Properties and applications of chemically functionalized graphene

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Abstract

The vast and yet largely unexplored family of graphene materials has great potential for future electronic devices with novel functionalities. The ability to engineer the electrical and optical properties in graphene by chemically functionalizing it with a molecule or adatom is widening considerably the potential applications targeted by graphene. Indeed, functionalized graphene has been found to be the best known transparent conductor or a wide gap semiconductor. At the same time, understanding the mechanisms driving the functionalization of graphene with hydrogen is proving to be of fundamental interest for energy storage devices. Here we discuss recent advances on the properties and applications of chemically functionalized graphene.

(Some figures may appear in colour only in the online journal)

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1. Introduction

Atomically thin materials are the thinnest materials which can be conceived and yet they have a unique combination of physical properties. Graphene is certainly the most celebrated and studied representative of this new family of materials [1–3]. This single layer of carbon atoms is the strongest known material, and the best electrical and thermal conductor which is mechanically flexible and transparent [1, 3]. In its pristine form the electrical conduction of graphene cannot be switched off, limiting the range of potential applications which will exploit the properties of graphene. At the same time, though graphene is nearly transparent (it absorbs only 2.3% of the light in the visible wavelength [4–6]), its electrical conductivity is still high for making pristine graphene suitable as a transparent electrode. However, the limitations of the physical properties of graphene can be overcome using chemical functionalization.
Indeed, recent experiments have shown that the optical and electrical properties of graphene can be controlled to fit the requirements of specific applications by chemical bonding of a molecule or a chemical element to the pristine material. For example, the functionalization with FeCl$_3$ of few-layer graphene results in a new graphene-based material which is the best known transparent electrical conductor and which outperforms the indium tin oxide (ITO) commonly used transparent electrode by the display companies. On the other hand, the functionalization with fluorine, hydrogen and oxygen makes graphene semiconducting. Engineering the properties of graphene with chemical functionalization is at the focus of current research since it holds the promise to expand significantly the potential range of novel applications which will be based on graphene materials.

2. Engineering the physical properties of graphene by covalent functionalization

The non-interacting first neighbour tight binding approximation predicts a gapless energy dispersion for single- and few-layer graphene (FLG) [7]. The lack of an energy gap is the direct consequence of the energetic equivalence between the onsite energy of the sublattices constituting the unit cell of these graphene materials (see figures 1(a) and (b)). Breaking this energetic symmetry between the sublattices directly leads to the opening of an energy gap. This can easily be accomplished in doubly gated transistor structures of FLGs with no mirror reflection symmetry [8] (e.g. AB-stacked bilayer, ABC-stacked trilayer, etc). In these devices the FLG is sandwiched between a back and a top gate which allow the independent control of a perpendicular electric field acting on the FLG and of the Fermi energy, see figures 2(a) and (b). More specifically, the voltages applied to the top and back gate originate a difference in the electrostatic energy in the layers composing the FLG, leading to the opening of a gate-tunable bandgap, see figures 2(c) and (d). Optical spectroscopy experiments in doubly gated AB-stacked bilayer graphene reported for the first time the direct observation of this gate-tunable energy gap whose value saturates of $\sim 200$ mV [9]. These experimental results are in stark contrast to previous electrical transport experiments, where the characteristic energy scales for the non-linearity reported in measurements of current versus voltage bias was at most 1 mV [10]. The contrast between the observations reported by optical spectroscopy and electrical transport experiments is yet unsolved. So far, the direct observation of a gate-tunable energy gap in electrical transport experiments remains elusive.

Although the doubly gated FLG devices are of great interest for both fundamental and applied research, the maximum values of bandgap which can be opened in these materials is limited to applications in the far-infrared range and not in the visible wavelength range. More specifically, while at low enough perpendicular electric fields ($E_{\text{perp}}$) the value of the energy gap increases linearly with increasing $E_{\text{perp}}$, at large $E_{\text{perp}}$ the value of the energy gap saturates due to screening caused by the finite density of states in the FLGs. The chemical functionalization of graphene offers a unique way to extend the limited range of bandgap energies achievable by doubly gated devices [8]. Indeed, a change in the hybridization of the graphene electronic orbitals from $sp^2$ to $sp^3$ can open large band-gaps ($>4$ eV in the case of fully fluorinated and hydrogenated graphene). This functionalization can be accomplished by chemically bonding a molecule [11], a functional group containing oxygen (i.e. graphene oxide) and/or an element such as fluorine or hydrogen to the carbon atoms of graphene as we will review in the following sections.

