Chemical Functionalization of 2D Materials

Chemistry–A European Journal
Editorial
doi.org/10.1002/chem.202001304

Chemical Functionalization of 2D Materials

Nazario Martín,*[a, b] Nikos Tagmatarchis,*[c] Qing Hua Wang,*[d] and Xiaoyan Zhang*[e]

Abstract: This Special Issue of *Chemistry–A European Journal* is dedicated to the *Chemical Functionalization of 2D Materials*, and features some great contributions from experts in the field of 2D materials. This issue was originally assembled to support the Symposium G "*Chemical Functionalization of 2D Materials*" at the European Materials Research Society (E-MRS) 2020 Spring Meeting, which was originally scheduled to be held in Strasbourg, France, from May 25th to 29th, 2020. Although the E-MRS 2020 Spring Meeting has been cancelled due to the COVID-19 outbreak, the publication of this Special Issue has proceeded and has become even more important as the contributors discuss diverse and timely research themes related to 2D materials. In this Editorial, a brief overview of the different types of 2D materials is given, together with the chemical functionalization schemes that can be applied to them to achieve new properties as well as enable improved performance in applications. Some of the articles featured in this Special Issue are also highlighted, with the hope that they will inspire readers and further advance the field.

The most well-known 2D material is graphene, a single layer of carbon. It was discovered in 2004 in the seminal experimental work by Geim and Novoselov, and completed the four dimensionalities of carbon nanomaterials, with the other three being fullerenes (0D), discovered by Kroto, Smalley and Curl in 1985, carbon nanotubes (1D), discovered by Iijima and Ichihashi and Bethune, and bulk carbon allotropes graphite and diamond (3D). Graphene is a single atomic layer of sp^2-hybridized carbon atoms in the form of a 2D hexagonal lattice. It can be considered as the fundamental structural component of the other aforementioned carbon allotropes. Since its initial discovery, graphene's superlative properties such as extremely high electron mobility, mechanical strength, and optical properties led to an extensive development of fundamental and applied research, and also paved the way for a further expansion of research on many other categories of 2D materials.

With respect to 2D materials, the typical methods of producing ultrathin nanosheets are mechanical exfoliation from a bulk layered material, bottom-up growth on a substrate by using methods like chemical vapor deposition (CVD), and liquid-phase or chemical exfoliation from bulk materials. Many efforts have been made to improve the quality and yield of materials produced by using these methods. In the top-down approach starting from graphite as the raw material, harsh oxidation can produce smaller fragments of nanographenes with heterogeneous sizes, forms and edges. In order to overcome these drawbacks, in recent years, there has been a lot of interest in using the bottom-up approach to obtain a wide variety of nanographenes with atomic precision by using the tremendous power of advanced organic synthesis. By this approach, a wide variety of nanographenes have been formed with precise control of size, shape, edges and chemical composition, allowing researchers to design fantastic polycyclic aromatic hydrocarbons (nanographenes) with amazing properties. Indeed, nanometer-scale carbon structures are currently receiving a lot of interest since they can be used to test fundamental ideas about the roles of dimensionality and confinement in materials of greatly reduced size as well as their topology.

Interestingly, in contrast to pristine graphene, which does not show fluorescence, the quantum confinement that exists in nanographenes results in highly fluorescent nanostructures, thus allowing for their use as optical probes or sensing devices. In addition, because of their reduced size and chemical functionality, their nature significantly differs from the others carbon nanostructures in terms of water solubility. Moreover, the singular electronic properties of graphene have been exploited for applications in materials science and extensively

[a] *Prof. N. Martín*
Departamento de Química Orgánica, Facultad de Ciencias Químicas
Universidad Complutense de Madrid
28040 Madrid (Spain)
E-mail: nazmar@ucm.es

[b] *Prof. N. Martín*
IMDEA-Nanoscience
C/ Faraday, 9. Campus de Cantoblanco, 28049 Madrid (Spain)
E-mail: nazmar@ucm.es

[c] *Prof. N. Tagmatarchis*
Theoretical and Physical Chemistry Institute
National Hellenic Research Foundation
48 Vassileos Constantinou Avenue, 11635 Athens (Greece)
E-mail: tagmatar@eie.gr

[d] *Prof. Q. H. Wang*
Materials Science and Engineering
School for Engineering of Matter, Transport and Energy
Arizona State University
Tempe, AZ, 85287 (USA)
E-mail: qhwang@asu.edu

[e] *Prof. X. Zhang*
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
Kemigården 4, 412 96, Göteborg (Sweden)
E-mail: xiaoyan.zhang@chalmers.se

The ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/chem.202001304.

