

# Nanoscale Mechanics of Graphene and Graphene Oxide in Composites: A Scientific and Technological Perspective

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Graphene shows considerable promise in structural composite applications thanks to its unique combination of high tensile strength, Young's modulus and structural flexibility which arise due to its maximal chemical bond strength and minimal atomic thickness. However, the ultimate performance of graphene composites will depend, in addition to the properties of the matrix and interface, on the morphology of the graphene used, including the size and shape of the sheets and the number of chemical defects present. For example, whilst oxidized  $sp^3$  carbon atoms and vacancies in a graphene sheet can degrade its mechanical strength, they can also increase its interaction with other materials such as the polymer matrix of a composite, thus maximizing stress transfer and leading to more efficient mechanical reinforcement. Herein, we present an overview of some recently published work on graphene mechanical properties and discuss a list of challenges that need to be overcome (notwithstanding the strong hype existing on this material) for the development of graphene-based materials into a successful technology.

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DOI: 10.1002/adma.201505469



## 1. Introduction

One of the most celebrated qualities of graphene, in both scientific papers and general media, is related to its mechanical properties. The hyperbolic definition “stronger than steel” has been often used for graphene, creating great expectations amongst laymen and industrial stakeholders.<sup>[1]</sup> The first commercial products using graphene composites further reinforced this hype by showing adverts where graphene-based tennis rackets were used to pierce metallic fences or shoot tennis balls faster than a fast racing car.<sup>[2]</sup>

Amongst the possible breakthrough applications of graphene, structural reinforcement in composites is often chosen as one of the most “mature” and promising, given that several products are already available on the market.<sup>[3]</sup> However, the performance of real, macroscopic graphene-based composites is still orders

of magnitude lower than that of the claimed properties of graphene.<sup>[4,5]</sup> This disparity between the great hype surrounding the ideal performance of graphene and the reduced performance observed in the current generation of real products may hamper the success of graphene as a new technology. It is difficult, thus, to foresee if graphene will become a truly disruptive technology in this field or just give an incremental advantage as compared to the existing materials already used for structural reinforcement.

We do not have a definitive answer to this question, but in the following sections we attempt to clarify the main challenges that need to be solved to exploit the full potential of graphene in composites materials: starting from some recent results published on the topic, we will discuss the importance of sheet size and shape, including how to correctly define it and its effect on materials performance on mesoscopic scale. We will also see how the performance of the material is influenced by the chemical properties of the sheet, where the presence of defects or chemical groups affects material failure, fosters interaction with the matrix, or allows an efficient dispersion of the graphene into the composite. Finally we will use all these topics to discuss how, and if, this extraordinary material will be used in the near future.

## 2. Strong but Flexible

A single, defectless sheet of graphene has a tensile strength of  $\approx 100$  GPa and a Young's modulus of  $\approx 1$  TPa.<sup>[5,6]</sup> Graphene

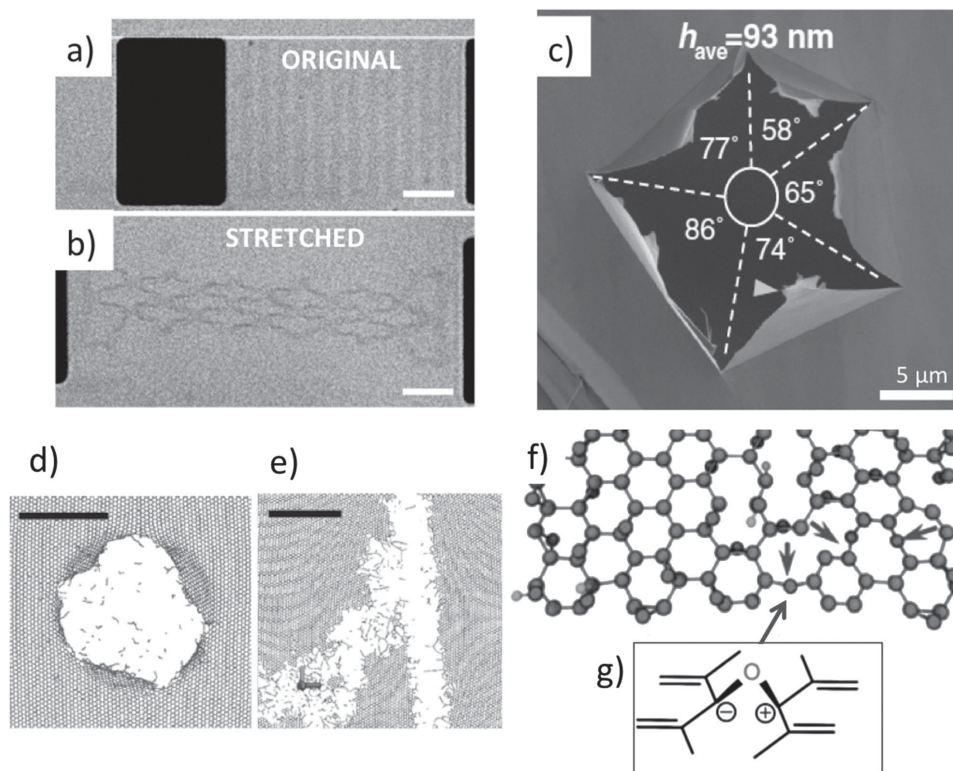
thus can be considered ideally as the strongest material known, though not the stiffest, as both diamond and carbyne have higher moduli. However, it is found when graphene is translated from a single-sheet to macroscale applications that the latter, graphene-based materials still do not outperform steel (strength  $\approx 1$  GPa and Young's modulus  $\approx 200$  GPa, respectively). The reasons for this underperformance of graphene on the bulk scale are primarily due to the crucial role of graphene defects and aggregation.

