistic and beneficial effect between the C-nanocarrier and the covalently grafted pyridinic groups. The clear-cut identity of the latter facilitated the elucidation of the presumed mechanistic path outlined on Fig. 3. Supported by model DFT calculations we demonstrated for the first time the key role played by CNTs as an electronic reservoir for the dangling pyridine active arms engaged in the catalytic cycle.

Finally, very recently, Liu and co-workers reported amino-functionalized CNTs able to promote N-formylation reactions in the presence of hydrosilanes (Guo et al. 2025). In particular, polyethylenimine (PEI) was grafted *via* classical amidation reaction on oxidized nanotubes and exploited in N-formylation of anilines with catalytic performance comparable to that reported for transition metal-based homogeneous catalysts. Authors showed that increased basicity and surface defects were beneficial for CO_2 adsorption and mass transfer, hence favoring catalytic activity.

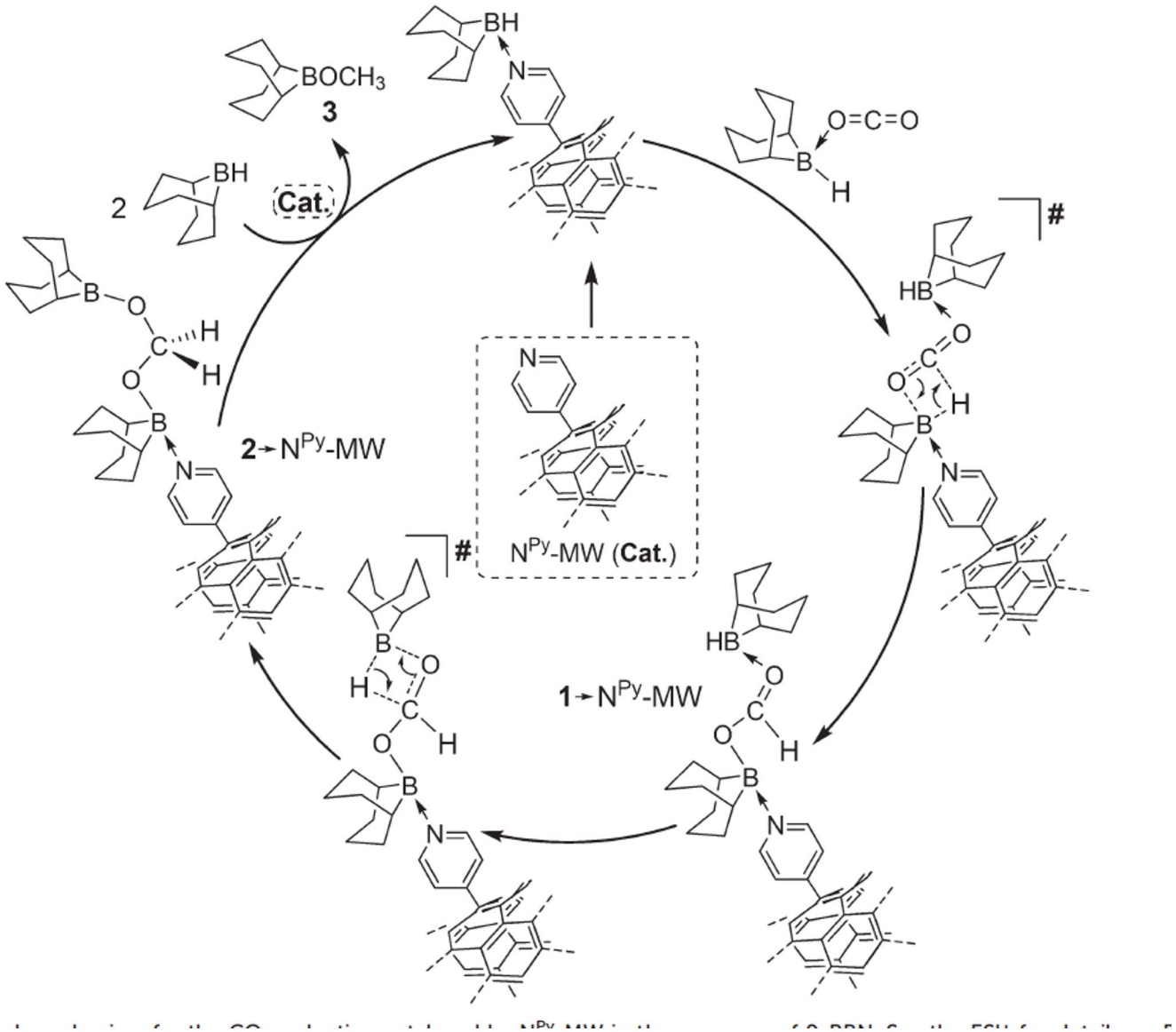


Fig. 3 Proposed mechanism for the CO_2 reduction catalyzed by $\mathbf{N^{Py}}$**-MW** in the presence of 9-BBN. Reproduced from Ref. (Tuci et al. 2017) with permission from the Royal Society of Chemistry