Part of a Special Issue focusing on the "Chemical Functionalization of 2D Materials", which supports the symposium on the topic held at the E-MRS 2020 Spring Meeting. To view the complete issue, visit Issue 29.

used for the development of advanced materials for optoelectronic devices and solar cells. Furthermore, the capability of carbon nanostructures to be photoexcited, to generate reactive oxygen species shows their great potential as photosensitizers for photodynamic therapy.

Beyond graphene, representative examples of 2D materials are the transition metal dichalcogenides (TMDs) having a MX_2 stoichiometry, where M is a transition metal and X is a chalcogen. TMDs are composed of a single sheet of transition metal atoms, such as molybdenum or tungsten, sandwiched between two thin layers of chalcogen elements, namely sulfur, selenium or tellurium. Interestingly, ultrathin layers of TMDs are also relatively easy to prepare by mechanical exfoliation or CVD, being almost as thin, transparent and flexible as graphene. During the past few years, more 2D materials, such as black phosphorus (BP or phosphorene), transition metal oxides (TMOs), layered double hydroxides (LDHs), transition metal carbides and carbonitrides (MXenes), and covalent organic frameworks (COFs), have attracted significant attention for applications in catalysis, energy conversion and storage, sensing, photonics, nanocomposites, and membranes. For instance, black phosphorous nanosheets have been a rising star among 2D materials due to their unique properties including tunable direct bandgap, high charge carrier mobility, and strong in-plane anisotropy.

The chemical functionalization of 2D materials is a very important and rapidly developing research area. By introducing foreign functional units onto 2D materials, chemical functionalization has been proven to be a powerful avenue to prevent the aggregation of 2D materials in solvents (preserving their large aspect ratio and high specific surface area), improve the dispersibility, wettability and processability, tune physicochemical properties, improve their environmental stability, and potentially impart new properties. Depending on the nature of the interactions, chemical functionalization of 2D materials can be classified into two types: (1) noncovalent interactions, by physical adsorption of organic units onto 2D materials through electrostatic, π–π, or hydrophobic interactions, and (2) covalent interactions, by direct bond linkage of organic moieties with 2D materials through cycloaddition, condensation, radical addition reactions, and so on. Noncovalent or covalent approaches have their own pros and cons: noncovalent interactions do not alter the structure of 2D materials while at the same time can largely preserve their intrinsic properties. Conversely, covalent interactions result in more stable and powerful hybrid systems, but a delicate control of the degree of functionalization is normally required. Chemical functionalization of 2D materials can be performed on substrates, in solvents or in the solid state (e.g., ball milling). Currently, there is an urgent need for the development of new chemical modification strategies, not only to enrich the chemistry available to different compositions of 2D materials but also to harness multifunctionality on 2D materials toward specific applications.

A main part of the contributions in the current Special Issue is devoted to graphene. In this frame, a modified graphene oxide (GO) coated with amorphous silica was employed to reinforce cement (Liu et al.). The innovative nature of functionalized GO sheets is found in their ability to form strong covalent bonds with cement hydration products, leading to increased strength. New routes for the chemical functionalization of GO were reported, exploiting the nucleophilic ring opening of epoxides decorating the basal plane of GO (Bianco and Menard-Moyon et al.). Further derivatization of the hydroxyl moieties through esterification or Williamson etherification reactions resulted in doubly functionalized GO sheets. Also, the asymmetric functionalization of fluorographene based on a facile nucleophilic substitution reaction led to the development of Janus graphene nanosheets featuring hydroxyl groups on one side and fluorine atoms on the other (Otyepka et al.). The development of such bifacially modified graphene sheets may be of particular importance for applications related to spintronics and actuators as well as for oil–water separation processes. In another report related to GO, the relation between the density of defects and the transport properties was studied by Eigler et al. The authors revealed an inversely proportional relationship of the field-effect mobility to the density of defects. Moreover, ZnO was coated with reduced-GO forming novel core–shell nanostructures, showing significant activity when employed as electrocatalysts towards the oxygen reduction reaction (Gregory et al.).

