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FEATURE ARTICLE

Not a molecule, not a polymer, not a substrate… the many faces of graphene as a chemical platform

Vincenzo Palermo*

What is, exactly, graphene? While we often describe graphene with many superlative adjectives, it is difficult to force this material into a single chemical class. Graphene's typical size is atomistic in one dimension of space, and mesoscopic in the other two. This provides graphene with several, somehow contrasting properties. Graphene can be patterned, etched and coated as a substrate. Though, it can also be processed in solution and chemically functionalized as a molecule. It could be considered as a polymer, obtained by bottom-up assembly of carbon atoms or small molecules, but it can be obtained also from top-down exfoliation of graphite (a mineral). It does not have a well-defined shape, such as that of fullerenes or nanotubes; conversely, it is a large, highly anisotropic, very flexible object, which can have different shapes and be folded, rolled or bent to a high extent. In this feature article, we will discuss the state of the art and possible applications of graphene in its broader sense with a particular focus on how its ''chemical'' properties, rather than its well-known electrical ones, can be exploited to develop original science, innovative materials and new technological applications.

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Introduction: what a material can be good for

Nearly five centuries ago some shepherds from Borrowdale, a small English village, discovered a new material. It was black, soft, mechanically weak and nearly useless, not solid enough to build houses, or malleable enough to make tools. Conversely, it tended to break easily when hit, yielding big shiny chunks that made fingers black. The best use that shepherds could make of it was to mark sheep, and that is what it was used for.[1]

The material discovered by the shepherds was graphite, of very high quality, and it did not take too long to find a proper use for it, an application of strategic/military relevance. Being a very good and heat resistant solid lubricant, graphite was used in cannon ball molding, a strategic military craft of the time. The British Crown became so jealous of this very unique material that the Borrowdale mine, the only one having graphite of this quality, was flooded with water when not in use, to discourage graphite thieves.

Not surprisingly, the military application was not the best one for this new material, but it took nearly 300 years to achieve large scale, cheap production of graphite for pencil making. Nowadays, graphite is used for many different applications, from pencils to nuclear reactors, while cannon ball molding is (luckily) just a niche application of this material.

Silicon, likely the most important material of our age, had a similar unpredictable story. Research on silicon was intense for applications like alloying and paints, and the huge success in

electronics came only at a later stage, nearly 130 years after silicon discovery.[2]

Graphene, a monoatomic sheet of honeycomb, sp^2 hybridized carbon atoms, is the latest and actually the most intensively studied among the "possibly revolutionary" materials. Its properties are outstanding; its potential applications, from microelectronics to composites to medicine, are so good that it can sometimes be hard to believe for the laymen.

Though, when it comes to graphene applications, we are more or less at the same level as the Borrowdale shepherds. It is just eight years that we have had this material in our hands, we feel that it shall be good for something, but it is still not clear who, first, will make it a technological success, and for which application.[3]

While we often describe graphene with many superlative adjectives, it is difficult to force this (superlative) material into a single chemical class.

Common electronic devices are fabricated by top-down techniques, such as optical lithography. Most nano-structured materials, such as carbon nanotubes and organic semiconductors, are instead produced by bottom-up self-assembly of molecules and atoms.[4]

Graphene can be produced in both ways, either by bottom-up assembly of smaller atoms and molecules[5–7] or top-down exfoliation of graphite stacks.[8,9] Luckily, Nature has provided us with large amounts of high-quality graphene sheets, stacked inside graphite mineral. Differently from carbon nanotubes, graphene can be produced on a ton scale without any high temperature process, and without the need for metal catalysts; at the same time, differently from organic materials, it can be produced at high temperature, in a clean vacuum, with no exposure to solvents needed for organic synthesis.

As a chemist, it is my opinion that the most peculiar properties of graphene lie in its truly 2D shape, its large availability in nature, its different possible sources for large scale production, and the huge amount of synthetic tools that can be readily used from organic synthesis, to play with graphene and transform it in the way we want.

This article will thus *not* describe any of the most appreciated electronic properties of graphene, it will not deal with its high charge mobility, ballistic transport, quantum hall effect, Dirac fermions, *etc.*

It will rather focus on the peculiar properties of graphene that make it an original chemical "object" and probably the first of a large family of 2D materials.

We will see at the end of this path that, to really assess the true potentiality of graphene, we should not compare it with silicon, but rather with the first man-made polymers that started the plastic revolution.

Graphene as a substrate: shaping molecules, shaped by molecules

Graphene's typical size is monoatomic (≈ 3.3 Å) in one dimension, and mesoscopic (up to tens of μm) in the other two; this would be the same aspect ratio of a 1 mm thin cotton blanket,

as large as a football field. Thus, while being one-atom thick, a sheet of graphene has a lateral size which is 10^2–10^5 times larger than the size of typical small molecules. This provides graphene with several, somehow contrasting properties. Graphene can be patterned, etched and coated as a substrate using conventional optical lithography. Original patterning techniques, using nanoparticle-induced etching,[10,11] nanosphere shadow masks[12] and evaporation-induced self-assembly,[13] have also been demonstrated. Thus, in a first approximation, graphene can be considered as a flat substrate, where molecules can adsorb or react in a predictable way. Luckily, we have a very good knowledge of how different kinds of molecules interact, in vacuum and in solution, with the parent material of graphene, which is graphite. Since the invention of a Scanning Tunneling Microscope (STM) in 1981, graphite has been the most used substrate to study the structure of organic molecules with unprecedented resolution, because it was very easy to obtain atomically flat and clean graphite substrates even in a normal atmosphere, thanks to scotch tape. To perform STM measurements, the first contaminated layers of a graphite chip were usually peeled off with scotch tape, exposing in this way the clean buried layers on which molecules could be deposited. The scientists of the STM community performed this basic procedure for years, dedicating their attention to the freshly cleaved bulk substrate, ignoring that a Nobel-prize winning treasure was hidden on the scotch tape they were throwing away.

