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*Editorial*

# Ultra-Thin Carbon Films: The Rise of $sp^3$-C-Based 2D Materials?

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We warmly thank all the colleagues who have enthusiastically participated in the project of this Special Issue on "2D Ultra-Thin Carbon Films", considering a globally unfavorable context characterized by (i) a myriad of publication options; (ii) strong pressure, by the highly competitive research (and researcher) funding and evaluation system, to publish in high impact factor journals, specifically for topics of worldwide interest; and (iii) all sorts of restrictions imposed by the sanitary crisis. Likewise, we are very grateful to all reviewers for their time and altruism considering this very particular context.

This issue focuses on different aspects of 2D Ultrathin Carbon Films. Both $sp^2$-bonded carbon and $sp^3$-bonded carbon materials are considered, although the latter are emphasized. We believe that this characteristic may be of particular interest considering the countless issues and reviews already dedicated exclusively to graphene. Moreover, although graphene initiated the booming field of two-dimensional (2D) and layered materials, since the seminal paper by Geim and Novoselov in 2004, which earned them the 2010 Nobel Prize in Physics, the craze for graphene might start to fade (see Figure 1).

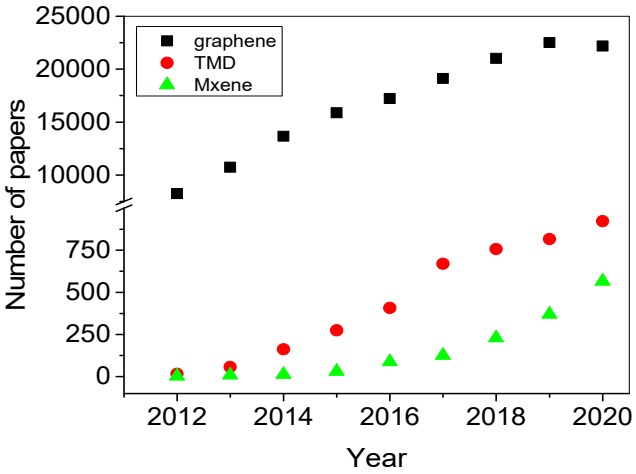


**Figure 1.** Number of published scientific articles per year since 2012 referring to graphene (black squares), TMDs (red circles) or MXenes (green triangles) in their abstract (source: Scopus, February 2021).

Indeed, no matter how beautiful the material is, single graphene is vitiated by a major deficiency, i.e., the lack of an electronic band gap. Due to this, other mono-elemental materials such as phosphorene [1] or silicene [2], and compounds such as transition metal dichalcogenides (TMDs) [3] or transition metal carbides, nitrides, or carbonitrides (MXenes) [4], have emerged and now increasingly attract the attention of the scientific community (Figure 1), dragging many research teams worldwide out of the carbon field. However,

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this is forgetting that carbon has kept providing scientific breakthroughs over the past 35 years.

The high interest in 2D materials is illustrated by the corresponding significant increase in the number of published scientific articles and the multiplication of dedicated conference sessions every year. Between 2015 and 2020, the number of published scientific articles per year which were indexed in Scopus and which were referring to 2D materials in their abstract has more than doubled, increasing from ~3400 to ~7300. The Materials Research Society will organize a symposium focusing on 2D materials during the 2021 Virtual MRS Spring Meeting and Exhibit (Symposium NM07-Beyond Graphene 2D Materials—Synthesis, Properties and Device Applications) following the success of similar symposia at the 2019 and 2020 MRS Fall meetings. 2D materials also get a dedicated journal since 2014 (see [5]), and a European experimental pilot line devoted to 2D materials was just launched in January 2021 as an initiative of the Graphene Flagship. Despite the interest in graphene is still quite high and remains well ahead of others (Figure 1) thanks, in particular, to the incorporation of nitrogen in the graphene lattice for energy storage applications and more recently twisted bi-layer graphene (TBG) for its superconductivity (1223 and 181 articles in 2020, respectively), the number of articles dedicated to graphene has started to decrease (by 1.4% from 2019 to 2020), while the current craze generated by newcomer materials is obvious.

