

EDITORIAL

Graphene-based nanocomposites for structural and functional applications: using 2-dimensional materials in a 3-dimensional world

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Graphene-based nanocomposites for structural and functional applications: using 2-dimensional materials in a 3-dimensional world

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Abstract

Graphene-based composites are currently the only application of graphene already commercialized on a large scale. However, the performance of such products is not comparable to that of pristine graphene sheets, measured at the nanoscale, which easily outperform well-established materials such as steel, silicon, or copper. A key reason for this difference in properties is that it is not yet fully understood how two-dimensional (2D)-based composites work at the nanoscale level and, more importantly, what is the ultimate performance (mechanical, electrical, etc.) that can be achieved when they are included in a bulk material. In the first year of the ramp-up phase of the Flagship, the ‘Nanocomposites’ work package has studied how to improve the processing, interaction, and performance of graphene and related materials (GRMs) in three-dimensional (3D) composites. This article offers a quick overview of some of the main results obtained within this rapidly evolving field.

1. Introduction

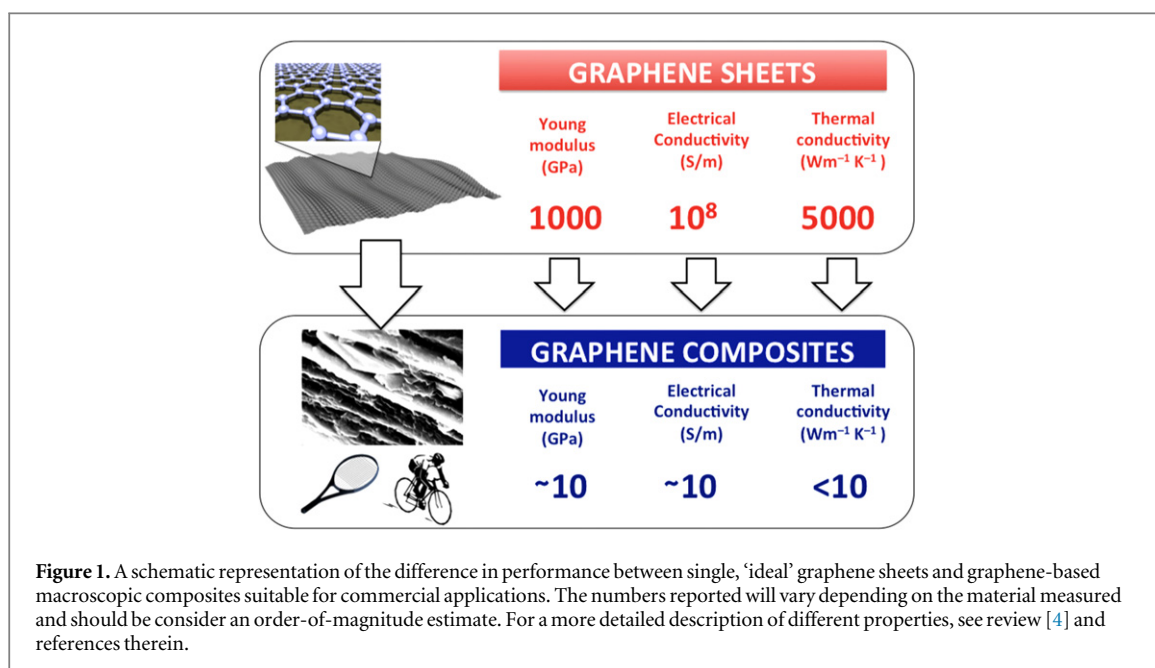
Graphene-based composites are currently the only application of graphene already commercialized on a large scale. The number of products containing these composites is increasing continuously, from tennis rackets, to bicycles, to skis [1, 2]. However, the performance of such products is not comparable to that of pristine graphene sheets, measured at the nanoscale, which easily outperform well-established materials such as steel, silicon, or copper.

A key reason for this difference in properties is that it is not yet fully understood how two-dimensional (2D)-based composites work at the nanoscale level and, more importantly, what is the ultimate performance (mechanical, electrical, etc.) that can be achieved when they are included into a bulk material. Figure 1 provides a schematic comparison of how the properties of graphene worsen when translated from the nanoscale to a macroscale material. More than 10 000 papers were published on graphene composite

materials in 2014 [3]. In these papers, the beneficial effect of graphene as an additive has been demonstrated for a great variety of bulk systems, but it is still not clear how extensively graphene will be used in future industrial applications, despite the importance of today’s carbon fillers. To understand if, and where, graphene and related 2D materials (GRMs) can be truly competitive at the industrial level, a strong combination of processing techniques, prototyping, characterization, and modelling is needed.

