

Editorial

Graphene and Other 2D Layered Hybrid Nanomaterial-Based Films: Synthesis, Properties, and Applications

Federico Cesano *  and Domenica Scarano * 

Department of Chemistry, NIS (Nanostructured Interfaces and Surfaces) Interdepartmental Centre and INSTM Centro di Riferimento, University of Torino, Via P. Giuria, 7, 10125 Torino, Italy

* Correspondence: federico.cesano@unito.it (F.C.); domenica.scarano@unito.it (D.S.);

Tel.: +39-11-670-7834 (F.C. & D.S.)

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Abstract: This Special Issue contains a series of reviews and research articles demonstrating actual perspectives and future trends of 2D-based materials for the generation of functional films, coatings, and hybrid interfaces with controlled morphology and structure.

Keywords: coatings; 2D materials; layered materials; graphene; reduced graphene oxide; transition metal dichalcogenides; WS_2 ; MoS_2 ; transition metal carbides; transition metal nitrides; transition metal carbonitrides; silicene; germanene; stanene; van der Waals heterostructures; interfaces

1. Introduction

Graphene is one of the most interesting and versatile materials of the last several years, especially since the Nobel prize in physics was awarded in 2010 to Geim and Novoselov for “groundbreaking experiments regarding the two-dimensional material graphene” [1]. The new material, being “isolated” in a controlled manner and recognised for its unique properties strongly different from those of the bulk counterpart, is a matter of interest for both fundamental studies and practical applications. Whilst the research on graphene has been extremely active since its discovery, a plethora of opportunities has appeared more recently, when other 2D layered systems and their combinations (i.e., van der Waals heterostructures) have been taken into consideration [2]. Moreover, two-dimensional (2D) systems, consisting of a single layer of atoms, have emerged among the main candidate materials for next-generation applications [3–5]. In general terms, the strict limit of the one atomic layer in thickness of these 2D crystals does not matter when new properties and applications with respect to 3D counterparts are taken into account. Accordingly, a material exhibiting some unique properties is, in fact, still considered a 2D material even if it is made of one/two/three or more layers. In such cases, they are described as being of monolayer, bilayer, three-layer, or few-layer thickness, but these materials have the potential to revolutionise electronics concepts and make new technologies feasible.

At the time of writing this Special Issue, a few dozen materials made of crystalline and one-atom-thick systems have been successfully obtained by exfoliation of 3D compounds (top-down approach) or by synthetic procedures (bottom-up approach) [6], but it is hard to give a more precise number of the 2D crystals due to the fast advancement in the field. Further, due to the discovery in 2017 of magnetic 2D materials, rapid progress in this field can also be mentioned. On this matter, significant examples can be highlighted, including magnetic single-layer CrI_3 (i.e., odd layer numbers, the magnetisation being absent for an even number of layers due to the antiferromagnetic coupling between the layers) [7] and ferromagnetic two-layered $Cr_2Ge_2Te_6$ [8]. Notice that, although all 2D materials are expected to be inorganics, chromium–chloride–pyrazine ($CrCl_2(\text{pyrazine})_2$) is the first

discovered organic/inorganic hybrid 2D material [9]. Together with its other prominent properties, 2D $\text{CrCl}_2(\text{pyrazine})_2$ exhibits magnetic properties.

2. 2D Materials: Quō Vādis?

Recently, Mounet et al. [10] showed that only a very small fraction of possible 2D crystals—belonging to transition metal carbides, nitrides, or carbonitrides (MXenes) [11]; silicene, germanene, or stanene (Xenes) [12]; transition metal dichalcogenides (MX_2) [6]; and graphene and graphene derivatives [13]—have been considered so far. Therefore, most 2D materials have not yet been discovered. In this regard, nothing can be said to be certain about the next one-atom-thick material. However, some possible highlights can be envisaged, including more simple fabrication techniques [14]; precise control of size and shape; greener production methods; 2D crystal doping [15]; superconducting properties of 2D crystals [16]; atom-by-atom assembling of 2D materials directly onto the surface of solids, such as photoactive TiO_2 polytypes [17]; or an energy breakthrough of 2D crystals (i.e., graphene) as a source of clean, limitless energy due to the layer motion (e.g., rippled morphology and temperature-induced curvature inversion) [18].