Thanks to plenty of STM work, we know pretty well what molecules do when adsorbed on graphite; long alkylic chains form highly packed 2D arrays, organic molecules can adsorb either face-on or edge-on, interacting with each other or forming complex binary mixtures.[14–18] Fig. 1a and b shows typical examples of the dynamic, reversible self-assembly of molecules on graphite.

The adsorption energy of several small organic molecules has been measured by thermal desorption spectroscopy and ranges from 0.5 eV for simple benzene to 2.1 eV for ovalene.[19] Adsorption energy of larger molecules can be extrapolated from these data obtaining, for example, an interaction energy of ~ 2.8 eV for hexa-benzocoronene (HBC, shown in Fig. 1a),
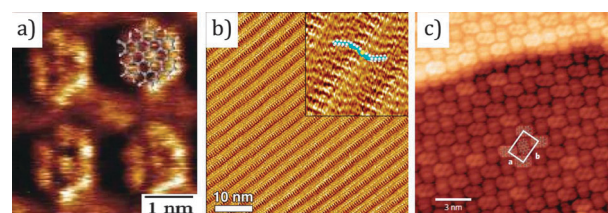
Fig. 1 STM images of small organic molecules self-assembled on highly oriented pyrolytic graphite (a and b) and on graphene (c). (a) Hexabenzo-coronene, adsorbed on graphite from solution. Reprinted with permission from ref. 20. Copyright (2002) American Chemical Society. (b) Stacked phenylene–thiophene–phenylene molecules with alkyl side chains on graphite. Reprinted with permission from ref. 17. In the inset a zoom-in is shown, together with the 3D model of the molecule. (c) Perylene molecules deposited on graphene by gas phase deposition in ultra-high vacuum. Reprinted with permission from ref. 22. Macmillan Publishers Ltd, copyright (2009). The monolayer continuously follows the graphene sheet over the SiC step edge.

which has a core of 42 C atoms and could be considered as a small hexagonal graphene sheet.

Density of HBC without (with) side chains is 6.15×10^{17} (3.36×10^{17}) molecules per m^2,[20] giving an estimated interaction energy of 277 (151) mJ m^{-2} between a uniform, ordered layer of HBC and a graphene layer, which is comparable to a graphite cleavage energy of ~ 260 mJ m^{-2} demonstrating that, at least in the first approximation, the interaction of graphene with small molecules can be as strong as inter-sheet interaction in graphite.[21]

Similar, ordered self-assembly of small molecules was also observed by Hersam and co-workers on graphene, using PTCDA (perylene-3,4,9,10-tetracarboxylic dianhydride) as a model system.[22] Graphene, though, is not graphite, and a different behaviour of the same molecule adsorbed on the two different materials gives different results.

The PTCDA monolayer interacts weakly with the epitaxial graphene and, unlike its behavior on highly ordered pyrolytic graphite (HOPG), is insensitive to surface defects and step edges, forming a continuous array anywhere the graphene sheet is uninterrupted (Fig. 1c).[22–24]

These domains of ordered molecules are thus much more robust and extended than in the case of graphite: they are held together by hydrogen bonds between the different molecules, and stick to graphene, thanks to π–π interactions, which are weaker than in the case of graphite but anyhow relevant.

The adsorption properties of PTCDA on bilayer graphene differ from those on HOPG, although the substrate lattice is the same. The area of 0.77 nm^2 $Å^{-1}$ $\pm$ 10% covered per molecule is much less, which implies an upright adsorption geometry.[25]

Thus, large amounts of molecules can be adsorbed and self-assembled on graphene, but this interaction will also work in the other way, and graphene can be deformed by the presence of adsorbed molecules; in this sense graphene, differently from normal bulk materials, can be considered a very ''reactive'' substrate, not in a chemical but in a truly mechanical way. Graphene is not perfectly rigid as a bulk substrate; conversely, it is a large, highly anisotropic, very flexible object, which can be stretched up to 20% of its size, rolled to form nano-scrolls,[26] or bent to a high extent.[27,28]

Graphene is so flexible that it can wrap and follow perfectly the shape of DNA molecules, replicating their shape with nanometric resolution.[29] In the presence of a droplet of a few thousands of water molecules, the simple interaction between molecules and graphene will force the latter to curl and deform due to surface tension, wrapping around the water drop.[30]

This curling due to adsorbed liquids can give nano-scrolls of varying size,[26] and has been observed experimentally in suspended graphene sheets.[31] Depending on the substrate on which graphene is supported (and on the liquid used), this interaction could be so strong to detach the sheet from the surface, forming graphene-based scrolls, capsules and sandwiches.[32,33]