The main goal of the ‘Nanocomposites’ work package of the Flagship is thus to translate the exceptional properties of GRMs from the single-sheet level to the macroscale, creating new composite materials that merge the exceptional thermal, optical, electronic, electrochemical, and structural properties of graphene with properties of more traditional, bulk materials.

In the first year of the ramp-up phase of the Flagship, the ‘Nanocomposites’ work package has studied how to improve the processing, interaction, and performance of GRMs in three-dimensional (3D)



composites. This article offers a quick overview of some of the main results obtained within this rapidly evolving field.

2. Composites production and processing

While for specific applications in electronics very small amounts of graphene are typically required, large-scale applications of GRM composites will require tons of starting material. Naturally the graphene cost for composites needs to be much lower than for other applications, and the quality can be lower compared to the 'ideal' graphene typically produced in a lab. Several published papers have demonstrated that graphene could improve the mechanical and electrical properties of composites even when added in very low quantities, such as a few volume percent or below. (For a comprehensive list of published works, see section 11 in the recently published graphene roadmap.) [4] An improvement in mechanical or electrical performance can be easily demonstrated on a lab scale for many graphene-polymer composites; however, full exploitation requires also the cost and scaling factors to be sufficiently competitive compared to established carbonaceous materials such as carbon black, carbon fibers, graphite powder, and carbon nanotubes. What most scientific works do not take into account is that even upon the addition of a few % of graphene in a polymeric material, the final cost will be significantly increased. Such a cost increase will hinder any industrial applications, especially if graphene is used for composites with cheap-commodity polymers and low added-value applications. This is the reason why GRM composites, similarly to other high-tech products, will be first commercialized for high added-value applications, such as sporting goods [2] and

aerospace and biomedical devices. It is thus essential to evaluate correctly and balance the trade-off between cost and quality when using GRMs in composites. There is a stark difference between the high-quality GRMs produced in academia, mostly obtained by chemical vapour deposition or liquid phase exfoliation, and the GRMs produced on a large, industrial scale, which typically use mechano-chemical and thermo-chemical exfoliation processes to reduce cost and avoid using organic solvents [5–7].

For this reason, we have prepared and compared different kinds of materials as starting components, ranging from liquid-phase exfoliated (LPE) graphene and electrochemically exfoliated graphene (e.g.) to chemically modified graphene oxide (GO), to cheap graphene nanoplatelets [8]. Some of these materials can already be produced on the gram or kilogram scale [5, 9].

Applications of graphene in composites need processing steps compatible with the current technology, thus requiring efficient ways to process graphene into polymer granules and liquid master batches. Graphene is stabilized in solution or in composites by the supramolecular interactions with organic solvents or surfactant [10]. In general, whatever molecule is used for the exfoliation, it will remain adsorbed on graphene sheets as well (at least in trace amounts), thereby reducing their interaction with the polymer matrix and the beneficial effects of graphene additives.

An ideal solution would be to use molecules that are already well established for the large-scale compounding of polymers, such as additives for polymer products [11, 12] or industrial colorants [12]. Interestingly, the same molecules shall be used also to solubilize other 2D materials such as boron nitride, tungsten disulphide, and molybdenum sulphides, selenides, and tellurides for electronic applications [13].

Covalent modification of graphene via its GO form is also a viable technique for applications in composites. GO has been for a long time the underdog of the graphene family, because the chemical defects that make it highly processable even in water environments, as well as adaptable for functionalization at the covalent and non-covalent level, ultimately destroy the nice physical properties of graphene. Nevertheless, in recent years production and successful application of different forms of GO and reduced GO have been demonstrated in different fields, from electronics to energy storage to polymer composites [4].

A main advantage of GO is that covalent chemistry approaches can be employed in order to tune, or maximize, the interaction of the GO sheets with suitable polymers and for test applications in bio-sensing or in tissue engineering. Differently from graphene, GO can be produced in water, with a high yield of monolayers featuring lateral sizes up to 100 μm , [14] much larger than the typical graphene sheets obtained by the LPE method.

Recently, in addition to supramolecular or covalent exfoliation of graphene in liquid media, electrochemical exfoliation was also demonstrated to be an efficient way to prepare powders and dispersions of e.g. and electrochemically exfoliated graphene oxide (EGO) using an upscalable method with a low and tunable grade of oxidation [14–16].

3. Characterization and modeling of GRMs in composites

Most of the composites containing GRMs have complex structures, with billions of 2D sheets interacting with the surrounding 3D matrix and with each other. Thus, besides production and applications, also the characterization and modelling of such materials is fundamental to improve their performance [17, 18].

The composition of GRM-based composites can be established using x-ray photoelectron spectroscopy and thermal gravimetric analysis. Raman spectroscopy is a most powerful technique to characterize the quality of graphene, including the presence of defects, the way it interacts electronically with (macro)molecules, etc; furthermore, it can be used to measure mechanical stress in graphene sheets embedded into composites [19, 20]. For example, recently we have used Raman spectroscopy to measure the tensile response of a prototype graphene touch-panel display, which can also be viewed as a model composite consisting of CVD graphene layers embedded within layers of polyethylene terephthalate (PET) [19].