A major motivation for 2D-material research is the synthesis of high-quality materials for electronic and optoelectronic applications. However, as stated in a recent article discussing a roadmap for electronic grade 2D materials [5], "for industrial production, 2D layer synthesis and engineering must lead to 'exfoliation-quality' 2D layers at the wafer scale". Hence, as pointed out by Luigi Colombo (Texas Instruments) some years ago during his invited talk at the MRS Fall meeting, it will be far more challenging to produce (and to integrate into devices) at wafer-scale an electronic grade 2D-compound material than a mono-elemental one. This is still a robust hypothesis for which we understand that 2D ultrathin carbon materials (2DC) offer a lot of promises for this sector of applications, especially as the field has recently evolved with new promising 2DC (besides TBG), namely 2D $sp^3$-bonded carbon materials. Another imperative incentive is the necessity of using materials and production processes, which are safe and compatible with sustainable development. As a matter of fact, carbon is one of the most abundant elements on Earth, whereas some elements necessary for other 2D materials, such as copper (or tin or indium) have started to become scarce. Additionally, our modern lifestyle produces excess gaseous forms of carbon ($CO_2$, $CH_4$), which are detrimental to the planet because of their significant contribution to the green-house effect. Hence, capturing the gaseous carbon forms into carbon materials is a promising double-winning strategy to consider. Likewise, 2DC can be produced by using green mass-production routes, which are also CMOS-compatible. 2DC materials open the door to significant advances in driving technologies, where they can compete with more complex materials, which are more challenging to manufacture and integrate, such as BN, TMDs, or MXenes. Further developments consisting of combining 2DC materials with each other, such as combining graphene with diamanoid, could motivate intense research to develop carbon-based electronics where both carbon materials would play a major role.

In 2018, in their perspective on current achievements and future challenges for carbon science, the editors of the journal *Carbon* considered that one experimental challenge that remained was the development of a bulk synthesis method for 2D diamonds and that a real breakthrough would be to use chemical vapor deposition (CVD) processes such as hot filament CVD in the presence of $H_2$ and $CH_4$, to yield scalable synthesis of 2D or 1D diamonds [6]. Actually, it was recently shown that hot filament CVD-promoted hydrogenation processes can be successfully used to induce the partial or full $sp^2$ to $sp^3$ conversion of carbon atom hybridization in 2D graphenic systems at low pressure and at low temperature to synthesize 2D crystalline $sp^3$-bonded carbon materials [7–11]. These results open the door to mass production of a variety of stable 2DC materials such as diamanes, diamanoids, and diamanoid/graphene hybrids (including TBG configurations),

merely by changing the type of graphenic 2DC to start with (from coherently stacked 2LG to few-layer graphene). Meanwhile, a major advantage is the use of the hot-filament-assisted CVD process, which is already a well-established method for the industrial production of other crystalline $sp^3$-bonded carbon materials, such as diamond films.

This is why the focus of this Special Issue is on new arising carbon materials, namely TBG and $sp^3$-carbon-related materials, the latter being wide band-gap semiconducting materials, which include genuine diamane, F-diamane, N-diamane, diamanoids, and amorphous carbon layers with high $sp^3$-bonded carbon fraction. Genuine diamane consists of two crystalline $sp^3$-bonded carbon layers, for which half of the carbon atoms are hydrogenated while the other half bond the two layers to each other. Diamanoids are crystalline $sp^3$-bonded carbon materials such as diamane, but they are composed of more than two layers while only the two outer ones are hydrogenated. The issue includes a contribution on F-graphene for the possibility of converting the material into F-diamane. The issue comprises a research article and four review articles. Experimental and first-principle works are included. Altogether, the manuscripts collected cover a variety of topics including synthesis, characterization, physical properties, applications, and cyto-compatibility.

