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Chemistry of 2-dimensional materials beyond graphene: closing remarks

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Since graphene exfoliation in 2004, two-dimensional (2D) materials have received great attention due to the qualitative changes in their physical and chemical properties associated to their nanosized thickness and the correlated quantum size effect. 2D planes allow the confinement of charge carriers, heat, and photon leading to remarkable electronic and optical properties of these materials. The Faraday Discussion "Chemistry of 2-dimensional materials: beyond graphene" has been an incredible showcase for a variety of highly interesting contributions in the field. This conference comprised a wide number of aspects of the topic: from the synthesis and the study of optical and physical properties to their numerous applications. These concluding remarks aim to capture the recent developments in 2D materials chemistry and physics that were presented and debated during this Faraday Discussion, and more generally in the research field in the last years. Particular attention will be paid to aspects like the synthesis of the materials, their toxicity and biodegradation, and some of their major applications in catalysis, such as Li-ion batteries, water filtration and sensing. As well we aim to highlight future challenges that still need to be addressed.

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Introduction: traveling through dimensions

The carbon nanotechnology field seems to jump in different directions among dimensions. The travel started with C60 fullerene and luminescent quantum dots, considered zero-dimensional (0D) materials. The next step was one-dimensional (1D) carbon nanotubes, in which the length is orders of magnitude bigger than the diameter. Before reaching three-dimensional (3D) materials, the last step was 2D systems where graphene was the ground-breaker, soon followed by a myriad of other related 2D materials. The huge potential of 2D materials was already predicted by Richard P. Feynman in 1959.[1] This pioneer of nanotechnologies during his lecture "There's Plenty of Room at the Bottom" planted the following questions "What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them?". This lecture inspired the upcoming researchers to investigated unexplored boundaries in this research field. Nowadays, more than 50 years after Feynman's lecture, we have clear in our minds that controlling the numbers of layers of a material is the way through tuning its physicochemical properties, and, as we saw during this Faraday Discussion, such fine
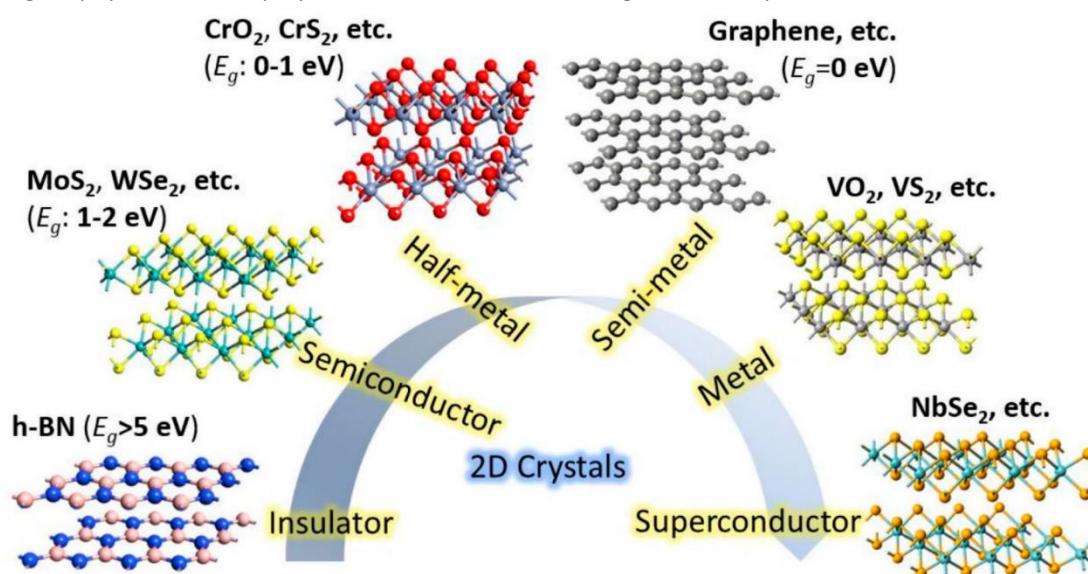

Figure 1. 2D materials beyond graphene. Reprinted from Ref. [4], Copyright © 2020 Society of Photo-Optical Instrumentation Engineers (SPIE).

control opened a wide number of possibilities in this field.