Guinea and co-workers also predicted that the folding could be driven and controlled by electric fields; besides being an interesting scientific result, this would allow us to produce graphene ''eyelid'' actuators,[34] or tunable ion channels, or controllable nanofilters,[26] or nano-oscillators operating at GHz frequencies.[35]

Not only small molecules can interact with graphene, but also larger ones, sometimes with dramatic results. As an example, insulin, which is a key regulator for the synthesis of fatty acids, can be denatured upon π–π adsorption on graphene in contrast to graphene oxide (GO), which instead binds with insulin electrostatically.[36]

Another, somehow surprising effect of the mechanical properties of graphene, as compared to graphite, is the acceleration of cell growth and differentiation, which was demonstrated in a recent work.[37] Graphene provides a promising biocompatible scaffold that does not hamper the proliferation of human mesenchymal stem cells (hMSCs) and accelerates their specific differentiation into bone cells.

The observed effect is almost certainly due to a complex interplay of mechanical, chemical, and electrical properties of graphene and the interactions between graphene and cells, as well as graphene and supporting substrates. This makes more difficult to identify the microscopic origin of the effect. In particular, the disparities between the results obtained with graphene and bulk graphite substrates point toward mechanical properties and surface morphology as the decisive factors.[37]

The ability of graphene to sustain lateral stress could play a more important role in the context of providing just the right amount of local cytoskeletal tension. Together with the observation that graphene allows for easy out-of-plane deformation, this may lead to the formation of strong anchor points of the cytoskeleton. Such tension may allow for the unfolding of the mechanically sensitive protein of interest and change the conformation. The fact that graphite is made out of weakly bound graphene planes may instead limit its effect as compared to graphene. In the presence of lateral forces, graphite easily shears off and is, therefore, commonly used in lubricants. In the specific context of cell adhesion and in view of the (lateral) contractual forces that cells exert on the surface, this effect may hamper strong cell adhesion on bulk graphite, as compared to a strongly adhered monolayer coating of graphene on a rough substrate.[37]

## Graphene as a molecule: a 2D tunable polymer

Besides providing a large surface onto which molecules can adsorb, graphene itself is a molecule, and as such can be dissolved in several solvents,[8] processed and most importantly, functionalized in solution on a large scale.[38–40] Its perfect aromatic backbone can be attacked by strong oxidants, radicals and reactive groups. The chemical defects hinder the perfect sheet stacking present in graphite, providing ''chemical handles'' such as –COOH, –OH and epoxy groups which can be used for further functionalization, even if the structure of chemically oxidized graphene is very complex and still poorly predictable.[41]

An extensive review of the different techniques used to chemically process graphene is out of the scope of this feature article; it is enough to say that, even if young, the chemistry of graphene is powerful and versatile. Overall, several optically active organic and inorganic molecules have been covalently grafted on GO by different chemical approaches.[42–44]

A graphene sheet in solution is a mesoscopic, highly anisotropic object, similar to a polymer, which extends in two dimensions, behaving differently from 0D objects (molecules, fullerenes) and 1D objects (nanotubes, polymer chains). In a nice experiment by Ferrari and co-workers, the Brownian motion of graphene in solution was studied by trapping graphene flakes with an optical trap.[45] While, for a linear nanostructure, Brownian mobility is larger along the optical axis, the large optical anisotropy of graphene aligns the flake orthogonal to the light polarization, with increased fluctuations in both longitudinal and transverse directions, due to a higher contribution from rotational motion with respect to nanotubes.

The strong optical anisotropy of graphene causes an orientation dependent radiation pressure, resulting in an orientation orthogonal to the incident polarization axis. Conversely, flat microparticles with a similar pronounced shape anisotropy, but no optical anisotropy, orient in an optical trap with their basal plane parallel to the incident polarization axis.

It is well known that a graphene sheet, even if only one atom thick, can be observed with a conventional optical microscope when deposited on a silicon substrate, due to a weak interference-like contrast. Without this simple yet effective way to scan substrates for single- or multiple-layer sheets, graphene would have probably remained undiscovered.[46] This method, which currently is the most practical way of identifying graphene sheets adsorbed on surfaces, works only on substrates having a suitable interference layer, like 300 nm thick SiO_2 and 67 nm thick Si_3N_4,[47–49] and thus cannot be utilized to visualize floating graphene sheets in solution. In 2009, we described a new technique able to visualize single graphene sheets on substrates such as glass and quartz, exploiting the quenching of the light emitted by a fluorescent layer of molecules, achieving an optical contrast of up to 0.8 (Fig. 2a and b).[50] This technique and similar ones, published soon after by Huang and Balasubramanian groups,[51] did not depend on light interference, and could also be used to visualize single sheets of solvated graphene, allowing us to follow its dynamics in solution in a fast and versatile way using a simple fluorescent microscope (Fig. 2d).
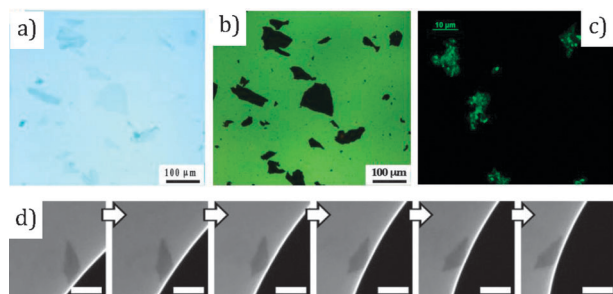
Fig. 2 (a) Optical microscopy (OM) image of GO sheets on 300 nm thick SiO_x functionalized with organic dye. (b) Fluorescence image of the same area. The image has not been processed in any way to enhance contrast or luminosity. Reprinted with permission from ref. 50. Copyright (2009) American Chemical Society. (c) Confocal fluorescence microscopy images of GO functionalized with fluorescent dyes on silicon. Reprinted with permission from ref. 68. (d) A GO sheet drifting in dye solution as observed using fluorescence quenching microscopy, from ref. 51. Copyright (2010) American Chemical Society.