We introduce the contributions to this Special Issue starting with $sp^2$-bonded carbon materials and continuing with $sp^3$-bonded carbon materials in order to follow the chronology of historical developments. Regarding the $sp^2$-bonded 2DC materials, the issue includes a review on Raman spectroscopy of TBGs [12]. Moutinho and coworkers review the main important effects observed in the Raman spectra of TBGs and twisted graphene/other phase heterostructures, with different twisting angles and recorded with different laser excitation energies. New Raman peaks appear in the Raman spectra of TBGs and twisted graphene heterostructures. Their positions depend on the twisting angle θ so that they can be used to provide a rough estimate of the latter. A large enhancement of the Raman G band occurs when the energy of the excitation laser line matches the energy separation between the van Hove singularities in the density of states (DOS) of TBGs with θ from 9° to 17°, when they are probed using laser excitation energies in the visible range. In the case of TBGs with low or high twisting angles, the Raman G band intensity is smaller than twice that of single-layer graphene. These results show that the G band enhancement is associated with the smaller quasi-periodic Moiré unit cell and not with the commensurate superlattice unit cell. It has been reported recently that the enhancement of the extra peaks associated with the Moiré patterns has two different resonance processes. Some peaks are enhanced, both below or above the G band position, for excitation laser energies where the G band is not enhanced. This resonance mechanism is called the intralayer electron-phonon process and is similar to the double resonance Raman process that activates the disorder-induced D band, but, in the case of TBGs, the momentum conservation of the double-resonance process is provided by the periodic potential of the Moiré superlattice.

Ahmad and coworkers provide a review on the preparation and applications of fluorinated graphenes [13]. Two preparation routes are considered: (i) the addition of fluorine atoms and (ii) the exfoliation of graphite fluoride. The chemical bonding in fluorinated graphene, the related properties, and a selection of applications are discussed. These include lubrication, energy storage, and gas sorption and sensing. The authors also address cytotoxicity issues, a very important field that is still often neglected when introducing new materials. However, a good reason for the latter is that it requires a totally different field of competence. Hence, the interest of a team with the needed expertise has to be attracted, which is hard to achieve as long as the actual technological interest of the targeted new material is not fully demonstrated. In the case of cells put in contact with fully fluorinated graphene, the cell viability is shown to decrease. In a general way, the biological response depends on the fluorine content. The adhesion and aggregation of blood platelets are shown to decrease with an increase in the fluorine content. On the other hand, a favorable antibacterial activity against *Escherichia coli* of partially fluorinated graphene is also evidenced.

The other articles concern $sp^3$-carbon-related materials, starting with the research paper by Pakornchote and coworkers, which deals with the modification of electronic and elastic properties of 2D [110] diamond by nitrogen substitution [14]. The authors theoretically demonstrate that 2D diamond derived from the [110] direction exhibiting a washboard conformation can also be stabilized by N-substitution, as was previously shown in the case of 2D diamond that is derived from the [111] direction. Three structural models of washboard-like carbon nitrides of different compositions ($C_6N_2$, $C_5N_3$, and $C_4N_4$) are studied together with the fully hydrogenated washboard-like diamane ($C_8H_4$). The results show that the band gap of washboard-like carbon nitrides is open if no dangling bond is left to be passivated. When comparing with the hydrogenated phase, the N-substituted phases have higher elastic constants and bulk modulus, suggesting that they are possibly harder than diamane, which is fully hydrogenated.

It can be seen that the previous paper includes a comparison with a diamane material. This reveals that diamanes and diamanoids are becoming important materials to the field of 2DC. Indeed, the application potential of diamanes and diamanoids is broad. Besides band-gap engineering, they could be used as an active laser medium in nano-optics. Due to its expected high thermal conductivity, they may be used in thermal management devices. Calculations have shown that diamane is a better host system for single-photon emission than diamond. Diamane-related materials are also expected to be mechanically very strong; therefore, they may be very attractive for ultrathin protective coatings, ultrahigh-strength components in composite materials for aerospace applications for instance, and nano-electromechanical systems. Due to the expected low friction coefficient of the hydrogenated surface, diamanoids may also be used to improve the wear resistance of coated mechanical parts and anti-adhesion surface properties. The expected strength, low coefficient of friction, and bio-compatibility could render diamane-related materials very competitive as building materials to make lower power and miniaturized electronics and biomedical devices. A diamane nanoribbon resonator was calculated to be better than single-layer graphene, bi-layer graphene, $MoS_2$, or other 2D-nanomaterial resonators (at least for the temperature range from 1 K to 300 K) [15]. Heterostructures of graphene and diamanoid would be attractive for tunnel devices, optical linear waveguides, high-efficiency optoelectronic sensors, lithium batteries, and supercapacitors.