The largest impulse in the field was given in 2004, when Novoselov, Geim and co-workers firstly isolated and measured the electronic transport on individual sp^2-hybridized carbon layers, that now is world widely known as graphene.[2] The discovery of graphene was a breakthrough in the modern history of science, but it was just the tip of the iceberg. Since then, several 2D materials followed and many others keep appearing. To date, the family of 2D materials comprises a wide selection of crystal compositions and includes most of the elements of the periodic table.[3] This is translated into a huge variety of electronic properties, going from metals and semimetals to semiconductors and insulators. For example, while graphene behaves as a zero-band-gap semiconductor, other 2D inorganic materials can act as insulators (*e.g.,* hexagonal boron nitride, hBN), semiconductors (*e.g.,* MoS_2, WS_2, WSe_2), and even superconductors (*e.g.,* $NbSe_2$, NbS_2) (Figure 1).[4] Furthermore, these properties can be modulated based on their crystal structures and stacking orientations.[5] As well the optical properties of 2D materials can range in a wide variety, with direct and indirect bandgaps spacing from ultraviolet to infrared.[6] Even if dozen of 2D materials have already been discovered, there is still a lot of room for investigation: 5619 compounds have been identified to have the potential to be easily exfoliated from their 3D parent compounds and await to be discovered.[7] Lately, graphene became very popular also outside the scientific environment, and the public media did not take long to recognize the potential of the material, considering it as the "miracle material of the 21st century".[8] Anyway, outside from the expert community, the terminology is a little confused, tending to call "graphene" an entire family of carbon materials that differ in chemical composition, dimensions, number of layers and physicochemical properties. In 2014 the necessity to bring order in the nomenclature of graphene related material brought several scientists active in the field to formulate an approach for an unequivocal.[9] Such categorization was

performed according to three fundamental properties: number of graphene layers, average lateral dimension, and atomic carbon/oxygen ratio (Figure 2). This classification is fundamental to understand the structure–activity relationships of this material and rationalize it in the context of its technological applications, human health and safety. Thus, this categorization avoids generalizations about the capabilities and limitations of graphene-based materials. For example, in applications where high charge conductivity is required, single layer graphene (SLG, $\sigma_G \sim 10^6$ S m^{-1}) is by far the best candidate and cannot be substituted for instance with graphene oxide.[10,11] Vice versa, graphene oxide prevails over other graphene related material when water colloidal stability is required. Anyway, trying to set ground rules for classifying materials in a field that is being developed at such a high speed is always complex, because new examples arise, breaking the pre-defined guidelines.

In this Faraday Discussion Zhuang and co-workers, proposed a more general classification method for carbon nanomaterials based on the meso-entropy of the matter (DOI: 10.1039/c9fd00115h). This new concept allows to introduce a broad relationship among different carbon materials, to distinguish and propose new polycyclic aromatic isomers, and to understand highly defective graphene derivatives.

When graphene's lateral dimensions are extremely reduced, other aspects are counted in the definition of the properties of the material, as in case of nano-graphene and nanoribbons. In these materials the conformation of the edge assumes a fundamental importance (Figure 3). For example, in armchair-edge graphene nanoribbons, quantum confinement activates electronic bandgaps directly correlated to their boundary conditions.[12] On the other side, nanostructures with zigzag edges have been reported to have spin-polarized electronic edge states with potential applications in graphene-based spintronics.[13] On this topic, we assisted to an inspiring opening lecture given by Professor Klaus Müllen.

Figure 2. Classification of graphene-related materials based on three physical-chemical descriptors: number of layers, lateral dimension, and atomic carbon/oxygen ratio.