Fluorescent quenching of organic fluorophores interacting with graphene (either in solid or in solution) can be due to either short-range charge transfer or long-range energy transfer,[52,53] and can have useful applications for bio-sensing.[54–57] As an example, a graphene oxide (GO)-based multicolor fluorescent DNA nanoprobe was demonstrated by Fan and co-workers[54] that allowed rapid, sensitive, and selective detection of DNA targets in solution. In this work, single stranded DNA fluorescent probes exhibited minimal background fluorescence due to GO quenching, while strong emission was observed when the probe formed a double helix with the specific targets. The large planar surface of GO can allow simultaneous quenching of multiple DNA probes labelled with different dyes, leading to a multicolor sensor for the detection of multiple DNA targets in the same solution.

The covalent grafting of functional organic materials to the GO surface also represents a valuable strategy to enhance the material performance in thin film transistors (TFT) or solar cells where the molecular surface organization and packing are key parameters for improving the final device performance. As an example, there is great interest in GO-oligothiophene (OT) hybrids, due to the widespread use of thiophene-based organic semiconductors in flexible electronics and photovoltaics. Liu et al. reported the synthesis of a GO-sexithiophene (T6) material with interesting optical limiting properties originated from the spatial proximity between the π-aromatic networks of both materials.[58]

We studied in the past how the performance of organic solar cells and transistors can be conveniently improved by controlling the self-assembly of the molecules in highly ordered 3D crystals[59–63] or attaching small molecules to 1D scaffolds such as linear, long polymeric chains (Fig. 3).[64–67] The use of a 2D scaffold such as a graphene sheet is expected to provide even more original materials. Indeed, 2D substrates allow molecules to be positioned over flat but highly flexible (and solution processable) sheets.[68] In addition, regiochemically defined grafting on the 2D surface can be achieved by exploiting the hydroxyl, carboxylic, epoxide groups present on the basal sheets or the edge sides as anchoring groups,[43] allowing us to tune the functional properties of the final hybrids by changing substitution pathways, the type of linker and spatial positioning on the sheet. The use of GO as a scaffold instead of synthetic polymers gives major advantages: GO can be produced on a large scale and at low cost by graphite oxidative exfoliation, and can form 2-dimensional sheets with sizes up to 100 μm, as compared to polymeric scaffolds which instead are 1-dimensional and have typical lengths of <1 μm. Single sheets of chemically modified graphite can be successfully observed by optical microscopy; by tuning the interaction between graphene and suitable fluorescent molecules, it is possible to visualize single sheets using fluorescence quenching (Fig. 2a and b) or, conversely, by watching the fluorescence emission of chemically functionalized sheets (Fig. 2c).

Any given molecule can be freely floating in solution, or covalently fixed on a solid substrate. When instead a molecule is interacting with graphene or GO we have a hybrid situation in which the molecule is "tethered" to a macroscopic substrate,
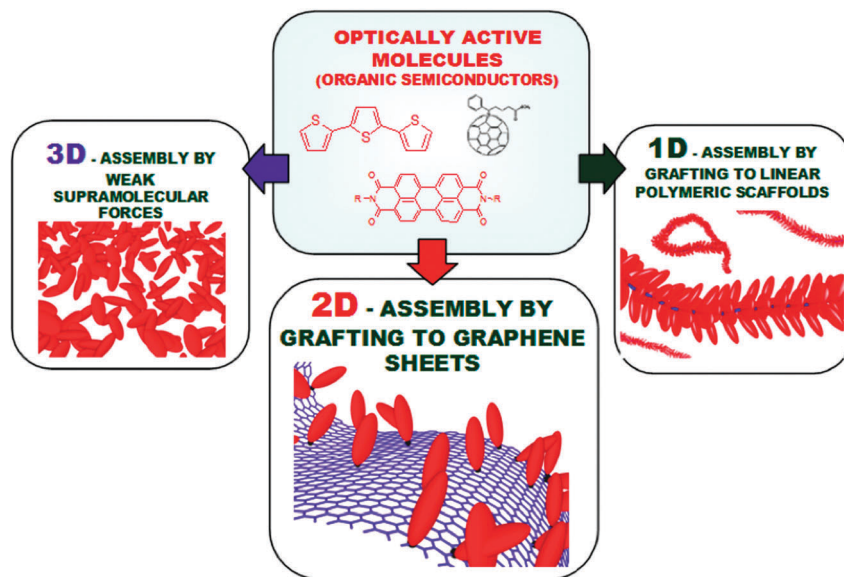
Fig. 3 Schematic representation of different ways to control the assembly of organic molecules by covalent or supramolecular interactions. Reprinted with permission from ref. 68.

which is nonetheless highly flexible and dynamically moving in the solvent. Indeed, even grafted molecules shall either lie on the graphene basal plane or float freely in the solvent, depending on the flexibility of the linker and the solvent used (Fig. 4).