2.1.4 Other thermic processes

Covalently decorated carbon nanomaterials have been also employed as oxidation catalysts. In particular, a well-known oxidation promoter such as N-hydroxylphtalimide (NHPI) has conveniently been anchored on different carbonaceous supports and used for the aerobic oxidation of benzylic hydrocarbons and cyclic alkenes (Blandez et al. 2018). To this end, NHPI was grafted either to MWCNTs, activated carbon (AC) and diamond nanoparticles (DH) through esterification. Authors demonstrated the central role of the chosen support, with higher catalytic efficiency registered for the NHPI/DH system. Due to the radical nature of the oxidation process, authors postulated a positive effect of the more inert DH surface to the generation and lifetime of radicals without interferences with the C-carrier surface. On the contrary, the conjugated and C_{sp2} enrich surface of MWCNTs and AC intercepted more easily the generated radical species hence preventing their action for oxidation. The nature of the support is therefore of pivotal importance in the process and requires to be accurately selected depending on the specific downstream catalytic application. In 2019, we reported a series of amino-decorated fullerenes (C_{60}) and graphene oxide (GO) as sustainable and efficient catalysts for glucose isomerization to fructose, a key process in the production of renewable chemicals from starch and cellulose (Chen et al. 2019). GO systems showed worse fructose yield respect to their fullerenes counterpart most likely due to mass transfer limitations in light of amine groups confinement on the material's defects and pores. On the other hand, C_{60} exhibited a well-defined morphology and admitted full reagent access thanks to the presence of tailored surface grafted functionalities introduced *via* a simple and well-consolidated functionalization protocols. The adopted *top-down* approach proved the crucial role of -OH groups in creating an ideal polar microenvironment that assists the solvation of grafted amine moieties while increasing their affinity toward the substrate. Indeed, intermolecular hydrogen bonding was thought to facilitate the intramolecular H-bond breaking among the sugar units.

2.2 Electrochemical processes

2.2.1 Oxygen reduction reaction (ORR)

Oxygen Reduction Reaction (ORR) represents the cathodic process at the heart of fuel cells, devices deputed to produce CO_2-free energy and contribute to the global energy transition. Pt-group metals catalysts still represent the benchmark systems for the process, and several research efforts have been devoted among the scientific community to replace them with low cost and sustainable alternatives. Since the seminal report by Dai and co-workers in 2009, (Gong et al. 2009) where in-situ prepared N-doped MWCNTs were demonstrated to be able to promote Oxygen Reduction Reaction (ORR), a huge number of studies reported N-doped carbon nanomaterials exploited as metal-free ORR catalysts. Other than remarkable ORR performance, metal-free systems generally demonstrated higher durability with respect to classical platinum-group metals (PGM)-based catalysts and complete methanol tolerance, an essential prerequisite for their successful exploitation at the cathode of direct methanol fuel cells. However, only a few papers deal with materials prepared through chemical functionalization with well-defined N-moieties that allows to finely control active sites chemical nature hence offering a privileged viewpoint on the underlying reaction mechanism. In 2011, Dai and co-workers prepared CNTs decorated with poly(diallyldimethylammonium chloride) (PDDA) that showed remarkable electrocatalytic activity imputed by these authors to the extended positive charge induced by ammonium groups present in the polyelectrolyte backbone (Wang et al. 2011). A few years later, Wang's group covalently linked nitrobenzene moieties to graphene with the aim of studying electronic effects on ORR performance (Dou et al. 2014). They found that the presence of strong electron-withdrawing groups boosted charge transfer from graphene to grafted moieties, favoring the overall process by increasing both current density and onset potential. In the same period, we prepared a series of MWCNTs covalently grafted with different N-heterocycles for their exploitation in alkaline ORR. Our strategy relies on the precise control of the chemical nature of N-active sites engaged in the process with the aim at shedding light on the controversial structure-reactivity relationship of this class of materials. Our studies unambiguously demonstrated the key role of carbon atoms adjacent to pyridine moieties in activating molecular O_2 and promote a $4e^-$ reduction pathway (Tuci et al. 2013, 2014, 2016b). A number of variably substituted pyridine moieties have been grafted to CNTs surface generating small variations of the atomic charges on the N-proximal carbon atoms of the heterocycles. Noteworthy, we found a rational trend between the electronic charge density distribution at the grafted N-heterocycles (Bader charge) and their final control on the potential value at which ORR started (onset potential). This phenomenological trend was attributed to the variation of the O_2 and/or its reduction intermediates adsorption energy onto the catalytically active sites (C atoms adjacent to pyridinic N). The key role of pyridinic N sites on ORR performance of carbon nanomaterials was also confirmed a decade later in the work by Titirici and Jones' teams (Xu et al. 2023). They prepared pyridine-decorated CNTs by cycloaddition of in-situ formed metastable pyridine intermediates and exploited them in ORR. Besides

reaffirming the active role of pyridinic moieties on the process, they found that high functionalization levels (up to 8 wt.%) translate into negative structural effects, such as poor electrical conductivity and reduced surface area, that resulted detrimental for ORR performance.