We have also recently developed a technique to quantify the orientation in graphene-based nanocomposites using polarized Raman spectroscopy. In this way, the orientation distribution function (ODF) of graphene in a bulk material can be quantified. The

ODF will be related to the mechanical properties of nanocomposites [21].

Modelling of GRM materials is difficult also, because the sheets obtained from LPE are typically of very variable shape and size. To circumvent this problem, we have developed a technique based on the automatized image processing of atomic force microscopy (AFM) data to measure, one by one, the exact shape and size of thousands of nanosheets obtained by exfoliation, and used different statistical functions to model the asymmetric distribution of the nanosheet sizes typically obtained [18]. Since the resolution of AFM is much greater than the average sheet size, analysis could be performed directly at the nanoscale and single-sheet levels.

4. Structural applications of GRM composites (aeronautics, automotive, mechanics, etc)

Most of the efforts to develop GRM-based composites are focused on polymer matrices, including thermosets, thermoplastics, and rubbers. Low loadings of GRMs are used as matrix modifiers for some applications (e.g., electrical conductivity and thermal stability), while high loadings have been also used for structural reinforcement applications. Importantly, these studies have used scalable methods for composite production, such as calendaring, twin-screw processing, and injection molding, which are suitable for industrial processing and applications of GRMs. Furthermore, techniques such as *in-situ* polymerization are being established to aid the dispersion for the graphene during processing. For example, an iron polymerization catalyst has been placed directly onto graphene flakes [7] prior to making a polyolefin composite.

Initial work on mechanical properties has established that the continuum micromechanic models used for traditional carbon fibre composites can be transferred to graphene composites, despite the reinforcement being one atom thick. For example, it has been shown that multi-layer graphene flakes follow the shear lag model, and, thus, there exists a critical graphene flake diameter, beneath which flakes are too small to reinforce the composite. This critical flake diameter is particularly pertinent due to a relatively poor interfacial strength of ~ 0.4 MPa between graphene and polymer matrix [20]. This predicted short-flake behaviour has now been demonstrated in both bulk amorphous (PMMA) [22] and semi-crystalline (PP) [23] systems, with few-layer graphene (FLG) flakes less than 5 microns in diameter giving little reinforcement, whereas larger flakes, 20 microns in diameter, give a linear improvement in a modulus to at least a 20 wt% loading.

On a mesoscopic scale we developed for this work package a 2D hierarchical fibre bundle model,

extending a previous one-dimensional (1D) code; the first application of this 2D code has been recently reported, predicting the stress-strain curves of graphene-composite nanofibers, finding a good agreement between simulations and experiments [24].

The surface chemistry of the graphene has also been shown to be crucial in determining the physical properties of the composites. The fracture toughness (K_{IC}) of the GRM-epoxy composites was found to be highest when incorporating thermally reduced GO (TRGO), due to its functional groups providing a strong interaction with the matrix [25]. This toughness improvement was significantly better than in the equivalent carbon nanotube system, with electron microscopy suggesting the difference was due to the ability of FLGs to absorb energy through both crack deflection and exfoliation of the FLG flakes. It was noted, however, that there was an optimal loading of GRMs, after which the fracture toughness started to decrease, in line with the reported behaviour for other nanocomposite systems. The functionality of the graphene fillers also determines the other mechanical properties, with TRGO giving a 1000% improvement in tensile strength in styrene-butadiene rubber (SBR) elastomers compared to a 200% improvement found for carboxylic acid-edge functionalized graphene [26]. Likewise, the TRGO had a conductivity of six orders of magnitude higher than any of the other graphene flakes studied.

One caution, though, when considering the role of functional groups, is that whilst GO flakes may give good specific properties, the absolute improvement that these flakes can provide is limited by their tendency to aggregate and increase the system's viscosity at very low loading. This may not be an issue for matrix-modification applications such as electrical conductivity, but it is a challenge for high-loading applications such as modulus reinforcement. However, the lower surface and less functionalized few- to many-layer graphene flakes can give improvements at loadings of 10–20 +wt% [6, 23]. Thus, there appears to be an optimal degree of functionalization, which will provide good specific properties whilst still ensuring processability at loadings sufficiently high to give useful property increases.

5. Functional applications of GRM composites (energy storage, catalysis, electronics, etc)

Graphene can interact with other materials and components not only to reinforce them, but also to generate new properties and functionalities [12]. Thanks to their high surface area, mechanical strength, flexibility, and chemical versatility, graphene-based nanosheets can be used as ultra-thin scaffolds and

combined with other materials to enhance their physical and chemical properties.