The length of the linker between organic dyes and the GO surface strongly affects the optical properties of the attached molecules and the degree of quenching.[69] Even the graphene properties can be deeply influenced by the presence of the molecule, due to charge-transfer and doping effects.[52]

We have recently developed a new approach to attach organic dyes to graphene oxide (GO) sheets with high loading and minimal perturbation of the electronic and optical properties of the dye. The dye unit used (a pH-sensitive terthiophene) is grafted to GO using a new modular synthetic approach, passing through a C6-aminic linker which makes GO more soluble in different organic solvents and allows straightforward attachment in high yield not only of terthiophene but also of many commercially available amino-reactive dyes. The main advantages of this approach (compared to those already reported in the literature) are: (i) high solubility of the amino ended GO intermediate in organic solvents which allow the convenient coupling with dyes under mild conditions, (ii) easy access to several commercial, stable succinimidyl ester dye derivatives, (iii) easy control of spacer length between the GO and oligothiophene dye, and (iv) high dye functionalization loadings (up to 5 wt%).

The covalent engraftment to GO does not perturb the absorption and emission properties of the dye, and in particular the pH sensing capability through amidic group reversible protonation.

By taking full advantage of synthetic chemistry, it is possible to create *a new class of 2D shaped materials*, where the sheets of graphene are used only as a template, to create 2D organic or inorganic sheets. Several groups have demonstrated in different works the use of graphene as a template to grow nanoparticles,[70] sheets[71] or ribbons[72] of iron oxide,
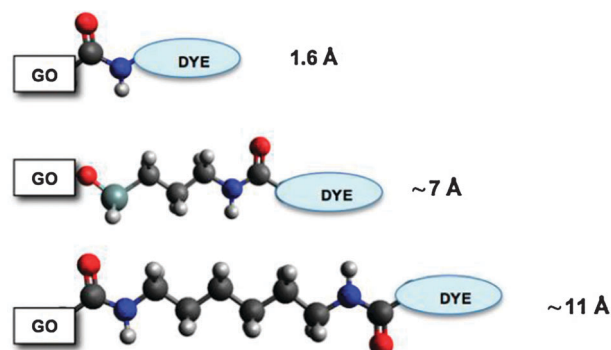
Fig. 4 Linkers used in synthetic approaches to oligothiophene-modified GO. (a) Reprinted with permission from ref. 58. (b) Reprinted with permission from ref. 42. (c) Reprinted with permission from ref. 68.

sandwich-like titania nanosheets,[73] rutile and anatase TiO_2 nanocrystals,[74] Mn_3O_4 nanoparticles,[75] and $Ni(OH)_2$ nanoplates.[76] For an extensive review on this topic see ref. 77 from Feng and co-workers.

By chemical or thermal treatments, these layers can be made robust enough to allow even the removal of the pristine graphene backbone. In this way, graphene will work just as a template for the creation of an infinite variety of 2D, ultra-thin, non-carbon-based materials.[73,77]

This process has analogies with either chemical functionalization in solution of a (macro)molecule or growth of nanoparticles and thin layers on a substrate, again highlighting the ambiguous, versatile nature of graphene.

Graphene as a coating: the perfect nano-wrapper

The 2D, highly anisotropic shape of graphene, of course, can be used as a perfect tool to "coat" micron-scale areas of a substrate
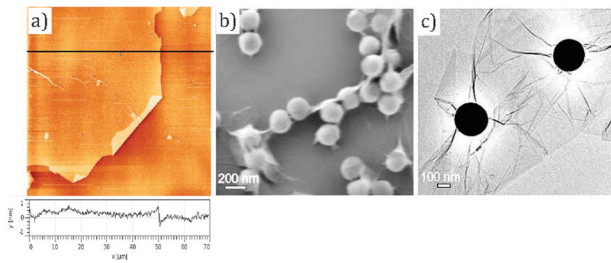
Fig. 5 (a) Single GO sheet, covering a surface of *ca.* 50 × 50 μm. In the inset, a height profile taken along the black line. Oscillations in the profile are an artefact due to incomplete image flattening, given the small thickness of the sheet (*ca.* 1 nm) as compared to the *xy* range of the AFM scan (70 μm). Reprinted with permission from ref. 50. Copyright (2009) American Chemical Society. (b and c) Typical images (b) SEM, and (c) TEM of graphene-wrapped silica spheres. Reprinted with permission from ref. 84.

with a perfect, mechanically robust, air stable monoatomic coating. By using a modified Hummers method, it is possible to prepare large sheets of GO, and to coat with them mesoscopic areas of arbitrary substrates (Fig. 5a).[50]

The high mechanical stability of monolayer graphene greatly exceeded initial expectation; a single sheet, suspended on a 1.5 μm circular hole, could withstand the force applied by an AFM tip up to 1600 nN, with deformations up to 100 nm out of plane. The ultimate strength measured by Hone and co-workers in this experiment was the highest for any material.[27,78] Most importantly, graphene could also withstand high pressure differences; graphene sealed micro-chambers could withstand a pressure difference of *ca.* 1 atm for several days;[28] eventually, gas leakage re-equilibrates the chamber pressure, but this is not due to gas passing through graphene, but to leaking at the sheet edges.