Beyond pyridinic sites, other N-functionalities have also been found to promote the $4e^-$ ORR. In 2016 we found that aziridine-decorated MWCNTs ($MW@N^{Az}$, see Sect. 2.1.2) were optimal metal-free electrocatalysts for the process (Tuci et al. 2016a, b). The covalent insertion of -NH groups onto CNTs sidewall was indeed claimed to generate a net redistribution of the electronic charge density at the N-neighboring carbon sites hence fostering O_2 activation and its successive reduction. The following year, Kim and co-workers developed amide-decorated rGO by classical oxidation/exfoliation of graphite followed by amidation of carboxylic groups available at the surface of graphene oxide and reduction with $NaBH_4$. Diamines such as 1,4-diaminobutane and 1,4-diaminobenzene were selected in order to obtain covalent junctions among different rGO layers and create hierarchical porous structures (Ahmed and Kim 2017a, b Ahmed and Kim 2017a, b). The increased SSA and conductivity as well as the facile interlayer charge transfer were claimed as key factors able to boost ORR performance of decorated materials.

Other than complete ORR, the partial 2-electrons oxygen reduction to hydrogen peroxide (H_2O_2) has gained great attention among scientific community. H_2O_2 is a product of primary importance with increasing world demand that is currently obtained through the energy-intensive, multi-step anthraquinone process. On this ground, the $2e^-$ selective electrocatalytic ORR has emerged as an alternative, cost-saving and sustainable technology (Deng et al. 2024). In 2019 Khataee et al. developed a hybrid material through covalent grafting of plain fullerenes to CNTs (Hasanzadeh et al. 2019). The as-prepared C_{60}-CNTs composite was found to promote H_2O_2 electrosynthesis due to the enhanced specific surface area and electron transport properties of the sample as well as to the increased content of C-sp^3 defective sites. Among hetero-doped materials, O-functionalities have been found to promote the selective $2e^-$ electrocatalytic ORR with the first reports dealing with simply oxidized materials bearing multiple surface O-moieties that substantially hampered any rational identification of the nature of active sites (Han et al. 2020; Kim et al. 2018; Lu et al. 2018; Tuci et al. 2024). To shed light on this matter, we recently developed MWCNTs decorated with tailored O-groups (*i.e.*, -COOH, -OH, ethers and ketones) and tested them with respect to their ability to perform ORR. In contrast with another report dealing with the electrocatalytic performance of tightly related functional materials, (Lee et al. 2023) the clear-cut identity of grafted groups allowed us to unambiguously identify phenol moieties - classically overlooked from the literature - as key functionalities for the process ensuring high selectivity (up to 80% for H_2O_2) as well as optimal onset potential (Fig. 4) (Tuci et al. 2023). Moreover, at odds to what reported on related literature works, (Lu et al. 2018; Zhou et al. 2019) we demonstrated that activity and selectivity in the process did not linearly correlate with the materials O-content but rather with the chemical nature and