The outstanding mechanical properties of graphene are due to the high stability of the  $sp^2$  bonds which form the graphene lattice. These bonds oppose strongly changes in length and angle, yielding a very high tensile energy when strained. Conversely, the bending of a graphene sheet does not lead to a significant deformation of these bonds, at least for the nanometric radii of curvature that are of practical interest. Thus the energy needed to bend graphene is much smaller than the energy needed to stretch it for a given degree of deformation.<sup>[7,8]</sup> It is this combination of high axial, tensile stiffness and strength coupled with a very high flexibility (due to the atomically thin thickness) that makes 2D materials, and especially graphene, unique. The first measurements of graphene Young's modulus and strength<sup>[9]</sup> took full advantage of these properties; a tip of an atomic force microscope (AFM) was used to nano-indent

suspended graphene sheets from which a graphene breaking strength  $\approx 130$  GPa was obtained (assuming zero bending rigidity). Even if these early measurements tended to overestimate the real tensile strength,<sup>[10]</sup> a value of about 100 GPa can be assumed for perfect graphene.<sup>[5]</sup>

Besides nano-indentation, graphene can also withstand large pressure differences due to its strength and flexibility and thus can behave as a unique gas separation barrier that is just one atom thick. Bunch et al.<sup>[11]</sup> suspended single graphene sheets over silicon micro-chambers. When the external pressure was varied respect to that in the cavity, the sheets sustained a pressure difference up to 90 KPa for many hours, bulging outward (or inward) without breaking. Graphene was used in this way to create the world's thinnest balloons.

An impressive demonstration of graphene's properties was recently obtained by cutting single layers of graphene in shapes inspired by Japanese kirigami (i.e., a variation of origami that includes cutting of the paper). These shaped layers could be stretched up to 240% of their initial length, bent using the radiation pressure of a laser beam or twisted with a magnetic field without breaking (Figure 1a,b).<sup>[12]</sup> The strength/flexibility combination was also key to produce suspended multi-layer graphene membranes that could survive the impact of high-speed microbullets, demonstrating a specific penetration energy for



**Figure 1.** Published examples on the high mechanical properties of graphene at the nanoscale. a,b) Kirigami structure of monoatomic graphene in its original (a) and highly stretched state (b). Scalebars are 10  $\mu\text{m}$ . Reproduced with permission.<sup>[12]</sup> Copyright 2015, Nature Publishing Group. c) Few-layers of graphene after being hit by a silica micro-bullet. Reproduced with permission.<sup>[13]</sup> Copyright 2014, The American Association for the Advancement of Science. d,e) Modeling of the catastrophic failure of graphene under indentation (d) or tensile strain (e). Scalebars are 5 nm. Reproduced with permission.<sup>[10]</sup> Copyright 2015, Royal Society of Chemistry. f) Modeling of GO plasticity when subjected to biaxial tension. Grey, red and green beads represent carbon, oxygen and hydrogen atoms, respectively. The dark-blue arrows highlight the locations where epoxide-to-ether transformations occurred. g) A schematic representation of the epoxide species formed. The formal charges indicated on the drawing should not be taken literally. Reproduced with permission.<sup>[14]</sup> Copyright 2014, Nature Publishing Group.

multilayer graphene  $\approx 10$  times larger than the one of macroscopic steel sheets (Figure 1c).<sup>[13]</sup>

The mechanical behavior of graphene and graphene oxide (GO) at the nanoscale has been also intensively studied using atomistic modeling<sup>[10]</sup> (Figure 1d,e), or correlating mechanical properties with structure and geometry of chemical bonds at atomic scale (Figure 1f,g),<sup>[7,14]</sup> as described in more detail in following sections. However, there is still no practical way to exploit in full the (nanoscale) mechanical properties of graphene in (macroscopic) graphene-based composites.