3. This Special Issue

This Special Issue, entitled “Graphene and Other 2D Layered Nanomaterial-Based Films: Synthesis, Properties, and Applications”, contains a collection of three reviews and eight research articles covering fundamental studies and applications of films and coatings based on 2D materials. Going into detail, the thermal growth of graphene and the advances in the field of free-standing graphene films for thermal applications are comprehensively reviewed by Tan et al. [19] and Gong et al. [20], respectively. The first review focuses on the mechanisms and main fabrication methods (epitaxial growth, chemical vapour deposition, plasma-enhanced chemical vapour deposition, and combustion), summarising the latest research progress in optimising growth parameters. Besides synthesis methods, the second review is dedicated to interface properties and the thermal conductivity of materials based on free-standing graphene nanosheets, as well as their thermal applications (e.g., heat dissipation materials, wearable flexible materials for thermal control). Along with surface-enhanced Raman spectroscopy (SERS), 2D-material-coated plasmonic structures are described in the review article by Xia [21]. In this review, the effects and advantages of combining 2D materials with traditional metallic plasmonic structures (i.e., higher SERS enhancement factors, oxidation protection of the metal surface, and protection of molecules from photo-induced damage) have been highlighted.

The preparation, properties, and applications of some 2D materials (i.e., graphene, graphene oxide, WS_2 , MoS_2 , and 2D carbon nitride nanosheets in a nickel–phosphorus alloy) are discussed in the eight research papers. Briefly, the fundamental work conducted by Lee et al. [22] provides a valuable insight into the nondestructive transfer of graphene from the surface of a metal catalyst to target substrates, without dissolving the metallic catalyst by chemical etching. Tsai et al. [23] report the preparation of a graphene-coated electrode by a spin-coating technique and the consequent effect on enhancing bacterial adhesion and increasing the power generation of the deposited film in microbial fuel cells (MFCs). Lv and Zhao et al. have investigated the preparation by a chemical vapour deposition (CVD) technique and photoluminescence properties of a WS_2 monolayer (which is a direct bandgap semiconductor) [24] in a first article and the preparation of mono- and few-layered MoS_2 by a CVD technique using water as a transport agent and growth promoter of the MoS_2 sheets [25] in a second paper. Mardle et al. [26] have evaluated the catalytic power performance of aligned Pt nanowires grown on reduced graphene oxide in proton-exchange membrane fuel cell (PEMFC) electrodes, while MoS_2 nanosheets supported on Pt nanoparticles have been obtained by Cheng et al. [27] to enhance the power conversion efficiency (PCE) of dye-sensitised solar cells (DSSCs) up to 7.52%. Alternatively, Shi et al. [28] have grown graphene/few-layered MoS_2/Si heterostructures by a CVD technique, and they investigated the double-junction properties in terms of enhancing the

photovoltaic performance of van der Waals heterostructures. Finally, Fayyad et al. [29] have obtained 2D carbon nitride (C_3N_4) nanosheets in a nickel–phosphorus (NiP) matrix by ultrasonication during electroless plating of NiP. The microhardness and corrosion resistance of the as-modified coatings have been evaluated and compared with those of the native NiP alloy.