Synthesis of 2D materials

The discussion opened with the session on "2D material production and generation of functional inks". In this session we saw several examples of optimization of conventional synthesis and the introduction of more innovative ones. In general, the synthesis of graphene related materials can be divided in bottom-up approaches, such as chemical vapor deposition and molecular assembly; and top-down, as mechanical and liquid phase exfoliation.[8] The last methodology is currently living a golden moment, as it is a not expensive, scalable, and highly versatile method to produce graphene flakes. In addition, exfoliation can be performed by various approaches (*e.g.*, Ionic intercalation, surfactant stabilization, sonication, or electrochemical intercalation), each with its own advantages (Figure 4).[14]

The popularity of liquid-phase graphite exfoliation is as well due to the growth of conductive inks and flexible electronics markets. Low-cost and industrially appealing printing techniques combined with conductive inks are getting ahead of the conventional solid-state and semiconductor technologies. Liquid exfoliated graphene is playing a pivotal role in this advancement furnishing inks with atomic thickness, mechanical flexibility and exceptional carrier mobility.[14] Throughout this Faraday Discussion, we saw several examples of liquid phase exfoliation. Casiraghi and co-workers demonstrated that exfoliation can be achieved using insoluble pyrene stabilisers if appropriately designed (DOI: 10.1039/c9fd00114j). They surprised the audience proving that water-stable suspension of exfoliated graphene can be achieved starting from two insoluble chemical species (graphite and bis-pyrene stabilizers). Galembeck and co-workers presented a spontaneous exfoliation of graphite in alkaline cellulose solution (DOI: 10.1039/c9fd00109c). Using this exfoliated graphene, the authors produced an ink that can be deposited on substrates by using different painting, coating and lithography techniques. In this formulation, cellulose simultaneously plays the roles of exfoliant, dispersant, stabilizer, adhesive and plasticizer. Xia, Palermo and co-workers showed that it is possible to monitor and investigate the electrochemical exfoliation process by *in-situ* Raman microscopy, giving new insights in the mechanism of the exfoliation process (DOI: 10.1039/c9fd00123a). Only a few
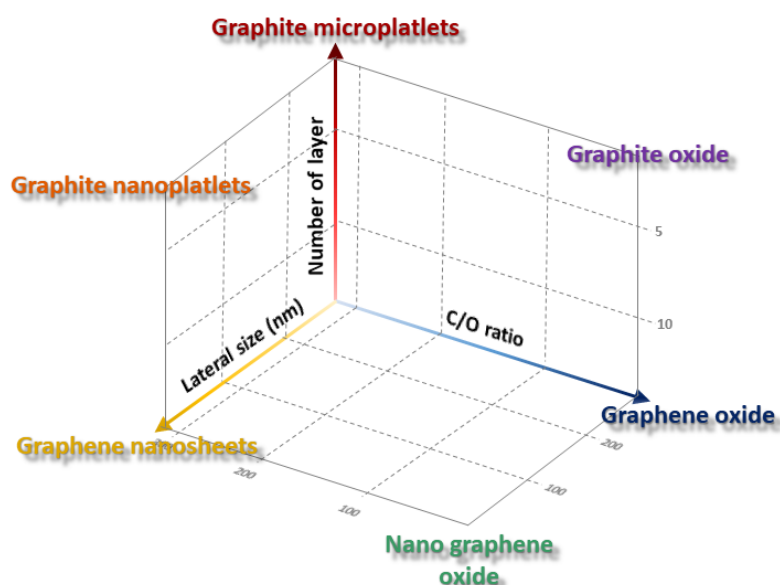
months ago, a recent article, published by the groups of Novoselov and Coleman, provided new perpectives for this process[15]. They demonstrated that ultrasonication liquid phase exfoliation, from graphite to graphene, takes place in three different stages (Figure 5). Firstly, sonication induces the formation of kink band striations on the graphite surfaces and the rupture of large flakes mainly along zig-zag directions. Next, graphite cracks along these striations, and thin graphite strips are peeled off from the surface, by the assistance of solvent intercalation. In the third and final stage, such strips are exfoliated into graphene. The cited work reveals that, even if liquid phase exfoliation is widely employed, there is still much to learn about its mechanism. A deeper comprehension of this process will be of immense value in the challenge to control the lateral dimensions, thickness, and yield during graphene and other 2D materials production.
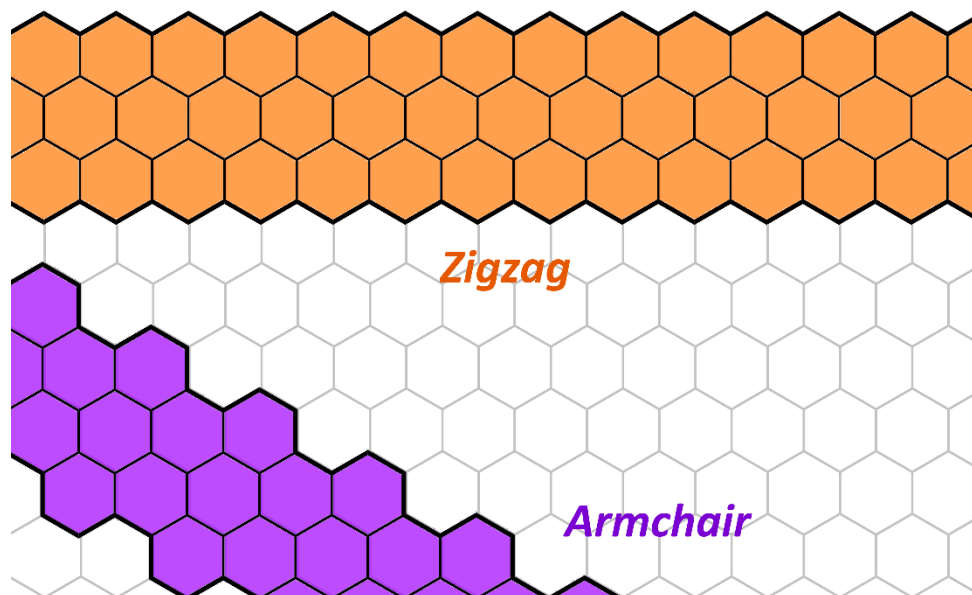