Significant progress on the doping of polycyclic aromatic hydrocarbons, en route the preparation of boron-nitrogen-doped nanographenes, was achieved by Bonifazi et al. In that work, substitution of C=C bonds with isoelectronic and isostructural B–N bonds was accomplished, opening a wide pathway for enriching the family of nanographenes with tailored optoelectronic properties. In addition, viologen-based ionic polyimides were synthesized and employed to prepare N-doped 2D porous carbon nanosheets with uniform thickness and large lateral size (Zhang, Ke and Zhuang et al.). Notably, the high specific surface area of those N-doped 2D carbon-based nanomaterials showed high electrocatalytic activity towards the oxygen reduction reaction, underscoring their potentiality for energy conversion and storage applications. Also, graphite intercalation compounds exploring Na in THF and dimethylacetamide were prepared and used to produce exfoliated graphene sheets (Shaffer et al.). Based on de-intercalation assays, a different behavior compared to that of KC_8 was observed, highlighting the implications the technique may have on reductive grafting of graphite. In addition, the poly-methyl-methacrylate assisted exfoliation of graphite and its use in polymer composite materials was examined by Bonaccorso et al. Moreover, the preparation of twisted graphene, GO and boron nitride sheets by covalently formed amide bonds was reported by Rao et al. In a different contribution, graphene sheets functionalized with optically switchable azabenzene moieties were employed to induce switchable behavior to graphene field-effect-transistors (Turchanin et al.). The preparation of an entirely supramolecular multi-chromophoric azaborondipyrromethene/zinc tetraphenylporphyrin/exfoliated graphene nanoensemble was accomplished by Tagmatarchis and D'Souza et al. Interestingly, porphyrin J-aggregates formed, as verified by UV/Vis assays, and graphene sheets seem acting as a nanoplatform for the aggregation of azaborondipyrromethene/porphyrin

supramolecular complexes. In a theoretical study, the electronic properties of 2D frameworks, structurally convergent with holey graphene, built by acene units, were studied by Melle-Franco et al. The authors found that the presence of holes decreases the bandgap of the material.

Moving on to TMDs, 2D heterostructures combining graphene sheets with MoS_2 and CdS nanoparticles were developed and tested for photocatalysis by Tasis et al. Particularly, the photodegradation of 4-nitrophenol was examined and it was found that the photocatalyst with the best performance was that with the coating of graphene around MoS_2, whereas semiconducting CdS nanoparticles were deposited homogeneously on either of the two 2D substrates. In another approach, a strategy for the development of WS_2/MoS_2 heterostructures, based on the electrostatic functionalization of exfoliated MoS_2 with a tungsten cluster followed by a dry thermal treatment was reported by Forment-Aliaga, Coronado, et al. Also, 2D metallic VSe_2-carbon nanotubes-reduced GO based ternary hybrid materials for high performance energy storage applications were reported by Rout et al. Regarding the chemical functionalization of MoS_2, a comprehensive study of MoS_2 functionalization with maleimides was reported by Pérez, Santamaría et al. It was noted that the presence of a base leads to the in situ formation of a succinimide polymer layer attached onto MoS_2. Furthermore, thiophenols were employed to controllably engineer sulfur defects in MoS_2 and the degree of functionalization was correlated with the intensity change of the corresponding Raman mode 2LA(M) normalized to that of A_{1g} (Hirsch et al.) In addition, the bottom-up preparation of MoS_2 nanosheets in situ functionalized with polymeric carbon nanodots was accomplished by Tagmatarchis et al. The hybrid material was examined against the hydrogen evolution reaction and showed significant electrocatalytic activity attributed to the synergistic effect between the two species within the hybrid material. In a theoretical and modeling study, the stability, structure and reconstruction of 1H-edges in MoS_2 was examined by Ewels et al., identifying stable edge nanostructures and a new disordered phase, which may play a key role in the edge site reactivity during thermally assisted chemical catalysis.