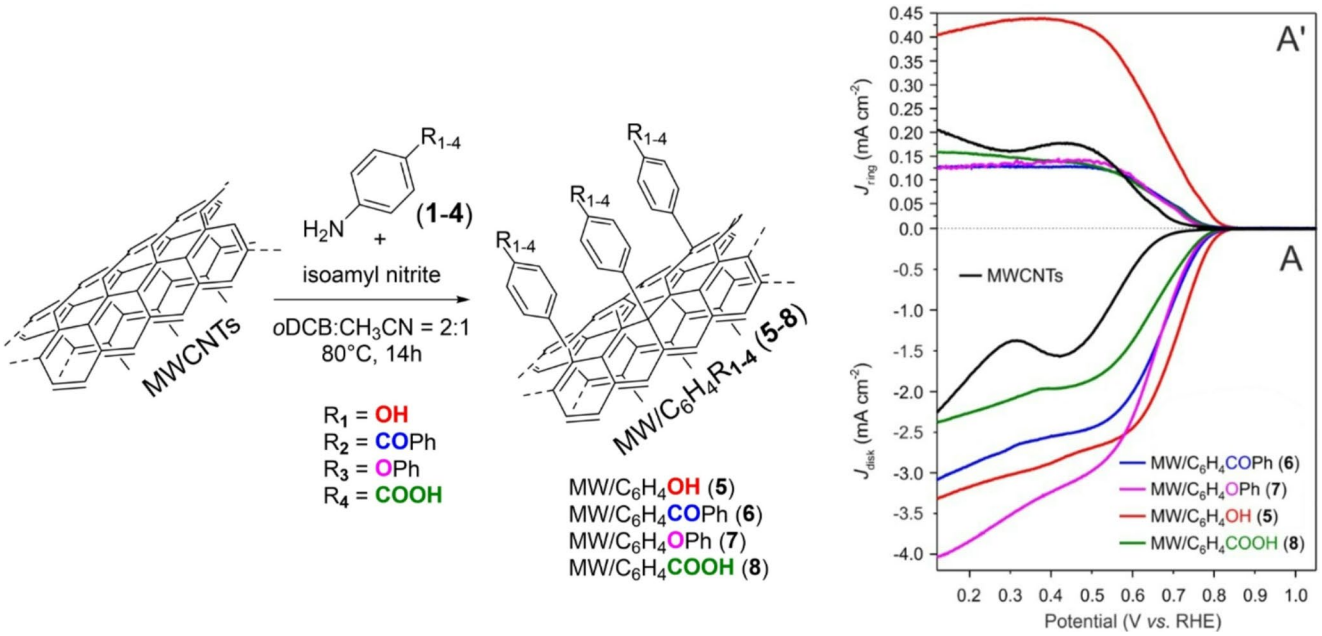


Fig. 4 Exohedral functionalization of MWCNTs with variably O-containing aniline derivatives and their corresponding **A**) Disk and **A**) Pt-ring RRDE Linear Sweep Voltammograms (LSVs) at comparison with pristine MWCNTs registered in an O_2-saturated 0.1 M KOH aqueous solution at an electrode spin rate of 1600 rpm. Reproduced with permission from (Tuci et al. 2023), Wiley-VCH GmbH

specific electronic properties of the surface exposed active sites. Analogously to what observed earlier for pyridinic sites in ORR (see above), DFT calculations allowed to correlate process activity and selectivity with the Bader charge of C-atoms neighboring O-moieties. In particular, C_α to hydroxyl groups of phenols ensured a favorable interaction with O_2 boosting the first electron transfer (rate determining step) at low overpotential values and bound the key intermediate HOO* with the "just right" strength for the second electron transfer to occur before O-O breaking (that would be expected to generate complete reduction to OH^- through a $4e^-$ path).

2.2.2 Hydrogen evolution reaction (HER)/water splitting

Water splitting is widely recognized as one of the greener approaches for sustainable large-scale hydrogen production (Fei et al. 2025; Oni 2025). On this ground, carbon-based metal-free catalysts are highly promising systems for the process (Ahmed et al. 2025). Li's group developed a series of MWCNTs decorated with imidazolium ionic liquid (IL) to be exploited as metal-free electrocatalysts for Hydrogen Evolution Reaction (HER), the cathodic process in devices for water electrolysis (Li et al. 2016, 2021). Authors found that grafted ionic liquids (ILs) boosted the hydrogen evolution reaction (HER) in two ways: they exhibited superior hydrogen adsorption and facilitated electron transfer. By using well-defined molecular structures, these researchers showed that the identity of the IL's counter-anion was critical. Electron transfer increased with the anion's hydrogen-bond basicity, following the trend $Cl^- > Br^- > BF_4^- > PF_6^-$. This correlation identified hydrogen-bond basicity as a coherent descriptor for optimizing HER performance in this class of metal-free electrocatalysts. Later on, the same authors (Li et al. 2018) and independently Sathe's group (Narwade et al. 2021) developed MWCNTs decorated with ethylenediamine fragments linked to the nanomaterial via an amide bond and used these metal-free systems for HER and overall water splitting, respectively. In both cases the activity was attributed to N lone pairs available within the grafted ethylenediamine dangling arms that were claimed to foster charge transfer hence improving the overall electrochemical activity, both on the HER and OER side.

2.2.3 CO_2 reduction reaction (CO2RR)

Electrochemical CO_2 reduction (CO2RR) holds great promise among carbon dioxide utilization approaches because of the mild operating conditions required and the possibility of being fed by electricity from renewable sources, hence making it a fruitful strategy for chemical energy storage (Fang et al. 2025). CO2RR promoted by metal-free, carbon-based materials is a challenging topic that has attracted the interest of catalysis community since a relatively long time (Kohli et al. 2025; Wang et al. 2024). However, despite several research efforts, the real nature of catalytically active sites engaged in the process remains a matter of debate hence making chemical functionalization an attractive and precious tool.