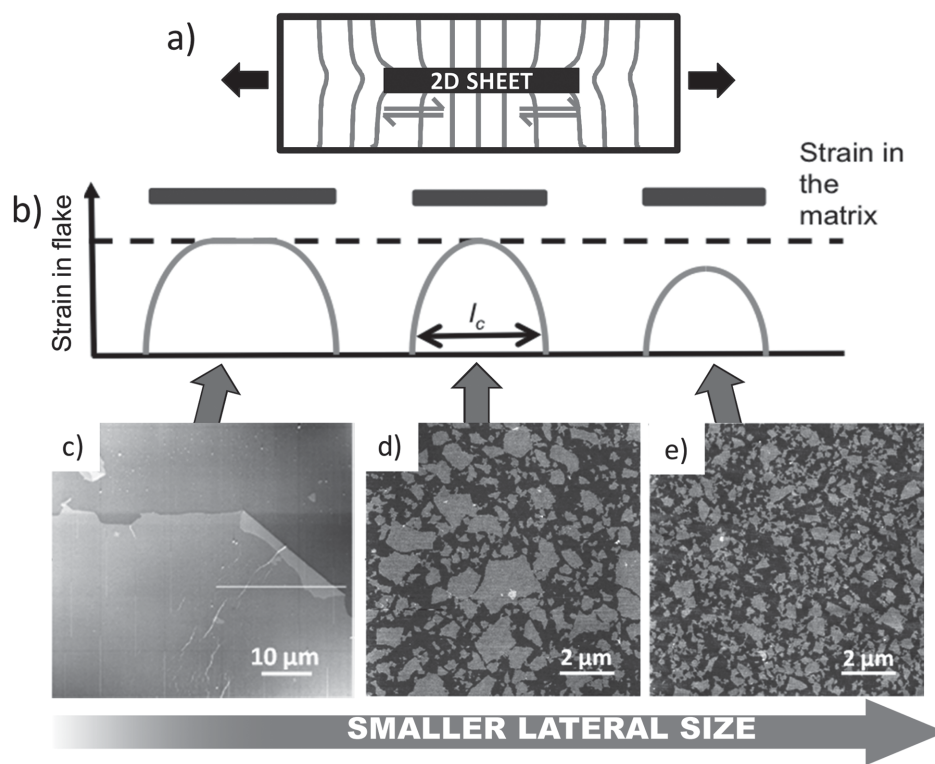
### 3. The Importance of Flake Size in Graphene-Based Composites

In order to achieve good mechanical reinforcement in graphene-polymer composites, the mechanical stress applied to the composite needs to be transferred to the graphene sheets via the polymer matrix. The stress transfer from the matrix to the sheet is traditionally modelled using shear lag theory.<sup>[15]</sup> This theory states that the stress transfer occurs via the shear forces generated at the interface between the polymer matrix and the reinforcement. Accordingly, consider Figure 2a: as a load is applied to the composite, the polymer matrix begins to deform around the graphene sheet. This deformation creates a shear force between the polymer and graphene concentrated at the ends of the flake, which then generates a strain within the graphene itself. This strain builds up going from the ends of the

graphene towards the center of the flake. The strain increases until the strain in the flake is the same as that within the matrix, i.e., when shear deformation (and stress) at the interface has dropped to zero as the two materials are equally deformed. The mechanical reinforcement arises in the composite due to the significant difference in Young's modulus between the polymer and the graphene; since both are at the same strain then the stress in the graphene is much greater than that in the polymer.

If the graphene is sufficiently large along the load direction, it can be assumed that its degree of reinforcement is equivalent to that of an infinitely long flake. However, if the flake is very short, then there is not sufficient length for the shear forces to develop a significant strain, and hence stress, within the graphene (Figure 2b). Thus a very short flake can never give any mechanical enhancement to the composite, regardless of how high its intrinsic elastic modulus. This issue with length is widely known in conventional fiber composites, where for example, the mechanical reinforcement is much higher for continuous carbon fibers than for short, chopped fibers.

It is conventional to define a critical length or aspect ratio above which the degree of reinforcement is independent of length and beneath which the end effects begin to dominate. This critical length,  $l_c$ , is given as two times the length required for the internal strain in the flake to reach 90% of that in the matrix (Figure 2b).  $l_c$  is larger in case of poor stress transfer (i.e., low interaction) between the sheet and the matrix.<sup>[15,16]</sup> The strain within single graphene sheets<sup>[17–19]</sup> or even in composites<sup>[20]</sup> can be measured and mapped using Raman



**Figure 2.** a) Cartoon showing the strain transfer between a polymer matrix and embedded 2D nano-reinforcement. b) Schematic representation of the strain applied in sheets of different length (red curves), as compared to the average strain present in the polymer matrix (dashed line). c–e) GO sheets with lateral size spanning from  $\approx 100$  nm to  $\approx 100$  μm, as visualized on different scales using scanning probe microscopy. Reproduced with permission.<sup>[27]</sup> Copyright 2009, American Chemical Society.

microscopy; for graphene an optimal length of  $10 l_c \approx 30 \mu\text{m}$  would be needed for good reinforcement assuming classical polymer matrix and interaction. Crucially, this length is one order of magnitude larger than the lengths of the graphenes typically obtained by exfoliation of graphite by ultrasound<sup>[21]</sup> or shear.<sup>[22]</sup>

This experimentally measured critical length is also much longer than that known for other materials. It is possible to calculate the interfacial shear stress of the polymer-graphene interface from the in situ Raman measurements and it is found to be about 10% of that found for other carbon-polymer interfaces, such as for carbon fibers. The reason for this low value in graphene composites is that non-functionalised, atomic flat graphene does not have either the functional groups or defects to give the chemical interactions or mechanical lock-in seen in other carbon materials.<sup>[15]</sup> Thus either routes to produce large sheets or highly functionalized sheets are required. An additional challenge with the latter is that bulky functional groups increase the cross-sectional area of the graphene and thus reduce its effective strength and Young's modulus.

Even the measurement and definition of sheet lateral size is not straightforward. Modeling of sheet size and shape distributions are not only important for mechanical reinforcement, but also to assess the electrical properties and conductivity in composites, as for example in conductive graphene inks<sup>[23]</sup> or thin layers,<sup>[24]</sup> or gas barriers,<sup>[25]</sup> which are all promising applications of graphene and other 2D materials.