In summary, this Special Issue of *Coatings* compiles a series of reviews and research articles demonstrating the potential of 2D-based materials for the generation of functional films, coatings, and hybrid interfaces with controlled morphology and structure.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. The Nobel Prize in Physics 2010. Available online: http://www.nobelprize.org/nobel_prizes/physics/laureates/2010/ (accessed on 15 November 2018).
2. Novoselov, K.S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A.H. 2D materials and van der Waals heterostructures. *Science* **2016**, *353*, aac9439. [CrossRef] [PubMed]
3. Zeng, M.; Xiao, Y.; Liu, J.; Yang, K.; Fu, L. Exploring two-dimensional materials toward the next-generation circuits: From monomer design to assembly control. *Chem. Rev.* **2018**, *118*, 6236–6296. [CrossRef] [PubMed]
4. Sun, Y.; Chen, D.; Liang, Z. Two-dimensional MXenes for energy storage and conversion applications. *Mater. Today Energy* **2017**, *5*, 22–36. [CrossRef]
5. Roldan, R.; Chirrol, L.; Prada, E.; Silva-Guillen, J.A.; San-Jose, P.; Guinea, F. Theory of 2D crystals: Graphene and beyond. *Chem. Soc. Rev.* **2017**, *46*, 4387–4399. [CrossRef] [PubMed]
6. Manzeli, S.; Ovchinnikov, D.; Pasquier, D.; Yazyev, O.V.; Kis, A. 2D transition metal dichalcogenides. *Nat. Rev. Mater.* **2017**, *2*, 17033. [CrossRef]
7. Huang, B.; Clark, G.; Navarro-Moratalla, E.; Klein, D.R.; Cheng, R.; Seyler, K.L.; Zhong, D.; Schmidgall, E.; McGuire, M.A.; Cobden, D.H.; et al. Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit. *Nature* **2017**, *546*, 270–273. [CrossRef] [PubMed]
8. Gong, C.; Li, L.; Li, Z.; Ji, H.; Stern, A.; Xia, Y.; Cao, T.; Bao, W.; Wang, C.; Wang, Y.; et al. Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals. *Nature* **2017**, *546*, 265–269. [CrossRef] [PubMed]
9. Pedersen, K.S.; Perlepe, P.; Aubrey, M.L.; Woodruff, D.N.; Reyes-Lillo, S.E.; Reinholdt, A.; Voigt, L.; Li, Z.; Borup, K.; Rouzières, M.; et al. Formation of the layered conductive magnet $CrCl_2(pyrazine)_2$ through redox-active coordination chemistry. *Nat. Chem.* **2018**, *10*, 1056–1061. [CrossRef] [PubMed]
10. Mounet, N.; Gibertini, M.; Schwaller, P.; Campi, D.; Merkys, A.; Marrazzo, A.; Sohler, T.; Castelli, I.E.; Cepellotti, A.; Pizzi, G.; et al. Two-dimensional materials from high-throughput computational exfoliation of experimentally known compounds. *Nat. Nanotechnol.* **2018**, *13*, 246–252. [CrossRef] [PubMed]
11. Hong Ng, V.M.; Huang, H.; Zhou, K.; Lee, P.S.; Que, W.; Xu, J.Z.; Kong, L.B. Recent progress in layered transition metal carbides and/or nitrides (MXenes) and their composites: Synthesis and applications. *J. Mater. Chem. A* **2017**, *5*, 3039–3068. [CrossRef]
12. Molle, A.; Goldberger, J.; Houssa, M.; Xu, Y.; Zhang, S.C.; Akinwande, D. Buckled two-dimensional Xene sheets. *Nat. Mater.* **2017**, *16*, 163–169. [CrossRef] [PubMed]
13. Inagaki, M.; Kang, F. Graphene derivatives: Graphane, fluorographene, graphene oxide, graphyne and graphdiyne. *J. Mater. Chem. A* **2014**, *2*, 13193–13206. [CrossRef]
14. Shim, J.; Bae, S.H.; Kong, W.; Lee, D.; Qiao, K.; Nezich, D.; Park, Y.J.; Zhao, R.; Sundaram, S.; Li, X.; et al. Controlled crack propagation for atomic precision handling of wafer-scale two-dimensional materials. *Science* **2018**, *342*, 833–836. [CrossRef] [PubMed]
15. Feng, S.; Lin, Z.; Gan, X.; Lv, R.; Terrones, M. Doping two-dimensional materials: Ultra-sensitive sensors, band gap tuning and ferromagnetic monolayers. *Nanoscale Horiz.* **2017**, *2*, 72–80. [CrossRef]
16. Saito, Y.; Nojima, T.; Iwasa, Y. Highly crystalline 2D superconductors. *Nat. Rev. Mater.* **2016**, *2*, 16094. [CrossRef]
17. Cravanzola, S.; Cesano, F.; Gaziano, F.; Scarano, D. Carbon domains on MoS_2/TiO_2 system via acetylene oligomerization: Synthesis, structure and surface properties. *Front. Chem.* **2017**, *5*, 91. [CrossRef] [PubMed]