In 2018, GO was decorated with different pyridinic cores by classical amidation/esterification of carboxylic groups (Yuan et al. 2018). Authors found a direct correlation between electrocatalytic performance and pyridinic N-loading together with an unusual selectivity towards C_2-C_3 products such as ethanol and acetone with Faradaic Efficiencies (FE) up to 36 and 9%, respectively. Selectivity was tentatively attributed to N lone pairs available at the pyridinic moieties that stabilized *CO intermediates allowing C-C dimerization rather than CO release. Anyhow, authors themselves admitted the high complexity of their material due to the presence of other O-containing groups and amide/ester fragments introduced upon the material functionalization together with the grafted pyridinic groups. As a consequence, a cooperative/synergistic role of these species available at the material surface could not be definitively ruled out and any conclusion on the actual reaction mechanism at work in the process and/or a clear-cut catalyst structure-reactivity correlation unavoidably remained speculative. In the same year, we reported the ability of aziridine-decorated MWCNTs ($MW@N^{Az}$, see Sect. 2.1.2) to chemo-selectively reduce carbon dioxide to CO with remarkably higher productivity than that obtained with pyridine-decorated counterparts (often claimed in the literature as the active species for CO2RR) (Tuci et al. 2018). The more precise control on the chemical nature of N-containing functionalities covalently grafted at the carbon nanomaterials surface allowed us to draw important mechanistic outcomes. In particular, we showed that the process driving force derived from the carbonation of the highly basic NH-aziridine moieties anchored to CNTs with the generation of a zwitterionic form (Fig. 5). The as obtained "chemical" CO_2 activation changed its geometry from linear to bent, hence facilitating the first and kinetically sluggish electron transfer step (rate determining step, RDS of the process).

A few years later, we prepared MWCNTs decorated with pyrrole rings or differently substituted pyridine cores in order to finely tune the electronic charge density distribution at the covalently linked N-heterocycles (Tuci et al. 2020). CO_2-to-CO productivity was lower respect to that measured with NH-aziridine groups, but the fine control on the chemical nature of grafted moieties allowed to unambiguously demonstrate the superior performance of pyridinic moieties compared to pyrroles while unveiling at the same time the existence of a "volcano"-type trend correlating FE_{CO}