Graphene was used as a 2D nanoscopic platform to create thin layers or bulk composite foams having 3D macroporous architectures with functional properties suitable for different applications such as transistors, catalysts, batteries, supercapacitors, etc

With this approach we could create 2D composites of GO and e.g. with silica, hematite, or conductive polymers. These composites have been used to produce metal-free catalysts in fuel cells, exhibiting superior performance to that of platinum-based catalysts; to enhance lithium storage in batteries, yielding capacity values comparable to commercially available batteries; to realize photosensors comparable to state-of-the-art, silicon-based inorganic photodetectors, and micro-supercapacitors with high capacitance.

Nitrogen-doped carbon nanosheets with size-defined mesopores were used as electrochemical catalysts for the oxygen reduction reaction (ORR), exhibiting superior performance to that of Pt/C in an alkaline medium and pronounced activity and stability under acidic conditions. This is a very rare example of metal-free graphene catalysts, exhibiting pronounced electrocatalytic performance in both alkaline and acidic media for the ORR [27].

Using a different, bottom-up approach, highly active nitrogen-doped, carbon-based, metal-free oxygen reduction reaction electrocatalysts were prepared using nitrogen-enriched aromatic polymers and colloidal silica particles as precursor and template, respectively, followed by ammonia activation. The prepared catalysts show porous graphene-like structures with a high surface area. They exhibit the highest oxygen reduction reaction activity (half-wave potential of 0.85 V versus reversible hydrogen electrode with a low loading of 0.1 mg cm^{-2}) in alkaline media among all reported metal-free catalysts. Significantly, when used for constructing the air electrode of a zinc-air battery, this metal-free catalyst outperforms the state-of-the-art platinum-based catalyst [28].

Electrochemically exfoliated graphene (EGO) paper also possessed excellent mechanical properties, with no significant change of electrical conductivity after bending to a 4 mm radius. All-solid-state flexible supercapacitors manufactured on the basis of e.g. films delivered a high area capacitance of 11.3 mF cm^{-2} and an excellent rate capability of 5000 mV s^{-1} . Boron-nitrogen co-doped graphene films were also produced via a layer-by-layer approach employing graphene oxide, cationic poly-L-Lysine, and H_3BO_3 as nitrogen- and boron-precursors. The resulting doped graphene films show high electrical conductivity. Micro-supercapacitor devices were for the first time fabricated based on such doped graphene films, delivering outstanding volumetric capacitance

of $\sim 488 \text{ F cm}^{-3}$ and an excellent rate capability of up to 2000 V s^{-1} [28].

Graphene-based foams (GFs) were prepared with EGO using a template-directed coating method and functionalized with an iron oxide porous layer to obtain bulk composites for lithium storage. The Fe_2O_3 :EGO ratio could be optimized to maximize its performance in lithium batteries, yielding an initial capacity of 701 mAh g^{-1} for an Fe_2O_3 :EGO ratio of 2:1 [15].

Functional composites of graphene with conducting polymers were also demonstrated as floating gates for memory devices [29] and as transparent electrodes for organic photodetectors [30]. As a proof of concept, some of these solution-processable graphene sheets have then been used as active layers in field-effect transistor (FET) devices. Interestingly, the addition of quantities $<1\%$ w/w of graphene in the active layer of the device has determined a 40-fold improvement of the charge mobility and 80% reduction of contact resistance [31].

Beyond graphene, we produced also MoS_2 /CdS nanocomposites that can be used as high-efficiency photocatalysts for H_2 production in the absence of a Pt cocatalyst. Under illumination with 0.5 sun (50 mW cm^{-2}), the catalyst exhibits excellent H_2 -generation activity (up to $\sim 137 \mu\text{mol h}^{-1}$) and a high apparent quantum yield ($\sim 10.5\%$ at 450 nm) [32].

6. Conclusions

Nanocomposites offer a further degree of tunability of the properties of graphene through their incorporation with other materials or even using altogether different 2D materials. The possibility that nanocomposites give to control the structure and, hence, properties of a material across multiple length scales gives access to a range of properties that may not otherwise be achievable. Our endeavour has produced composites from the bulk scale to porous, highly structured films and foams. These systems have been tested in various prototypes of functional devices including FETs, photodetectors, supercapacitors, and batteries.

In the first year of the Flagship, the potentialities of GRM composites have been demonstrated in a wide range of scientific works and have fostered broad industrial interest and academic-industry collaborations. The transfer of GRM composites from basic research to commercialization is already ongoing. However, to ensure long-lasting impact, a deeper understanding of the structure and performance of GRM composites will be needed, as well as an extensive evaluation of how these materials perform compared to conventional composites, taking into account performance, cost, and processability.

There is practically no limit to the number of 2D composites that can be constructed based on a

graphene backbone structure, using chemistry to modify them.

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