Therefore, the next two papers deal with diamane and diamanoids. It includes a contribution from the group that pioneered the research on these new materials by being the first to hypothesize them [16,17]. Chernozatonskii and coworkers provide a review on theoretical and experimental studies on diamane-related materials with various atomic structures and types of functionalization (with either hydrogen or fluor) [18]. This article includes recent results on diamane systems exhibiting Moirés, i.e., involving domains with slight rotational misorientations. It is shown that diamanes are mechanically stronger than graphene and graphane and have wide bandgaps ranging from 3.1 to 4.5 eV depending on the structure. The potential applications are briefly reviewed.

Finally, this Special Issue ends with a review on the experimental synthesis of genuine diamanes and diamanoids including diamanoid/TBG [11]. Genuine diamane is prepared from the exposure of bi-layer graphene (2LG) to hydrogen radicals produced by the hot-filament process at low pressure and temperature. A sharp $sp^3$-bonded carbon stretching mode, assigned to the diamond/lonsdaleite stretching mode between $sp^3$–C (diamond $E_{2g}$ mode; lonsdaleite $A_{1g}$ and $E_{2g}$ modes) is observed in ultraviolet Raman spectra, while no $sp^2$-bonded carbon peak is simultaneously detected. By replacing 2LG with few-layer graphene (FLG), diamanoid/graphene hybrids are formed from the partial conversion of FLG due to the prevalent Bernal stacking sequence. Raman spectroscopy, electron diffraction, and Density Functional Theory calculations show that partial conversion generates TBG located at the interface between the upper diamanoid domain and the non-converted graphenic domain underneath. Carbon–hydrogen bonding in the basal plane of hydrogenated FLG, where carbon is bonded to a single hydrogen over an area of 150 $\mu m^2$, is directly evidenced by Fourier transform infrared microscopy, and the actual full

hydrogenation of diamane is supported by first-principle calculations. Raman mapping and FTIR observations indicate the hydrogenation and subsequent $sp^3$ conversion over surface areas of up to 2000 $\mu m^2$. Importantly, it is believed that dimensions are only limited by the dimensions of the starting material, not by the process. Therefore, those results open the door to mass production of diamanes, diamanoids, and diamanoid/graphene hybrids by means of the hot-filament-assisted CVD process. It is believed that the key to producing homogenous diamane films is to start with very high-quality 2LG material, ideally, single-crystal AB flakes as large as possible. Finally, from a more fundamental standpoint, those recent results should reanimate a 50-years-long discussion on the origin of some crystalline $sp^3$-bonded carbon grains in extraterrestrial environments.

2D materials will definitely play an important role in the close future of technology. What part will carbon materials (2DC) take in it? We do believe that this Special Issue is merely one hint among many others that show that 2DC will maintain a top level of research interest. There are two major reasons for this: (1) as opposed to carbon, alternate non-carbon materials may exhibit fatal drawbacks in the mid/long term with respect to sustainability (scarcity of feedstock sources, intrinsic toxicity) and processing difficulty; (2) the versatility of carbon makes it highly inventive. Beyond graphene, this Special Issue shows several examples of the potential ability of $sp^3$-carbon-related materials to fulfill electronics needs. There might be the future of carbon for such applications, which was unexpected a few years ago, when only graphene was considered. This would not be the first time there was such a change of mind. Recall that not so long ago, energy storage could not do without the most conductive carbon material, namely graphite, while other carbon materials were discarded because of their low electrical conductivity; however, nowadays, in spite of this, using so-called "hard" carbons (i.e., graphenic carbon materials unable to graphitize) instead of graphite is currently the route that is boosting the research activity in this field. Hence, with fullerenes, nanotubes, and graphenes, $sp^2$ carbons might have given their best, while, for decades, $sp^3$ carbons were not seen able to give better than nanodiamonds. The time may have come for $sp^3$-carbon-based 2D materials.

We were very pleased to guest-edit this Special Issue, and we hope that it will reach the widest audience of materials science researchers, in particular those working in the field of carbon-related materials, and that it will contribute to boosting further scientific and technological advances.

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