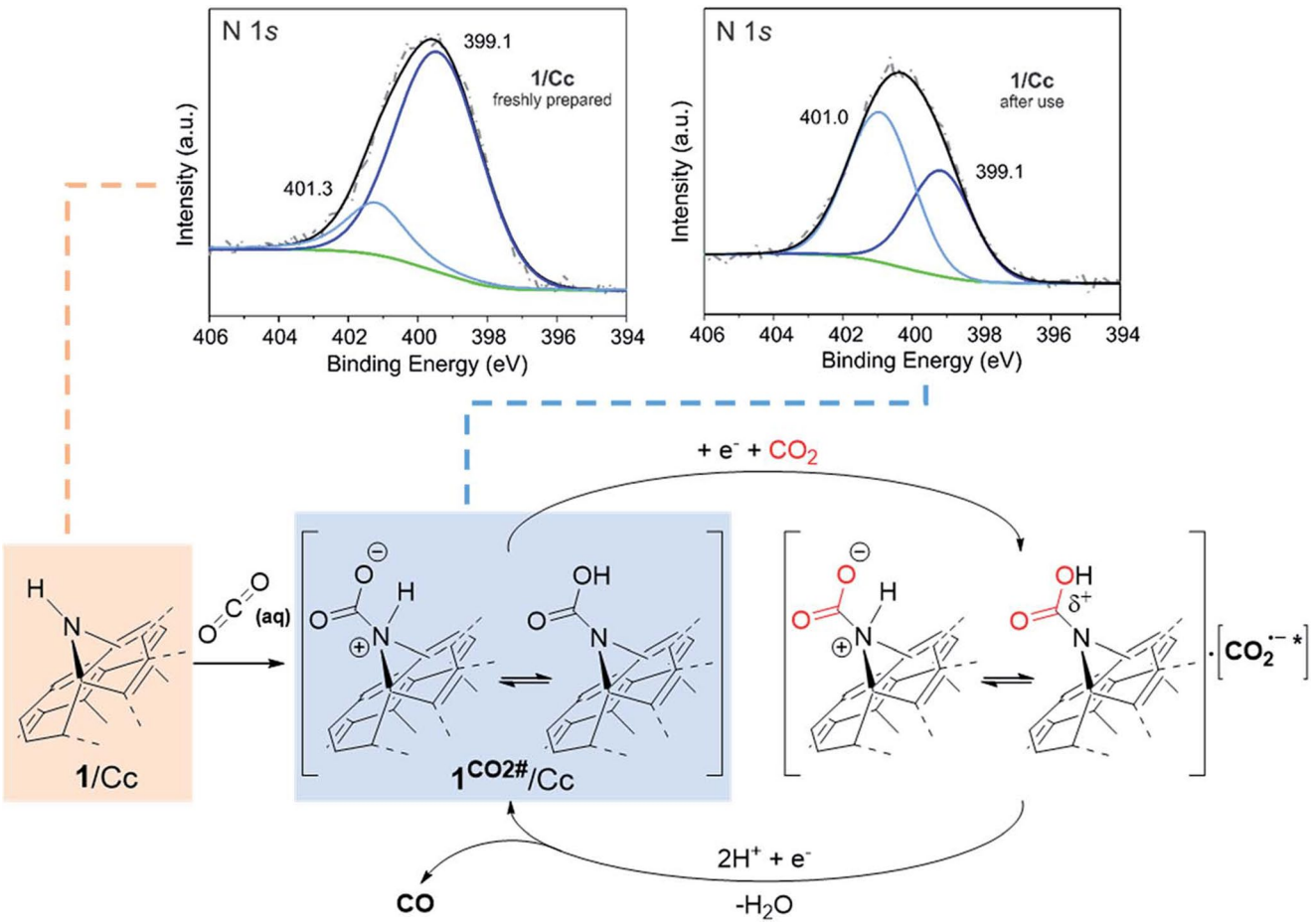


Fig. 5 CO_2 electroreduction process via $CO_2^{(aq)}$ chemisorption to NH-aziridine groups (amine carbonation - $CO_2^{\#}$). A first $1e^-$ reduction step takes place on $CO_2^{\#}$ followed by aziridine-NH re-carbonation and stabilization of the radical ion ($CO_2^{\cdot -*}$). An additional $1e^-$ reduction gives rise to [CO + H_2O] and regenerates $CO_2^{\#}$ ending the catalytic cycle. N 1s core regions and relative fits for the high resolution XPS spectrum of **1/Cc** before (left) and after (right) the electrocatalytic run are also shown in the upper part of the scheme. N 1s components at higher binding energies (401.3 and 401.0 eV) are attributed to the formation of amine carbonate whereas components at 399.1 eV belong to free aziridine groups. Reproduced from (Tuci et al. 2018) with permission from the Royal Society of Chemistry

with the electronic properties of the selected N-containing groups at the CNTs surface. Experimental evidences combined with DFT calculations allowed to infer that both the basic character of each heterocycle as well as the electronic charge distribution at the N-neighboring carbon atoms played a role on the ultimate electrocatalytic performance of these metal-free systems. While the former feature was supposed to foster CO_2 interaction with N-dangling groups, the latter was expected to stabilize the process intermediates hence providing a useful base for the rational preparation of more catalytically active systems for the process.

3 Transition metal dichalcogenides (TMDCs)

The first attempts to TMDCs surface engineering through covalent functionalization for catalytic purposes are relatively recent and deal with the exploitation of the 2-H semiconducting phase. In this regard, Tascon's group decorated 2-H MoS_2 nanosheets with acetic acid moieties by means of chemical (Paredes et al. 2016) or electrochemical (García-Dalí et al. 2021) grafting strategies. The as obtained composites were exploited for nitroarene and organic dyes reduction with $NaBH_4$ as a reductant. Functionalized MoS_2 offered enhanced performance with respect to undecorated materials considering its higher dispersibility in aqueous medium and increased accessibility to active sites. Indeed, especially for electrochemically decorated materials, the derivatization process favored the generation of sulfur vacancies - the postulated catalytic active sites for nitroarenes/dyes reduction - and the moderate steric hindrance of anchored carboxylic species did not hinder reagents update.

Due to the metallic character of TMDCs 1T phase, this polymorph offers high potential for electrocatalytic applications. The main drawback is linked to its intrinsic instability