Figure 3. Structure of armchair- and zigzag-edge graphene nanoribbons.

One of the most efficient methods to produce exfoliated graphene is the chemical intercalation of graphite with alkali metals[16]. In addition, this methodology provides one of the most effective strategies for the covalent functionalization of graphene, compared to the approaches that involves non-charged graphene. However, this approach depends on different parameters that must be controlled, such as the type of intercalating agent, the nature of starting graphite and the solvent used, among others. Indeed, our laboratory carried out a systematic study about the influence of different commonly used solvents in the reactivity of negatively charged graphene intercalated with potassium cations.[17] We found that its dispersibility and functionalization ability depends on the balance between solvation of K^+ and flocculation in solvents.

Another methodology for the synthesis of carbon-based 2D materials has been presented by Turchanin and co-workers (DOI: 10.1039/c9fd00119k). They investigated the role of electron irradiation energy inducing chemical reactions to produce carbon-based materials. In particular, they found that low-energy electron irradiation causes crosslinking of aromatic self-assembled monolayers resulting in 2D carbon nano-membranes.

As mentioned above, graphene derivatives are only a fraction of the 2D reported materials. Accordingly, the contributions on the synthesis of other types of 2D materials, which include many metal-based and metal-free materials, could not be missed in this Faraday Discussion. Most of the techniques employed for the production of graphene can also be applied to the majority of 2D materials, such as liquid and chemical exfoliation or chemical vapor deposition. In this Faraday Discussion, Hersam and co-workers reported the production of hBN nanoplatelets by exfoliation in ionic liquids (DOI: 10.1039/c9fd00113a). Furthermore, by adding imidazolium ionic liquid and ethyl lactate after exfoliation, the authors obtained ionogel ink printable by high resolution aerosol-jet printing.