The recent progress in the design of MoS_2-based nanostructures for rechargeable batteries was reviewed by Ciucci, Kim et al., unveiling how the properties of the material can be improved in order to employ MoS_2-based electrodes in electrochemical energy-storage systems. In addition, a critical Review involving TMDs beyond MoS_2 as active materials in alkali metal-ion batteries and supercapacitors was presented by Soares, Singh et al. Two other Minireview articles discuss the progress in transition metal based materials (Lee et al.) and phosphorene (Zhang and Sun et al.) as bifunctional electrocatalysts for water splitting and electrocatalysis, respectively, whereas another Review focuses on 2D metal–organic framework (MOFs) and covalent organic framework (COF) nanosheets for supercapacitors, batteries, oxygen reduction and hydrogen evolution (Xu and Pang et al.). The physicochemical exfoliation methods leading to the realization of layered 2D nanomaterials for energy and environmental applications was also reviewed by Kim and Yoon et al. Furthermore, hydrothermal synthesis approaches for 2D materials, including their chemical functionalization, were reviewed by Kellici et al., who highlighted benefits and challenges. Unlike the highly reviewed graphene and TMDs, a Minireview discussing 2D nanoarchitectonics by Ariga et al. is featured in this Special Issue, focusing on dynamic 2D media at the liquid surface, air–water interface and cell membrane surfaces.

Finally, with respect to other 2D materials beyond graphene and TMDs, the exfoliation of Sb_2S_3, Bi_2S_3, Sb_2Te_3 and Sb by bipolar electrochemistry was reported and their hydrogen evolution ability was screened by Pumera et al. In addition, GeS_2 nanosheets were prepared by Geng and Li et al., examined as anodes for lithium-ion batteries and showed superior lithium storage performance. A ruthenium-arene complex functionalized black phosphorus heterostructure was formed (Chen et al.). Interestingly, it was found that the electrons transferred were localized at the interfacial region and the heterostructure effectively performed as a photodetector. In addition, the synthesis of modified carbon nitride-based materials featuring electron donor-acceptor domains, with significant photo- and electrocatalytic activity was reported by Shalom et al. Furthermore, the covalent functionalization of a magnetic NiFe layered-double-hydroxide with silanes was reported by Abellán, Coronado et al., opening the way to the development of more complex architectures and hybrids. Also, a postsynthetic modification of imine-based COFs was reported by Segura, Zamora et al. In addition, a new class of halide-organothiolate-mixed 2D hybrid material featuring a five-coordinated lead atom with an inorganic backbone composed of two benzenethiolate layers was synthesized and examined by Liao, Dou et al. On a different note and in order to conclude this concise presentation of the Special Issue, palladium nanodots were immobilized onto 2D conjugated polymers, providing a facile route for the preparation of metal-catalysts supported on 2D materials (Li et al.).

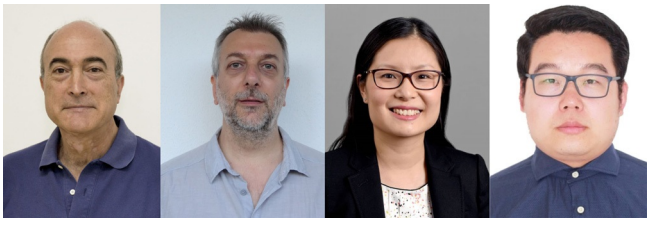

Figure 1. From left to right: Nazario Martín, Nikos Tagmatarchis, Qing Hua Wang, Xiaoyan Zhang.

As the Guest Editors (Figure 1) of this Special Issue, we consider the many excellent works on chemical functionalization of 2D materials gathered in this venture as a useful and updated tool for those specialists in the field as well as for a broader readership. The diversity of original contributions on various topics is a timely and useful source of information for the reader. We firmly consider that the science contained in this issue will inspire the imagination of scientists interested in the

beauty and significance of graphene(s) and other non-carbon 2D materials.

Finally, we would like to express our gratitude to all the contributors to this Special Issue, who eagerly accepted to participate. We would also like to thank all those scientists whose names are cited along the issue for their former seminal works. This gratitude is also for the Wiley-VCH team and, in particular, for the team of handling editors at *Chemistry–A European Journal*, for putting this issue together and for their support and excitement when they received our proposal of editing this Special Issue devoted to the chemical functionalization of 2D materials. Our special thanks go to Leana Travaglini, who was in charge of the editorial side of this Special Issue at Wiley-VCH.