Unfortunately, exfoliation always yields a polydispersed range of nanosheet thicknesses and lateral sizes. When characterizing these 2D sheets, their average size are commonly reported with the corresponding standard deviation, often assuming that their size follows a symmetric "Gaussian" (i.e., "normal") distribution. Conversely, experimental evidence shows that the size and shape distributions of these materials are non-Gaussian, and should be modelled using asymmetric distributions, similarly to that conducted with polymers.<sup>[26]</sup>

#### 4. Chemical Defects at the Nanoscale Control the Mechanical Properties at the Macroscale

It is possible to obtain large quantities of monoatomic, soluble nanosheets with tunable length up to  $100 \mu\text{m}$  (Figure 2c–e) by chemical oxidation of graphite, yielding GO.<sup>[27]</sup> GO is obtained by oxidation and exfoliation of graphite with strong oxidants, typically a mixture of sodium nitrate, sulphuric acid and potassium permanganate, which create in solution a highly reactive dimanganese heptoxide ( $\text{Mn}_2\text{O}_7$ ) that can attack the stable lattice of graphene.

The high processability of GO is due to the presence of many hydrophilic moieties on its surface (carboxyl, hydroxyl or epoxy groups) that make it water-soluble and also hinder sheet restacking. However, the presence of these groups destroys the excellent electrical properties of graphene, and also degrades its mechanical properties.

Due to its high defective nature, GO has long been the underdog of the graphene family. However, this prejudice is now being challenged and GO is used for many interesting potential applications.<sup>[4,28]</sup> For example, GO is an excellent material for processing into high ordered structures.

Xin et al. recently spun GO sheets of different sizes into coagulated fibers. The inner fiber structure consists of large-sized graphene sheets forming a highly ordered arrangement intercalated with small-sized graphene sheets filling the space and microvoids. The optimized graphene fiber, subjected to thermal annealing at  $2850 \text{ }^\circ\text{C}$ , possessed thermal and electrical conductivities of up to  $1290 \text{ W m}^{-1} \text{ K}^{-1}$  and  $2.21 \times 10^5 \text{ S m}^{-1}$ , respectively.<sup>[29]</sup> Alternatively, GO can be used as a precursor for foams that have a very low specific density, high surface area<sup>[30]</sup> and in some cases, reversible compressibility.<sup>[31]</sup>

Electrochemical approaches have also been used to enhance the chemical reactivity, and thus the exfoliation, of graphene in solution. Such approaches have obtained a high degree of exfoliation of graphite in few minutes by using electrolyte solutions less troublesome than the strong acids required for GO production via the Hummers' method.<sup>[32,33]</sup> A main advantage of electrochemical exfoliation is that it allows to fine-tune the sheet oxidation, giving sheets that are larger and more soluble than those obtained by ultrasound exfoliation, but have less defects than the GO sheets produced by the Hummers' method. (For a systematic comparison of sonication, chemical and electrochemical exfoliation techniques see ref. [32]).

While the oxidized  $\text{sp}^3$  carbon atoms and vacancies present on the graphene sheets act as defects, degrading its mechanical strength, they also increase its interaction with other materials. For example the groups control the interaction between the graphene and the polymeric matrix of a composite, maximizing strain transfer and thus reducing the critical length,  $l_c$ , needed to achieve mechanical reinforcement. Efficient reinforcement in graphene-based composites requires thus a fine tuning of sheet size, shape, number and surface chemistry.<sup>[17]</sup>

#### 4.1. Role of Atomic Vacancies on the Fracture Strength of Graphene

Graphene oxide sheets with defects are more rugged and structurally robust than expected. Thermal and electrical transport in graphene is very sensitive to presence of defects (e.g., disruptions in the  $\text{sp}^2$ -bonding network). Conversely, its mechanical properties can better tolerate defects and imperfections; the breaking strength of graphene in presence of isolated  $\text{sp}^3$  defects is  $\approx 14\%$  smaller than in perfect graphene. Instead, in case of several missing carbon atoms, nanometer-sized voids are formed in the lattice, resulting in a quick drop in stiffness and strength.<sup>[34,35]</sup>

The presence of atomic vacancies decreases the ideal mechanical strength  $\sigma_f^{(0)}$  of perfect graphene or other 2D materials (for graphene  $\approx 100 \text{ GPa}$ ) by triggering a brittle crack propagation. Even in high-quality graphene obtained by chemical vapor deposition (CVD), grain boundaries between different crystalline domains will trigger fracture in tensile loading with the onset of crack nucleation near 5–7 Stone-Wales defects.<sup>[10]</sup> Under tensile loads, the uniform stress field applied to the graphene sheet provides a driving force for the catastrophic propagation of crack after its nucleation (Figure 1d,e). The effective strength of highly defective graphene (or GO or other 2D materials) is difficult to evaluate, because it depends not only on the



amount of defects or atomic vacancies present in the lattice, but also on how they are grouped together at the nanoscale.