Bidimensional transition metal dichalcogenides (2D-TMDs) are an emerging family of 2D materials with adjustable chemical and optoelectronic properties.[18] In addition, they can exist in various phases that are associated to different features.[19] The preparation method enables the phase engineering of these 2D-TMDs. A well-known example is the chemical exfoliation of layered crystal MoS_2, which possesses a semiconducting

2H phase. By treatment with *n*BuLi or NaK alloy, exfoliated MoS_2 enriched in metallic 1T phase can be obtained.[20,21]

Phase engineering can also be performed by chemical vapor deposition. One example is the synthesis of niobium disulfide, whose metallic 2H phase NbS_2 has been predicted as highly efficient electrocatalysts for HER.[22] But the phase of this material is dependent on the thickness. Chhowalla and coworkers reported the synthesis of the metallic 2H phase of niobium disulfide with additional niobium (2H $Nb_{1+x}S_2$, where x is ~0.35) by chemical vapor deposition under certain conditions.[23] Then they tested the catalytic performance for HER of this metallic material with improved conductivity via elimination of van der Waals gaps between layers. During the discussion, Chhowalla also showed that the variation of the growth environment in the chemical vapor deposition method can lead to changes in the thickness, obtaining metallic mixed 3R and 2H $Nb_{1+x}S_2$ nanoflakes (DOI: 10.1039/c9fd00132h).

Beyond that, different and more specific approaches can be used to produce these materials as the solvo/thermal treatment.[24] For example, Sui and co-workers showed a sol-gel synthesis of 2D TiO_2 (DOI: 10.1039/c9fd00108e). They reported a simple and scalable method consisting of the reaction of titanium isopropoxide with acetic acid at 333 K in isopropanol, followed by calcination at 673 K to remove the organic ligands.
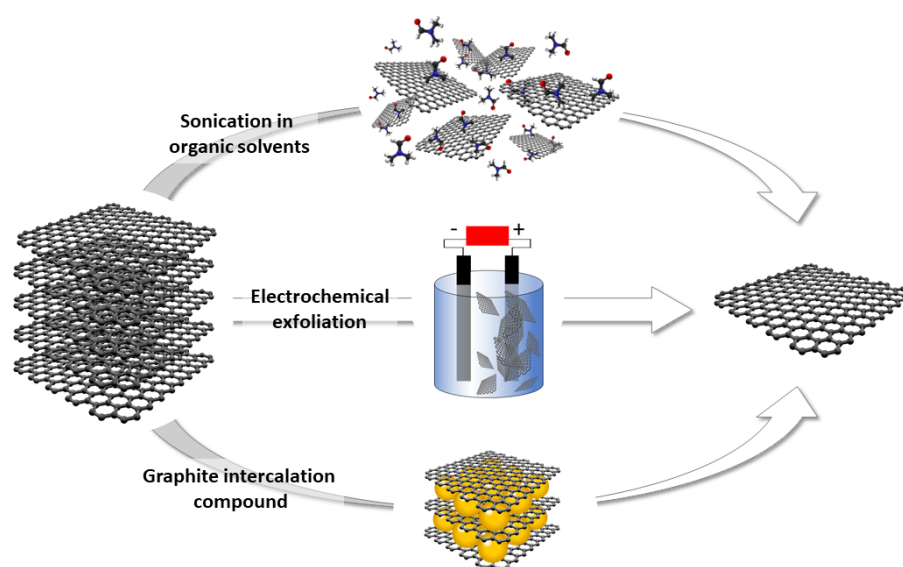

Figure 4. Schematic representation of various exfoliation routes of graphene.