This very low gas permeability of graphene could be effectively used to protect metals from corrosion, either by growing graphene directly on the metal or by mechanically transferring it,[79] establishing graphene as the thinnest known corrosion-protecting coating.[80]

Of course the industrial interest in this kind of graphene application is high, and a collaboration between the University of Buffalo and Tata steel is trying to develop rust-proof steel with a graphene-based composite; this material could serve as a nontoxic alternative to coatings that contain hexavalent chromium, a probable carcinogen.[81]

Even in the case of coatings, a major advantage of graphene is that its gas permeation can be tuned by chemical functionalization, as demonstrated by Geim and co-workers: they found that submicrometer-thick membranes made from graphene oxide could be completely impermeable to liquids, vapors, and gases, including helium, but these membranes allow unimpeded permeation of water (H_2O permeates through the membranes at least 10^{10} times faster than He).[82] These seemingly incompatible observations were explained assuming a low-friction flow of a monolayer of water through two-dimensional capillaries formed by closely spaced graphene sheets.

This *pseudo*-2D liquid flow could be compared to what already obtained using Temperature Enhanced Solvent Vapour Annealing (TESVA),[60,62,63] where it is possible to form a continuous

layer of solvent on a surface with a thickness of a few nanometres by controlling the amount of solvent condensing on the substrate. This very thin layer is sufficient to boost molecules' mobility on the surface, allowing them to travel over very large distances (50–100 μm) with a rather high lateral diffusion, while being at the same time constrained in close proximity to the surface, in the thin layer of liquid, which can thus be described as a quasi-2- dimensional solution. Due to the different dimensionality, molecular diffusivity is higher than typical diffusivities observed by UHV STM for organic molecules on surfaces (10^{-11} cm^2 s^{-1}), but lower than what is observed in liquids (10^{13} cm^2 s^{-1}).[60] Controlled flow through well-ordered, highly defined graphene sheets could be an even more extreme case of a 2D liquid system, in which every molecule of the liquid is in contact with two graphene sheets, whose chemical surface will deeply influence the diffusivity of the solvent molecules.

Besides membranes, graphene coatings at the nanoscale have been used to wrap and protect MnO_2 nanoparticles for supercapacitors,[83] SiO_x and CO_3O_4 nanoparticles for lithium storage (Fig. 5),[84] DNA single strands on surfaces,[29] or even bacteria.[85]

Controlled permeation through chemically modified nanoholes in graphene membranes could also find straightforward applications, for example for water de-salinization[86] or even, in a more long term visionary application, DNA sequencing.[87]

Besides giving protection against the outer environment, a single layer of graphene can also tune the electronic properties of the surface, enhancing charge transport, modifying the work function or the wetting properties, which make graphene coatings of great interest for electronics.

Recently, we have devised a simple approach to fabricate graphene-based field-effect-transistors (FETs),[88] where the work function of each electrode could be tuned independently by coating it with GO sheets. The process relies on the site-selective reduction of GO sheets deposited from solution onto a substrate, in between or on the surface of micro/nano-electrodes (Fig. 6 and 7). The same electrodes are first used for voltage-induced electrochemical GO reduction, and then as the source and drain contacts of FETs, allowing for the straightforward production and characterization of ambipolar graphene devices. By using nano-electrodes, we could reduce different selected areas belonging to one single sheet as well (Fig. 8). The changes due to GO sheet deposition and reduction were monitored using Kelvin Probe Force Microscopy.[89,90] Alternatively, the tip of a scanning probe microscope could also be used to reduce selected conductive patterns on the GO-FET surface. The areas patterned in this way showed an increase of conductivity up to 8 orders of magnitude as compared to the untreated areas.[91]