By applying quantized fracture mechanics<sup>[5]</sup> the strength  $\sigma_f^{(n)}$  as a function of the number  $n$  of atomic vacancies and their spatial arrangement for a defective 2D material can be predicted.<sup>[36]</sup>

If we consider an ideal strength of graphene of 100 GPa, a conventional GO thickness of 0.75 nm and a nearly identical fracture force for graphene and GO, we obtain an upper limit of  $\sigma_{fGO}^{(0)} = 100 \times 0.34 / 0.75 = 45$  GPa, valid for GO without any holes. We shall then consider the presence of nearly circular holes in the GO layer of  $\approx 5$  nm<sup>2</sup> (as estimated experimentally by TEM<sup>[37]</sup>), giving thus  $n = 190$ . A smaller value of  $\approx 1.7$  nm<sup>2</sup> (as estimated by Raman spectroscopy<sup>[34]</sup>) would give  $n \approx 67$ . Assuming circular holes we have:<sup>[38]</sup>

$$\sigma_f^{(n)} = \sigma_f^{(0)} \sqrt{\left(1 + \frac{2}{9} \sqrt{\frac{n}{\pi}}\right) / \left(1 + 2 \sqrt{\frac{n}{\pi}}\right)} \quad (1)$$

obtaining a fracture strength  $\sigma_{fGO}^{190} = 18$  GPa for voids of  $\approx 5$  nm<sup>2</sup>, and  $\sigma_{fGO}^{67} = 20$  GPa assuming voids of  $\approx 1.7$  nm<sup>2</sup>. These numbers are lower, but comparable to those measured experimentally by AFM indentation of GO (24.7 GPa)<sup>[39]</sup> and of highly defective, plasma treated graphene (30 GPa).<sup>[34]</sup>

Defects are not always undesirable, as in some cases they can improve the mechanical properties of GO due to mechanically activated chemical reactions. For example, the surprising plasticity and ductility of GO observed in AFM nano-indentation experiments was found to be due to an epoxide-to-ether transformation (Figure 1f,g).<sup>[14]</sup>

Upon mechanical strain, an epoxide ring-opening reaction takes place through cleavage of the C–C bond (Figure 1g), differently from the most thermodynamically favorable C–O bond-cleavage. In this way, it is possible to tune the mechanical properties of GO sheets by transforming epoxide groups in more stable ether groups. While the defect-free C–C bonds of graphene give brittle failure, the cyclic epoxide groups on GO dissipate strain energy and can thus hinder crack propagation, making GO more ductile.

## 4.2. Processing of Graphene Sheets in Composites

In graphene-based materials, the mechanical failure of the sheet itself is only one of the possible issues. A macroscopic composite, made of billions of graphene sheets embedded in a polymer matrix, can break down also due to poor interaction between graphene and the matrix; this leads to sheet pull-out, or to poor, irregular dispersion of the sheets into the matrix, with the formation of large graphite-like aggregates that act as macroscopic defects in the material. For this reason, the typical performance of graphene-based (macroscopic) composites is two orders of magnitude worse than the one of (nanoscopic) graphene.<sup>[4,5,35,38,40]</sup>

Processing the graphene sheets in a polymer is often one of the most challenging steps in the creation of a composite. The graphene sheets will tend strongly to re-aggregate, stacking over each other due to their planar shape and to the presence of strong  $\pi$ – $\pi$  interactions between different sheets. For this

reason, as well, chemical functionalization is key to promote a uniform distribution of the sheet in the matrix, avoiding re-aggregation and thus ensuring uniform mechanical properties at the microscale.<sup>[41,42]</sup>

Processing techniques such as blending in solution, co-extrusion, three-roll milling or simple mechanical mixing are currently used to disperse graphene in polymer matrices, but optimal conditions depend on the graphene type used, the polymer matrix and the final application targeted by the composite. An ideal technique to ensure uniform distribution of the graphene sheets in the polymer relies on surface functionalization of graphene with groups able to trigger polymerization.<sup>[43]</sup> In this way the sheets are dispersed into the monomers, and polymer chains grow directly from the surface of the sheet, ensuring good dispersion of the sheets in the matrix, negligible aggregation and a high degree of interaction between the polymer and the sheet.<sup>[20]</sup> As example, this powerful in situ approach allowed the production of elastomeric polyurethane (PU) nanocomposites by polymerization of diisocyanate with functionalized graphene nanosheets dispersions in polyether polyols,<sup>[41]</sup> or electrodes for capacitors by oxidative polymerization of polypyrrole on GO<sup>[42]</sup> and electropolymerization of polyaniline on GO paper.<sup>[44]</sup>

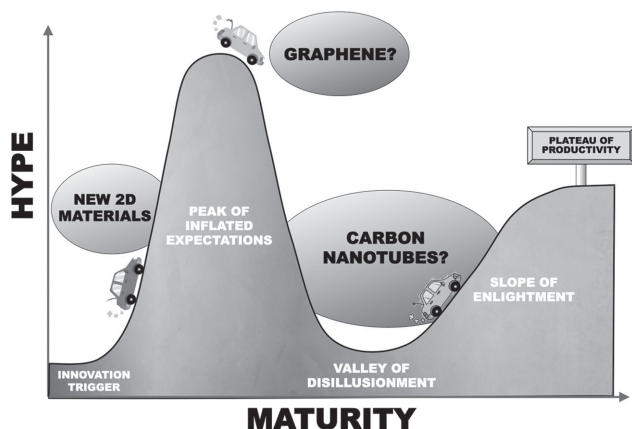
Such approaches have the advantage of avoiding high shear forces, which may reduce the graphene size, produce composites with a very high graphene loading and give a high degree of graphene alignment.