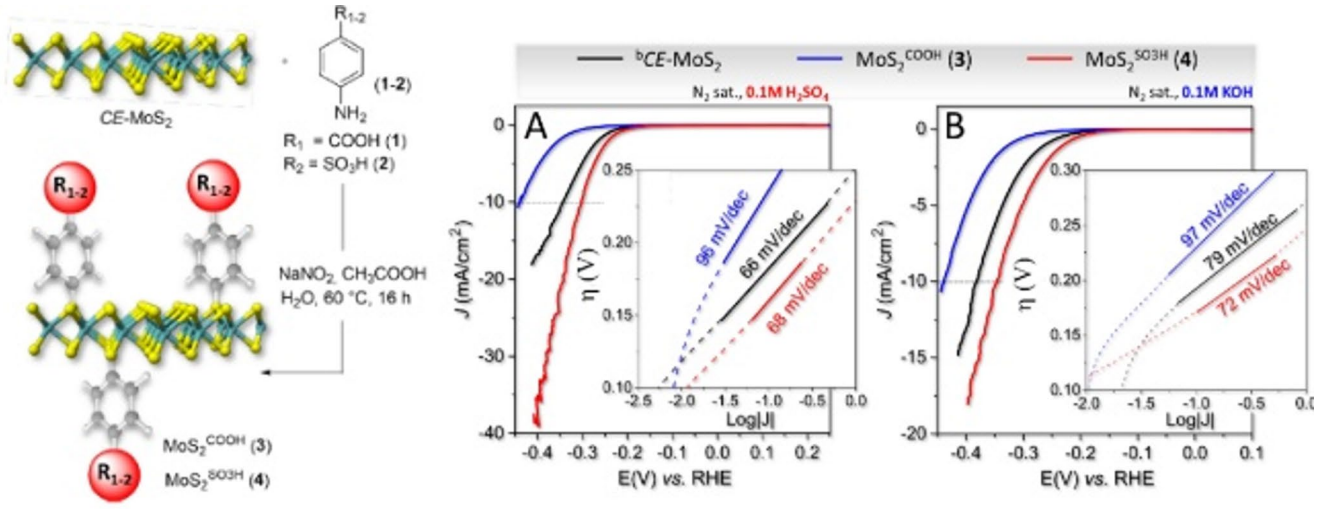


Fig. 6 (left) Exohedral Covalent Functionalization of *CE*-MoS_2 via Aryl-Diazonium Salt Chemistry. (right) Electrocatalytic HER performance of different samples in acidic (**A**) and alkaline (**B**) electrolytes. *iR*-corrected LSVs were recorded in N_2-saturated 0.1M H_2SO_4 (**A**) and N_2-saturated 0.1 M KOH (**B**) at a scan rate of 5 mV/s. The insets display Tafel analysis derived from *iR*-corrected LSVs obtained at a scan rate of 0.5 mV/s. Reproduced with permission from (Pugliesi et al. 2025), American Chemical Society

and its tendency to revert to the more thermodynamically stable, semiconductive 2-H phase. On this regard, chemical functionalization of 1T-TMDCs is a "*one stone*, *two birds*" approach because it stabilizes the 1T metallic phase, modulates TMDCs surface properties and enhances its electrocatalytic performance. In 2018, a pioneering paper by Miller and co-workers reported 1T-MoS_2 chemical grafting of different aromatic species bearing either electron-withdrawing or donating substituents by means of classical aryldiazonium salts protocols (Benson et al. 2018). Their results showed for the first time a strong correlation between the electronic properties of anchored species and their ultimate HER performance. In particular, donating groups were demonstrated to boost electron-transfer kinetics while electron-withdrawing organic substituents removed charge from MoS_2 nanosheets thus lowering the activity in HER. A few years later, a Chinese team prepared 1T-MoS_2 covalently decorated with *n*-butyl groups and exploited them in HER as well as a counter electrode catalyst in DSSC (Dye-Sensitized Solar Cell) (Vedhanarayanana et al. 2021). Improved performance with respect to undecorated MoS_2 were attributed both to electronic factors and the induced interlayer spacing among MoS_2 flakes. In 2024 Maroneze's group prepared MoS_2 decorated with acetic acid moieties upon reaction with the corresponding iodide (Hostert et al. 2024). Quite strangely, the 2-H/1T ratio was reported to increase after MoS_2 functionalization but the reduction of the metallic phase was claimed to be compensated by the surface electronic effects induced by the grafted organic species that improve the overall HER performance. The latter was ascribed by authors to the decrease in charge transfer resistance (as measured from EIS analyses) and to the optimal hydrogen adsorption free energy (ΔG_H) as argued by DFT calculations. Very recently, we investigated MoS_2 decorated either with strong or weak acid moieties for their exploitation on HER in a wide pH range (Pugliesi et al. 2025). Indeed, the alkaline environment is known to offer important technical and economic benefits with respect to acidic media, but HER kinetics are much slower at high pH with highly reduced electrocatalytic efficiencies (Wang et al. 2020; Xu et al. 2022). To tackle this issue we developed MoS_2 nanoflakes decorated with Brønsted acid-capped aryl fragments, namely aromatic carboxylic (Ar-COOH) and sulfonic (Ar-SO_3H) acids. Our electrocatalytic outcomes revealed the superior ability of MoS_2^{SO3H} to boost HER efficiently regardless of the electrolyte pH (Fig. 6). In contrast to literature, electron withdrawing substituents on the aryl grafted moieties did not inhibit HER performance hence proving that the electronic donating/withdrawing character of the decorating species is not the unique descriptor of HER activity of MoS_2 hybrids. By means of DFT calculations and molecular dynamics studies, it is inferred that sulfonic groups improve the material hydrophilicity and create an ideal surface microenvironment that boosted water tunneling and its activation/dissociation at the electrocatalyst surface, thereby increasing HER kinetics even under alkaline media where water dissociation typically represents the rate limiting step.