18. Ackerman, M.L.; Kumar, P.; Neek-Amal, M.; Thibado, P.M.; Peeters, F.M.; Singh, S. Anomalous dynamical behavior of freestanding graphene membranes. *Phys. Rev. Lett.* **2016**, *117*, 126801. [[CrossRef](#)] [[PubMed](#)]
19. Tan, H.; Wang, D.; Guo, Y. Thermal growth of graphene: A review. *Coatings* **2018**, *8*, 40. [[CrossRef](#)]
20. Gong, F.; Li, H.; Wang, W.; Xia, D.; Liu, Q.; Papavassiliou, D.V.; Xu, Z. Recent advances in graphene-based free-standing films for thermal management: Synthesis, properties, and applications. *Coatings* **2018**, *8*, 63. [[CrossRef](#)]
21. Xia, M. 2D materials-coated plasmonic structures for SERS applications. *Coatings* **2018**, *8*, 137. [[CrossRef](#)]
22. Lee, J.; Lee, S.; Yu, H.K. Contamination-free graphene transfer from Cu-foil and Cu-thin-film/sapphire. *Coatings* **2017**, *7*, 218. [[CrossRef](#)]
23. Tsai, H.-Y.; Hsu, W.-H.; Liao, Y.-J. Effect of electrode coating with graphene suspension on power generation of microbial fuel cells. *Coatings* **2018**, *8*, 243. [[CrossRef](#)]
24. Lv, Y.; Huang, F.; Zhang, L.; Weng, J.; Zhao, S.; Ji, Z. Preparation and photoluminescence of tungsten disulfide monolayer. *Coatings* **2018**, *8*, 205. [[CrossRef](#)]
25. Zhao, S.; Weng, J.; Jin, S.; Lv, Y.; Ji, Z. Chemical vapor transport deposition of molybdenum disulfide layers using H₂O vapor as the transport agent. *Coatings* **2018**, *8*, 78. [[CrossRef](#)]
26. Mardle, P.; Fernihough, O.; Du, S. Evaluation of the scaffolding effect of Pt nanowires supported on reduced graphene oxide in PEMFC electrodes. *Coatings* **2018**, *8*, 48. [[CrossRef](#)]
27. Cheng, C.-K.; Lin, J.-Y.; Huang, K.-C.; Yeh, T.-K.; Hsieh, C.-K. Enhanced efficiency of dye-sensitized solar counter electrodes consisting of two-dimensional nanostructural molybdenum disulfide nanosheets supported Pt nanoparticles. *Coatings* **2017**, *7*, 167. [[CrossRef](#)]
28. Shi, W.; Ma, X. Photovoltaic effect in graphene/MoS₂/Si van der Waals heterostructures. *Coatings* **2017**, *8*, 2. [[CrossRef](#)]
29. Fayyad, E.M.; Abdullah, A.M.; Hassan, M.K.; Mohamed, A.M.; Wang, C.; Jarjoura, G.; Farhat, Z. Synthesis, characterization, and application of novel Ni-p-carbon nitride nanocomposites. *Coatings* **2018**, *8*, 37. [[CrossRef](#)]



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