## 4.3. Conclusions: Perspectives of Graphene Applications in Bulk Composites

It is difficult to summarize the status and perspectives of graphene-based structural composites, given the huge range existing of target applications (structural reinforcement, electrical conductivity, gas barrier, etc.), starting materials (graphene, GO, graphite nanoplatelets, other 2D materials, etc.) and possible polymer matrices (thermoplastics, thermosets, elastomers, etc.).<sup>[45]</sup> However, some general challenges that should be overcome to improve the use of 2D, e.g., graphene, sheets in 3D structural composites shall be singled out by the great mass of published data available at the moment.

Successful development of graphene-based reinforced composites into a widespread technology will require progress in:

- 1) **Metrology** – 2D nanosheets are a completely new class of materials, and require new ways to define and quantify average flake size, shape, concentration and density of (typically oxidative) defects present at chemical level.<sup>[46]</sup> Several works are already addressing this issue by proposing new concepts for characterization and classification of 2D materials.<sup>[26,47]</sup>
- 2) **Modeling** – completely new concepts should be developed to model the mechanics of 2D nanosheets reinforced 3D composites. Mechanical behavior under stress and electrical fields, interaction between adjacent sheets, etc., should be better understood to estimate the final level of performance that shall be achieved by such novel 2D-reinforced 3D composites, and how to reach this performance. Even if most work on graphene modeling is focussed on charge transport



**Figure 3.** The typical hype curve for new technologies. The (indicative) placement of different nano-materials is also indicated, according to the authors' opinion.

in highly ordered systems (e.g., graphene nanoribbons), several computational and theoretical models are already used to study more realistic and disordered materials.<sup>[5,19,48]</sup>

- 3) **Chemistry** – a fine control of the surface chemistry of the nanosheets will be required to tune the density and nature of chemical defects, to maximize the interaction between the sheets and the polymer matrix and hence ensure uniform dispersion in the composite and efficient stress transfer between the different phases of the composite material with moderate intrinsic flake strength reduction.

A commonly used way to describe the evolution of new technologies is the so-called “Gartner curve” (Figure 3).<sup>[49]</sup> For any new technology, an initial stage of fundamental research is followed by a peak of hype, where many disruptive applications seem possible with the new technology. Yet, when the first applications face competition from the already established, optimized and cheap technologies, many of the possible applications result to be impossible, uneconomic, non-competitive or simply too late to market to have a real impact; thus many early adopters give up and move to other newer and more fashionable topics. In a few, lucky cases, though, some of the tested applications yield the creation of new products, able to occupy niche markets or to create new ones. With time, production techniques are optimized, cost decreases, quality increases and the new technology eventually becomes dominant.

Graphene and other nano-materials have been positioned in the Gartner curve, as shown in Figure 3. It is easy to demonstrate that new, 2D materials beyond graphene (e.g., boron nitride, transition metal dicalchogenides, phosphorene, etc.) are still in the ramp-up part of the hype curve. This is the same position, for example, where the Gartner puts other emerging technologies such as 3D bioprinting or quantum computing.<sup>[49]</sup>

“Older” materials such, as for example, carbon nanotubes (CNT), are much past the hype peak. CNT are currently used on a moderate scale in composites and batteries, to enhance electrical conductivity, and also in transparent displays. They continue to be intensively studied for application in digital electronics, (see as example recent work published by IBM research labs)<sup>[50]</sup> where they have a clear advantage on graphene due to

their finite bandgap and high aspect ratio and thus low percolation threshold. This is the same position where Gartner locates, for example, hybrid cloud computing or augmented reality.<sup>[49]</sup>

Graphene can be placed (in our opinion) still high on the hype curve, together with “hot” technologies such as internet-of-things or consumer 3D printing.<sup>[49]</sup> Many possible applications of graphene in different fields are still very promising, even if critical points on the disparity between graphene actual production compared to market request have recently been raised.<sup>[51]</sup> Overall, the real evolution of graphene technology will depend on how effectively the research community will be able to face the challenges in metrology, modeling, processing and chemical tunability that we have briefly described in this review.

## Acknowledgements

We acknowledge the European Union Seventh Framework Programme under grant agreement no. 604391 Graphene Flagship, the European Research Council (ERC StG Ideas 2011 BIHSNAM no. 279985 on ‘Bio-inspired hierarchical supermaterials’, ERC PoC 2013–1 REPLICIA2 no. 619448 on ‘Large area replication of biological anti-adhesive nanosurfaces’, ERC PoC 2013–2 KNOTOUGH no. 632277 on ‘Super-tough knotted fibers’, ERC PoC 2015 SILKENE no. 693670 on ‘Bionic silk with graphene or other nanomaterials’, EPSRC (EP/I023879/1) and the Provincia Autonoma di Trento (‘Graphene nanocomposites’, no. S116/2012–242637 and reg. delib. no. 2266).