In another approach,[92] we produced FETs based on a blend of reduced graphene oxide (RGO) and poly(3-hexylthiophene) (P3HT). By using sequential deposition of the two components (Fig. 9a), the surface coating of RGO sheets could be tuned linearly (Fig. 9b), thereby modulating their contribution to the charge transport in the transistors, and the onset of charge percolation. Fig. 10 shows a typical output of an RGO–P3HT based FET.
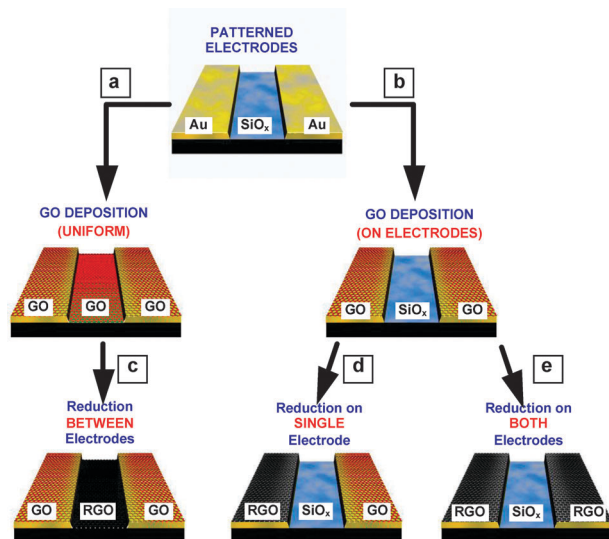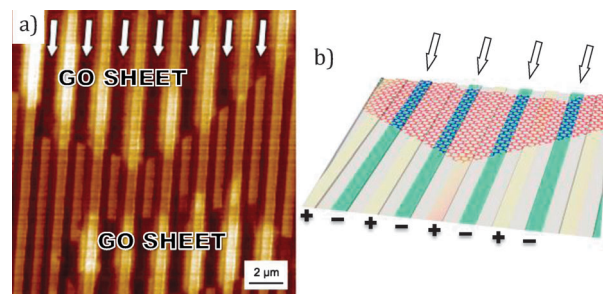
Fig. 6 Schematic representation of the different FET architectures which could be achieved by selective deposition and electrochemical reduction of graphene oxide. Reprinted with permission from ref. 88. Copyright (2011) American Chemical Society.
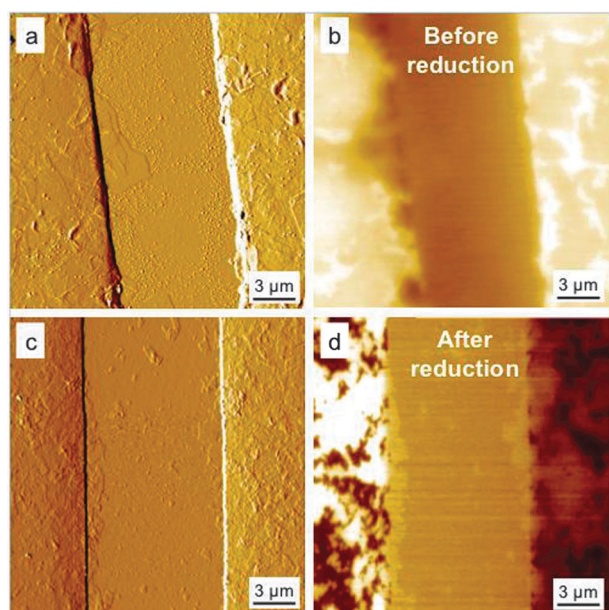
Fig. 7 (a and c) Gradient filtered AFM topography and (b and d) corresponding potential images of GO sheets selectively deposited on drain-source electrodes before (a and b) and after (c and d) selective reduction of the sheets on the right electrode. Z range = (a and c) 100 nm μm^{-1}, (b and d) 160 mV. Reprinted with permission from ref. 88. Copyright (2011) American Chemical Society.

FETs based on P3HT with different amounts of RGO show significant improvements in hole mobility, while electron transport remains unaffected and the I_{ON}/I_{OFF} ratio is >10^3. By comparing charge transport for different RGO coverage, with or without P3HT, it is possible to observe that graphene sheets can improve charge transport in continuous P3HT layers by acting as preferential paths for charges, reducing the effective channel length and increasing the overall hole mobility.

Fig. 8 (a) Selective reduction on single GO sheets on inter-digitated electrodes. Each electrode is *ca.* 500 nm in width. White arrows indicate the electrodes to which the negative voltage has been applied. (b) Schematic representation of the process. Reprinted with permission from ref. 88. Copyright (2011) American Chemical Society.

More than the high charge mobility of graphene (which in this work was not present because we used reduced GO), the main advantage of using graphene was the high processability of GO, which allowed us to tune the surface coating of the surface linearly, as demonstrated by SEM and AFM, just by tuning GO concentration in solution (Fig. 9b). In this work, an attempt was made to combine two materials together in a composite, to merge together the properties of graphene (high charge mobility, transparency, chemical stability) with those of organic semiconductors (tunable band-gap, photoluminescence, tunable acceptor–donor doping properties, *etc.*).

Discussion and conclusions

The general overview presented above of different properties and use of graphene does not mean to be an exhaustive review of all the work currently undergoing on this nice material. Its only aim is to show, through a (personal) selection of examples, how the versatility of graphene and its ambiguous nature are a great opportunity to create new science, new materials and innovative applications.

Though, the high versatility and tunability of graphene are also causing some confusion in the scientific community, which is by its own nature composed of experts coming from different areas. Many researchers complain about the abuse of the term "graphene" to indicate instead graphene oxide, chemically modified graphene, few layers graphene or even expanded graphite, graphite nanoplatelets and flakes, *etc.*