Even if it is possible to synthesise several 2D materials, some of them are not stable under environmental conditions and can be subjected to oxidation when exposed to oxygen. Encapsulation is a good strategy to preserve the chemical composition, structure and properties of the material. On this topic, Ferrari and co-workers showed how it is possible to stabilize InSe and GaSe monolayers by encapsulation in hexagonal boron nitride followed by Raman characterization (DOI: 10.1039/d0fd00007h). Analogously, Molle and co-workers proposed the sequential encapsulation of Xenes in Al_2O_3 as a solution to face degradation in environmental condition (DOI: 10.1039/c9fd00121b). They proved the encapsulation effectiveness by virtue of the interaction between silicene and a silver substrate. The authors as well generalized their encapsulation scheme other metal-supported Xenes like epitaxial phosphorene-on-gold.

Applications of 2D materials

Atomic thickness, wide surface and exceptional electronic, mechanical, and optical properties make 2D materials promising for a high number of applications.[25] These materials show a huge potential in electronics, optoelectronics, photonics, composites, catalysis, sensing, and biomedicine. All over this Faraday Discussion we have seen several examples of 2D materials applications, and in the following paragraphs we will briefly summarize all these contributions.

The step from 3D bulk materials to 2D atomic crystals induces considerable changes in the electronic structure, increasing the surface-to-volume ratio. For this reason, this class of materials have attracted considerable interest in electrocatalysis, conventional heterogeneous catalysis and photocatalysis.[26] A variety of catalytic mechanisms has been described but, in general, it has been observed that the catalytic properties are related to a particular electronic structure due to a quantum confinement effect. Moreover, the crystalline structure can be modified by introducing defects (such as dislocations, vacancies, edges, impurities, and functional groups), that are able to modify the density of states in the material and therefore its catalytic activity.[27]

During this Faraday Discussion, there were three presentations dealing with application of 2D materials to catalysis. Firstly, Caps and coworkers showed that natural graphite can be used as a templating matrix to grow non-stoichiometric cobalt oxides (DOI: 10.1039/c9fd00110g). In particular, the authors grew reduced cobalt oxides starting from cobalt nitrate and sodium borohydride. The highly porous graphene-supported cobalt oxide nanosheets showed superior catalytic performance in the CO oxidation reaction at low temperature.

In recent years, 2D metal-free materials has received much interest as efficient, green, and sustainable photocatalysts for energy conversion and organic transformations.[28] In particular, 2D carbon nitride is one of the most promising photocatalyst because of its easily accessible synthesis, adsorption in the visible region, excellent thermal and chemical stability and chemical modification capability.[29,30] Although carbon nitride can present different structural arrangements, graphitic carbon nitride (g-CN) is the most stable form. In the last years, Antonietti and coworkers have reported new syntheses of g-CN derivatives that permit the fine-tuning of their photocatalytic activity. On one hand, they reported the synthesis of mesoporous graphitic carbon nitride (mpg-CN) with a much larger surface area than g-CN.[31] More recently, they described the preparation of poly(heptazine imides) (PHI) by using molten salts in the conventional melamine thermo-polymerization.[32] Both g-CN analogs are remarkably efficient in performing photo-oxidation of organic molecules.[29,33] Related to the structural modification of carbon nitride, our group recently reported post-synthetic modifications of g-CNs to improve the photocatalytic performance in perfluoroalkylation reactions.[34] In particular, important findings about the mechanism were obtained by innovative NMR studies, evidencing the importance of halogen bond strength between the reagent and the catalyst surface. In this direction, relevant contributions to this field were reported in this Faraday Discussion. Moura, Teixeira and co-workers demonstrated that by adding single atoms of selected transition metals to graphitic carbon nitrides it is possible to tailor its electronic and chemical properties, modulating the activity in photocatalysis (DOI: 10.1039/c9fd00112c). The authors demonstrated that Ni^{2+}, Pt^{2+} or Ru^{3+} single atoms may either improve or impair the degradation of rhodamine B and methyl orange, depending on the proper matching of the net charge of these molecules and the surface potential of the catalyst. Computer simulations supported the experimental evidence, demonstrating that even a single transition metal cation can dramatically change the electronic structure of the material. Martsinovich and co-workers arrived at similar conclusions performing density functional theory calculations on a series of structures based on graphitic carbon nitride (DOI: 10.1039/c9fd00147f). They designed in silico different carbon nitride structures by replacing nitrogen with other atoms (phosphorus, boron) or aromatic groups (benzene, s-triazine and substituted benzenes). Several of the computed structures were predicted to have electronic properties superior to pristine carbon nitride and favorable catalytic properties for water splitting reaction. These two studies demonstrate how chemical modification of carbon nitride is a powerful method to tune this material's electronic properties and improve its photocatalytic activity.