Received: November 5, 2015

Revised: December 4, 2015

Published online: March 9, 2016

- [1] G. Sechi, D. Bedognetti, F. Sgarrella, L. Van Eperen, F. M. Marincola, A. Bianco, L. G. Delogu, *Nanomedicine* **2014**, *9*, 1475.
- [2] Head Homepage, <http://www.head.com/g/us/graphene> (accessed: November 2015).
- [3] Head Skis, <http://www.head.com/ski/products/skis/women/super-joy/7988/>; Catlike Helmets, <http://www.catlike.es/global/en/innovation/helmets-technologies/graphene/>; Vittoria Race Wheel, <http://www.vittoria.com/wheel/race/> (accessed: November 2015).
- [4] P. Samorì, I. A. Kinloch, X. Feng, V. Palermo, *2D Mater.* **2015**, *2*, 030205.
- [5] N. M. Pugno, R. S. Ruoff, *Philos. Mag.* **2004**, *84*, 2829.
- [6] A. K. Geim, *Science* **2009**, *324*, 1530.
- [7] J. Atalaya, *Ph. D. Thesis: Nonlinear Mechanics of Graphene and Mass-loading Induced Dephasing in Nanoresonators*, Chalmers University of Technology, Gothenburg, Sweden **2012**.
- [8] J. Atalaya, A. Isacson, J. M. Kinaret, *Nano Letters* **2008**, *8*, 4196.
- [9] C. Lee, X. Wei, J. W. Kysar, J. Hone, *Science* **2008**, *321*, 385.
- [10] J. Han, N. M. Pugno, S. Ryu, *Nanoscale* **2015**, *7*, 15672.
- [11] J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead, P. L. McEuen, *Nano Lett.* **2008**, *8*, 2458.
- [12] M. K. Blees, A. W. Barnard, P. A. Rose, S. P. Roberts, K. L. McGill, P. Y. Huang, A. R. Ruyack, J. W. Kevek, B. Kobrin, D. A. Muller, P. L. McEuen, *Nature* **2015**, *524*, 204.
- [13] J.-H. Lee, P. E. Loya, J. Lou, E. L. Thomas, *Science* **2014**, *346*, 1092.
- [14] X. Wei, L. Mao, R. A. Soler-Crespo, J. T. Paci, J. Huang, S. T. Nguyen, H. D. Espinosa, *Nat. Commun.* **2015**, *6*, 8029.
- [15] R. J. Young, I. A. Kinloch, L. Gong, K. S. Novoselov, *Compos. Sci. Technol.* **2012**, *72*, 1459.