Even when comparing two graphene-based materials having the same chemical composition, the sheet size, sheet size distribution and exfoliation grade can be different, and this makes it difficult to compare different scientific works. The most evident example of this issue comes from the biological applications of graphene where, similarly to what happened in the past for carbon nanotubes, different and somehow contrasting properties are attributed to graphene; graphene-based materials have been demonstrated to be toxic for cells or bacteria in some cases, in others they did not show significant toxicity, and in others they were also used for *in vivo* drug delivery and imaging. For an extensive review on this, see ref. 93 and 94.
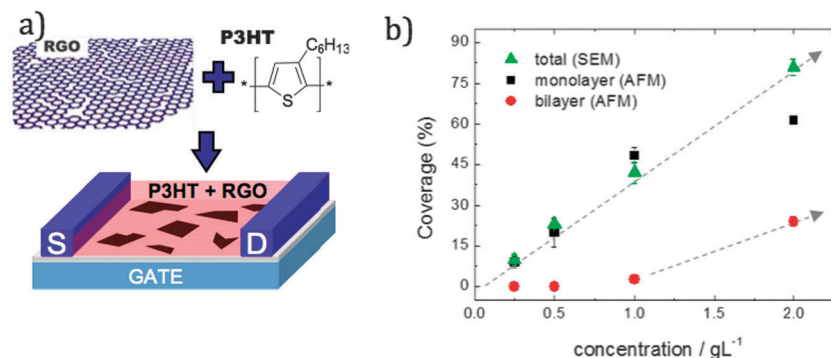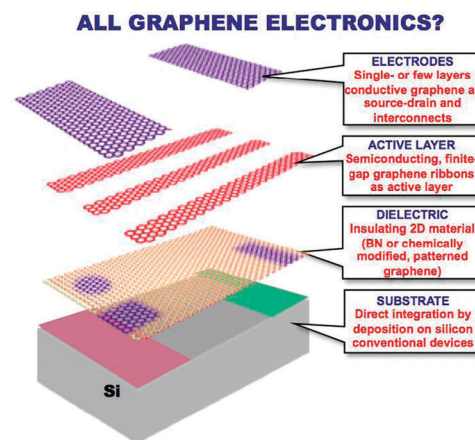
Fig. 9 (a) Cartoon depicting the structure of FET based on RGO and P3HT. (b) Area coverage *vs.* solution concentration, as measured by SEM (total coverage, ▲) and AFM (mono-■ and bi- layers ●). Reprinted with permission from ref. 92.
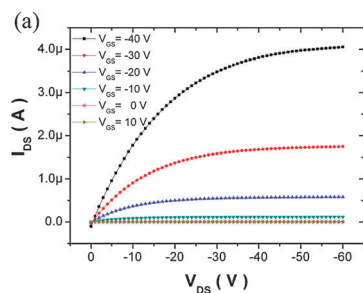
Fig. 10 Typical output characteristics for a RGO + P3HT FET device. Reprinted with permission from ref. 92.

Fig. 11 Schematic representation of the many different possible uses of graphene in an electronic device.

Even if it is clear to all the researchers of the field that these contrasting results are due to different functionalization and size of the graphene sheets used, this issue is a serious threat to the large scale application of graphene for consumer products, and can provoke a negative reaction of public opinion against the use of this new material.

To face this potential threat, serious efforts should be made to develop graphene metrology. Even if this can sometimes look like a hard task, we shall learn from the field of polymer science, where standard properties of the polymer used (chemical composition, molecular weight, polydispersity, *etc.*) are routinely determined and used to characterize different materials.

Overall, the right way to classify graphene is not as an outstanding, unique material, but as the first example of a new class of 2D materials.

When the first 1D polymer was produced in the 19th century (celluloid, also known as Parkesine or Xylonite) it was just used to replace amber and tortoiseshell (replacing ivory billiard balls was also attempted, but the balls tended to explode upon impact). The main importance of celluloid is not due to its initial applications, which were limited, but because it was the first example of a new class of plastic materials that changed deeply our lives with a wide range of different applications, which could not be predicted in the 19th century.

We are already producing different kinds of graphene; all these different graphenes will find applications in different fields. Even in microelectronics, the possibility of patterning, etching, self-assembling and functionalizing graphene shall

provide a huge versatility of applications, allowing us to envision devices in which the active layer, the wiring and the dielectric are all made of graphene or similar 2D materials (Fig. 11). In this direction, all-carbon solar cells containing graphene, fullerenes and nanotubes have been recently demonstrated.[95] Most of these applications will not be in competition with existing technologies, but should be in combination with them, if not for technical reasons, but for economical ones.

There are of course high hopes in the exploitation of the high charge mobility of graphene for electronics applications but, in my opinion, the first and most outstanding applications of this material will not be to make faster transistors. We should avoid the classical mistake of judging a fundamentally new technology merely by what it might do for already existing applications.

As stated by Nobel Prize winner H. Kroemer, the principal applications of any sufficiently new and innovative technology have always been – and will continue to be – applications created by that technology.[96]

In conclusion, we shall say that:

(1) The properties of graphene as a chemical object provide a wide range of different applications and challenging science; the most promising applications, where the properties of graphene will shine at their best, are the ones which take

advantage of these properties, such as the use as a coating for corrosion or cell-growth, the creation of new sandwich materials for energy applications, or the use of graphene composites for electronics and mechanics.

(2) These properties will likely yield the first and most prominent applications more quickly than the microelectronic ones, based on the most famous physical properties of graphene.

(3) To foster industrial success of these applications, a critical issue will be to find clear answers to the questions about graphene toxicology and biological activity, in order to avoid a negative first impact of these materials on public opinion.

(4) Standardization and metrology will be fundamental to select fundamental outcomes among the plethora of different results published on this topic, allowing a clear and objective distinction between the different members of the graphene family, and the quality of materials produced in different labs.

(5) To correctly describe these new 2D nano-objects an approach similar to the one used for 1D polymers shall be useful, allowing us to create a new terminology to classify this original, new class of materials.

"*Stat rosa pristina nomine, nomina nuda tenemus*"

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