2D materials, and in particular graphene, have been widely applied as electrodes for Li-ion batteries. The atomic thickness and the robust mechanical properties make graphene the ideal candidate for flexible electrodes with high electrochemical performance. Feng and co-workers demonstrated a general and straightforward co-assembly approach to prepare flexible electrodes for Li-ion batteries (DOI: 10.1039/c9fd00120d). Electrochemically exfoliated graphene (EG) was used as conducting matrix and doped with different metal oxides ($Li_4Ti_5O_{12}$, $LiCoO_2$, Li_2MnO_4, $LiFePO_4$). The resultant EG–metal oxide hybrids exhibit elevated flexibility and can endure rolling, bending, folding, and even twisting. When serving as the anode for Li-ion batteries, these hybrid materials present flat discharge plateau, small polarization, high-rate capability, and excellent cycling stability.

2D materials finds several applications as well in the biomedical fields.[35] Palermo, Melucci and co-workers (DOI: 10.1039/c9fd00117d) showed, for example, how composite materials formed of graphene oxide and polyethersulfone–polyvinylpyrrolidone hollow fibers can be used as microfilters for biologicals fluids and contaminated waters. The filters based on this technology, differently to conventional ones, allow not only to remove cells and proteins from the stream, but as well small molecules such as antibiotics. Biosensing is another major field in which 2D nanomaterials are highly promising. In this Faraday Discussion we had an example of biosensor for the detection of ferritin reported by Singh and co-workers (DOI: 10.1039/c9fd00111e). The authors included hexagonal boron nitride quantum dots (hBN QDs) in the design of an electrochemical impedance immunosensor. The obtained device showed high selectivity, wide linear range, did not deviate in the presence of interfering agents, and was also highly reproducible. A little more
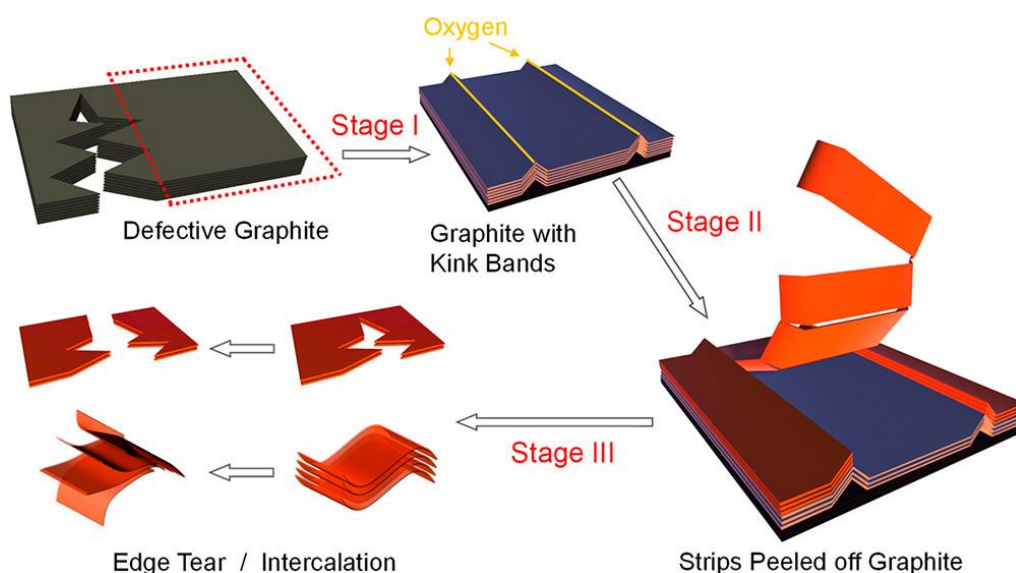