Apart from the 1T-phase, the semiconducting 2-H polymorph of TMDCs is highly attractive for photo(electro)catalytic applications. In 2020 Agnoli, Blanco *et al*. decorated $MoSe_2$ nanosheets with different thiolated-end capped tetraphenyl porphyrins (well-known for their light-harvesting properties) and exploited them in the photo-assisted HER

(Blanco et al. 2020). Covalent decoration with discreet macrocycles allowed to infer the role of functional groups on photo HER. In particular, authors outlined the key role of -OH species in the phenyl moieties of porphyrins that acted as a proton relay for boosting H_2 production, especially under mildly acidic pH conditions. Very recently, De and co-workers exploited the semiconducting properties of 2-H-$MoSe_2$ for promoting the photo-mediated conversion of benzylamines to benzimidazoles (Jaiswal et al. 2025). Authors functionalized their TMDC with 3-mercaptopropionic acid (3-MPA) and exploited the as prepared hybrids for the efficient photo-catalyzed synthesis of a toolbox of benzimidazole analogues. The conjugation with 3-MPA imparted enhanced stability, dispersibility and reactivity to the hybrid as well as red-shift of the absorption maxima towards the blue region. The local lattice distortion due to the presence of two types of chalcogens together with the optical band-gap reduction were claimed as the driving force for enhanced catalytic performance. Despite the still controversial nature of the thiol conjugation to the chalcogenide (claimed either as covalent and non-covalent), (Chen et al. 2016) these two papers highlight the importance of surface decoration with discrete organic molecules for modulating and boosting the intrinsic photocatalytic properties of TMDCs.

4 Conclusions and perspectives

The potential of surface covalent functionalization for a rational modulation of catalytic performance of both organic and inorganic materials has been described. The use of carbon-based materials as metal-free catalysts is a well-established field. Thanks to the many available techniques for surface functionalization, researchers can now create a wide variety of custom-designed materials that perform effectively in numerous applications. In the last two decades, functionalized CNMs have found applications in thermal (hydrolysis/esterification/transesterification, C-C bond forming reactions, processes for CO_2 valorization, aerobic oxidation and monosaccharides isomerization) and electrochemical (ORR, HER, OER and CO2RR) transformations, showing in many cases better performance, higher stability/durability with respect to benchmark metal-based catalysts of the *state-of-the-art* or to the 'randomly' hetero-doped CNMs classically obtained through *bottom-up* procedures. Moreover, tailored chemical functionalization offers a unique tool for the clear-cut identification of the active species engaged in a specific catalytic process and provides a unique perspective to the comprehension of the reaction mechanism at work. As an additional benefit, chemical functionalization is a non-invasive technique that allows to mimic a specific functional moiety (commonly found in *bottom-up* prepared materials together with many others) without altering any other chemico-physical properties of the underlying macromolecular carrier (*e.g.*, electrical conductivity, porosity, type and density of topological defects, wettability). All these features represent essential tiles for completing the complex puzzle of chemical/electronic/structural surface properties determining the overall performance of metal-free CNMs-based heterogeneous catalysts and open to a rational design of more effective and durable systems. Despite several heterogeneous transformations have been already investigated with such *top-down* designed CNMs, many other challenging (electro)chemical reactions are still waiting to be explored. On the side of thermal processes, chemical oxidation/reduction are rarely studied; at the same time, also electrochemical ammonia synthesis from N_2 or CO_2 electroreduction to $\geq C_2$ added-value products deserve further investigation. In addition, beyond common N and O, other light heteroelements - such as B, P and S – still deserve to be carefully explored as dopants of carbon nanomaterials with the potential to further extend the field of (electro)catalytic application for these metal-free systems.

On the 2D TMDCs side, chemical functionalization emerged only recently as a powerful strategy to tune materials chemico-physical properties. At odds with CNMs, the chemical grafting of organic species to these inorganics does not mimic surface active sites but offer a fine tuning of TMDCs properties hence impacting on their ultimate performance in (electro)catalysis. Covalent functionalization offers a strategic pathway for the surface engineering of TMDCs. It enables targeted modification of catalytic active sites residing on basal planes and edges, while preserving intrinsic material properties such as defect density, morphology, and phase, potentially impacting their performance. Covalent functionalization is moreover able to avoid the spontaneous conversion of the metastable 1T phase, largely exploited in electrochemical applications, into its thermodynamically favored 2-H counterpart, hence making grafted 1T-TMDCs robust and durable electrocatalysts. One main hurdle that should be overcome in the near future is the still limited number of functionalization protocols available for this class of materials, especially for the 2-H polytype, that somehow restricts the possibility to impart them multimodality and versatility in an easy and well-established manner. Nevertheless, even if the field of covalently grafted TMDCs for targeted catalytic applications is still in its infancy it has already offered precious hints to the comprehension of underlying mechanisms at work in key processes such as (photo)electrochemical HER. The potentiality of this class of materials is however far from being fully exploited and chemical functionalization is expected to bring in the incoming years important hints to

the development of efficient TMDCs materials for various applications spanning from thermal to photo- and electrochemical catalytic transformations.

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Declarations

Competing interests The authors declare no competing interests.

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