- [16] N. M. Pugno, *J. Mech. Phys. Solids* **2010**, *58*, 1397.
- [17] L. Gong, R. J. Young, I. A. Kinloch, I. Riaz, R. Jalil, K. S. Novoselov, *ACS Nano* **2012**, *6*, 2086.
- [18] G. Tsoukleri, J. Parthenios, K. Papagelis, R. Jalil, A. C. Ferrari, A. K. Geim, K. S. Novoselov, C. Galiotis, *Small* **2009**, *5*, 2397.
- [19] C. Androulidakis, E. N. Koukaras, O. Frank, G. Tsoukleri, D. Sfyris, J. Parthenios, N. Pugno, K. Papagelis, K. S. Novoselov, C. Galiotis, *Sci. Rep.* **2014**, *4*, #5271.
- [20] Z. Li, R. J. Young, I. A. Kinloch, *ACS Appl. Mater. Interfaces* **2013**, *5*, 456.
- [21] J. N. Coleman, *Acc. Chem. Res.* **2013**, *46*, 14.
- [22] K. R. Paton, E. Varrla, C. Backes, R. J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O. M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. o. Coelho, S. E. O'Brien, E. K. McGuire, B. M. Sanchez, G. S. Duesberg, N. McEvoy, T. J. Penrycook, C. Downing, A. Crossley, V. Nicolosi, J. N. Coleman, *Nat. Mater.* **2014**, *13*, 624.
- [23] GNext Graphene Applications, <https://www.youtube.com/watch?v=dhLV278gG18> (accessed: November 2015); Graphene Based Ink, <https://www.youtube.com/watch?v=ri5ntLoEUhg> (accessed November 2015).
- [24] A. Vianelli, A. Candini, E. Treossi, V. Palermo, M. Affronte, *Carbon* **2015**, *89*, 188.
- [25] D. Pierleoni, Z. Y. Xia, M. Christian, S. Ligi, M. Minelli, V. Morandi, F. Doghieri, V. Palermo, *Carbon* **2016**, *96*, 503.
- [26] K. Kouroupis-Agalou, A. Liscio, E. Treossi, L. Ortolani, V. Morandi, N. M. Pugno, V. Palermo, *Nanoscale* **2014**, *6*, 5926.
- [27] E. Treossi, M. Melucci, A. Liscio, M. Gazzano, P. Samorì, V. Palermo, *J. Am. Chem. Soc.* **2009**, *131*, 15576.
- [28] a) M. Melucci, S. Ligi, V. Palermo, *Sigma Aldrich – Materials Matters* **2015**, *10*, 45; b) T. Liu, M. Leskes, W. Yu, A. J. Moore, L. Zhou, P. M. Bayley, G. Kim, C. P. Grey, *Science* **2015**, *350*, 530.
- [29] G. Xin, T. Yao, H. Sun, S. M. Scott, D. Shao, G. Wang, J. Lian, *Science* **2015**, *349*, 1083.
- [30] Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach, R. S. Ruoff, *Science* **2011**, *332*, 1537.
- [31] H. Hu, Z. B. Zhao, W. B. Wan, Y. Gogotsi, J. S. Qiu, *Adv. Mater.* **2013**, *25*, 2219.
- [32] Z. Y. Xia, S. Pezzini, E. Treossi, G. Giambastiani, F. Corticelli, V. Morandi, A. Zanelli, V. Bellani, V. Palermo, *Adv. Funct. Mater.* **2013**, *23*, 4684.
- [33] a) Z. Y. Xia, G. Giambastiani, C. Christodoulou, M. V. Nardi, N. Koch, E. Treossi, V. Bellani, S. Pezzini, F. Corticelli, V. Morandi, A. Zanelli, V. Palermo, *ChemPlusChem* **2014**, *79*, 439; b) A. M. Abdelkader, A. J. Cooper, R. A. W. Dryfe, I. A. Kinloch, *Nanoscale* **2015**, *7*, 6944; c) K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Müllen, *J. Am. Chem. Soc.* **2014**, *136*, 6083.
- [34] A. Zandiatashbar, G.-H. Lee, S. J. An, S. Lee, N. Mathew, M. Terrones, T. Hayashi, C. R. Picu, J. Hone, N. Koratkar, *Nat. Commun.* **2014**, *5*, #3186.
- [35] N. M. Pugno, *Appl. Phys. Lett.* **2007**, *90*, #043106.
- [36] N. Pugno, *Int. J. Fracture* **2006**, *141*, 313.
- [37] K. Erickson, R. Erni, Z. Lee, N. Alem, W. Gannett, A. Zettl, *Adv. Mater.* **2010**, *22*, 4467.
- [38] N. M. Pugno, *Acta Mater.* **2007**, *55*, 5269.
- [39] C. Cao, M. Daly, C. V. Singh, Y. Sun, T. Filleter, *Carbon* **2015**, *81*, 497.
- [40] A. Carpinteri, N. Pugno, *Nat. Mater.* **2005**, *4*, 421.
- [41] A.-K. Appel, R. Thomann, R. Muelhaupt, *Polymer* **2012**, *53*, 4931.
- [42] H. P. de Oliveira, S. A. Sydlík, T. M. Swager, *J. Phys. Chem. C* **2013**, *117*, 10270.
- [43] Y. F. Yang, J. Wang, J. Zhang, J. C. Liu, X. L. Yang, H. Y. Zhao, *Langmuir* **2009**, *25*, 11808.
- [44] D.-W. Wang, F. Li, J. Zhao, W. Ren, Z.-G. Chen, J. Tan, Z.-S. Wu, I. Gentle, G. Q. Lu, H.-M. Cheng, *ACS Nano* **2009**, *3*, 1745.
- [45] A. C. Ferrari, F. Bonaccorso, V. Fal'ko, K. S. Novoselov, S. Roche, P. Boggild, S. Borini, F. H. L. Koppens, V. Palermo, N. Pugno, J. A. Garrido, R. Sordan, A. Bianco, L. Ballerini, M. Prato, E. Lidorikis, J. Kivioja, C. Marinelli, T. Ryhanen, A. Morpurgo, J. N. Coleman, V. Nicolosi, L. Colombo, A. Fert, M. Garcia-Hernandez, A. Bachtold, G. F. Schneider, F. Guinea, C. Dekker, M. Barbone, Z. Sun, C. Galiotis, A. N. Grigorenko, G. Konstantatos, A. Kis, M. Katsnelson, L. Vandersypen, A. Loiseau, V. Morandi, D. Neumaier, E. Treossi, V. Pellegrini, M. Polini, A. Tredicucci, G. M. Williams, B. Hee Hong, J.-H. Ahn, J. Min Kim, H. Zirath, B. J. van Wees, H. van der Zant, L. Occhipinti, A. Di Matteo, I. A. Kinloch, T. Seyller, E. Quesnel, X. Feng, K. Teo, N. Rupasinghe, P. Hakonen, S. R. T. Neil, Q. Tannock, T. Lofwander, J. Kinaret, *Nanoscale* **2015**, *7*, 4598.
- [46] V. Palermo, *Chem. Commun.* **2013**, *49*, 2848.
- [47] P. Wick, A. E. Louw-Gaume, M. Kucki, H. F. Krug, K. Kostarelos, B. Fadeel, K. A. Dawson, A. Salvati, E. Vázquez, L. Ballerini, M. Tretiach, F. Benfenati, E. Flahaut, L. Gauthier, M. Prato, A. Bianco, *Angew. Chem. Int. Ed.* **2014**, *53*, 7714.
- [48] a) S. Panzavolta, B. Bracci, C. Gualandi, M. L. Focarete, E. Treossi, K. Kouroupis-Agalou, K. Rubini, F. Bosia, L. Brely, N. M. Pugno, V. Palermo, A. Bigi, *Carbon* **2014**, *78*, 566; b) Z. Li, R. J. Young, I. A. Kinloch, N. R. Wilson, A. J. Marsden, A. P. A. Raju, *Carbon* **2015**, *88*, 215; c) A. W. Cummings, D. L. Duong, V. L. Nguyen, D. Van Tuan, J. Kotakoski, J. E. Barrios Vargas, Y. H. Lee, S. Roche, *Adv. Mater.* **2014**, *26*, 5079.
- [49] Gartner's 2015 Hype Cycle for Emerging Technologies Identifies the Computing Innovations That Organizations Should Monitor, <http://www.gartner.com/newsroom/id/3114217> (accessed: November 2015).
- [50] Q. Cao, S.-J. Han, J. Tersoff, A. D. Franklin, Y. Zhu, Z. Zhang, G. S. Tulevski, J. Tang, W. Haensch, *Science* **2015**, *350*, 68.
- [51] M. Peplow, *Nature* **2015**, *522*, 268.