Figure 5. The three stages involved in the liquid phase exfoliation mechanism. Stage I: flake rupture and kink band formation. Stage II: peeling off of thin graphite strips. Stage III: exfoliation to thin flakes. Reprinted from Ref. [15], Copyright © 2020, American Chemical Society

unusual application of 2D materials was presented by Strano and co-workers (DOI: 10.1039/d0fd00030b), that showed how autoperforation of two-dimensional materials can be employed to generate colloidal state machines capable of locomotion. Colloidal state machines (CSMs) are particulate devices capable of integrating sensing, memory, and energy harvesting onto a single particle. The innovation in this paper was the use of an inversion molding technique compatible with autoperforation that allows the patterning of an external catalytic surface (Pt layer), which enables locomotion in an accompanying fuel bath. Finally, Palma and co-workers presented DNA-driven dynamic assembly of MoS_2 nanosheets demonstrating that DNA can be employed to drive the static and dynamic assembly of MoS_2 nanosheets in aqueous solution (DOI:10.1039/c9fd00118b). Even though it does not represent a direct application, the control of the self-assembly of 2D materials with molecular precision can have a great impact in several fields, such as optoelectronics, energy, and drug delivery.

When speaking about biomedical applications of 2D materials, it is necessary to evaluate their potential impact on the environment and human health.[36] The paper on the biodegradation of graphene materials catalysed by human eosinophil peroxidase presented by Bianco and co-workers (DOI: 10.1039/c9fd00094a), in the session dedicated to biomedical applications, opened an animated discussion on the toxicity and fate of graphene related materials. The paper shows how this important enzyme secreted from immune cells is able to degrade graphene oxide in less than 90 h. Such results should make the scientific community reflect over the fate of 2D materials once introduced in the human body or in the environment. Furthermore, these results clearly show that it is not enough to assess the toxicity and environmental impact of the pristine material. It is fundamental as well to identify the subproduct deriving from graphene biodegradation and the toxicity and polluting profiles. While these studies are already active in the field of graphene, and an entire working package of the graphene flagship is dedicated to it, such investigations are still scarce for new emerging 2D materials.

Conclusions

More than 100 attendants participated into this online *Faraday Discussion*, chaired by Paolo Samorì (ISIS Strasbourg) and Vincenzo Palermo (CNR Bologna and Chalmers University), which included one introductory lecture by Klaus Müllen (Max Planck Institute, Mainz), 19 communications and one concluding remark lecture, in addition to a number of lightning presentations.

This *Faraday Discussion* showcased the current state-of-the-art for 2D materials in synthesis, characterization and applications. These materials promise to revolutionize not only science and technology but also our everyday's life. However, there is still a lot of room for improvement. For example, large scale production of graphene still necessitates a suitable way for characterizing purity and quality. Until this aspect is exhaustively solved, it will be difficult to understand the nature of the materials we will introduce in applications.

During this conference, new methods of synthesis of 2D materials were described, with emphasis on liquid phase exfoliation, either chemical or electrochemical. New insights into relevant characterization techniques were described, extremely important for the advancement of this branch of science. Applications in electronics, optoelectronics, photonics, composites, catalysis, sensing, and biomedicine have been highlighted.

As was clear from these three days of vibrant discussion, 2D materials represent an incredibly lively field of research, joining scientists from many different disciplines. The most exciting aspect of these materials is that the race for new discoveries is not over yet. "What is next is great and breathtaking", said President Joe Biden a few days ago about the future of science. We look forward the great future of 2D materials, confident that new milestones and amazing breakthroughs wait for us along the way.

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Conflicts of interest

There are no conflicts to declare.

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