2.1. Graphene oxide

Graphene oxide (GO) is formed when oxygen containing functional groups are covalently bonded to the network of $sp^2$ hybridized carbon atoms of graphene. Several functional groups have been shown to exist in GO, such as carboxylic, hydroxyl and epoxy groups. GO has triggered research interest due to its wide range of physical and chemical properties [13–15], but also to its potential for the production of graphene on the ton scale [16, 17] by using different methods to remove the oxygen and create the so-called reduced GO. The chemistry of GO is still under debate, with several models that have been proposed for the chemical structure of GO and comprehensive reviews that have recently appeared on this topic [18, 14]. The most accepted model which is supported by solid-state 13C NMR spectroscopy [19] is shown in figure 3(a). In this model there are epoxy and hydroxyl groups which lie above and below the layer of $sp^2$ carbon atoms, whereas carboxylic groups are thought to
Figure 2. (a) Cross section view of a suspended and doubly gated few-layer graphene device. (b) False colour SEM image of a suspended and doubly gated ABC-stacked trilayer graphene taken under a tilted angle. Reproduced from [12]. (c) Schematic band structure of ABC-stacked trilayer graphene with broken energetic symmetry between the outer planes, for example by means of an external voltage ($V_G$) applied to the top and back gates as illustrated in (a). (d) The resistance versus back-gate voltage ($V_{bg}$) measured at $T = 300$ mK and for different values of fixed top-gate voltage as indicated in the graph in a doubly gated ABC-stacked trilayer. Reproduced with permission from [12]. Copyright 2012 American Institute of Physics.

Figure 3. (a) Schematic model for the structure of GO indicating the presence of different oxygen functional groups. Reproduced with permission from [18]. Copyright 2009 Royal Society of Chemistry. (b) High-resolution transmission electron micrograph of GO, illustrating its amorphous character. The inset represents a selected area electron diffraction pattern in which diffraction dots are absent and only diffraction rings are visible, confirming the disordered, amorphous nature of GO. Reproduced with permission from [20]. Copyright 2008 American Chemical Society. (c) Atomic resolution, aberration-corrected transmission electron micrograph of reduced GO. The defect-free crystalline graphene area is displayed in the original light grey colour, whereas the different structures have been highlighted with different colours: dark grey, contaminated regions; blue, disordered single-layer carbon networks or extended topological defects; red, individual adatoms or substitutions; green, isolated topological defects; yellow, holes and their edge reconstructions. Reproduced with permission from [50]. Copyright 2010 American Chemical Society. (d) Comparison of transmittance at 550 nm as a function of sheet resistance of GO films after undergoing different reduction treatments. Reproduced with permission from [15]. Copyright 2010 Wiley. (e) Photograph of unreduced GO (leftmost) and a series of high-temperature reduced GO films of increasing thickness. Reproduced with permission from [30]. Copyright 2008 American Chemical Society.
populate the edges of the layers. Due to the presence of these functional groups, which are randomly adsorbed, GO has a disordered, amorphous structure which has been revealed by both x-ray diffraction and high-resolution transmission electron microscopy (HRTEM) studies [20] (see figure 3(b)).

There are several methods to produce GO which are based either on wet chemistry or plasma oxidation. The most common wet chemical techniques consist of oxidation of graphite in strong acids, followed by a liquid exfoliation process. Graphite oxide can be produced by either the Brodie [21], Staudenmaier [22] or Hummers method [23]. The Brodie and Staudenmaier methods use a mixture of potassium chlorate with nitric acid, whereas the Hummers method is based on a solution of potassium permanganate and sulfuric acid. The liquid exfoliation of GO from graphite oxide can be achieved by simple sonication of graphite oxide in water and various organic solvents. These techniques have been extensively discussed in several reviews [18, 17]. Although the wet techniques employed to synthesize GO are suited for large-scale production, they inevitably introduce contamination in the final product. Therefore, alternative plasma-based routes to produce GO have been recently developed. These methods are based on exposure of graphene sheets to low-power oxygen plasma [24–29]. After exposure to oxygen plasma, a transition from semimetallic to semiconducting behaviour in graphene has been reported, which was due to the functionalization of graphene with oxygen atoms [26, 27]. More controlled plasma-oxidation techniques include the use of a water vapour plasma [28] or downstream oxygen plasma [29]. For instance, Liu used a water vapour plasma to oxidize graphene through a nanosphere lithography mask, which ensured that the oxidation occurs in a mild and controllable manner [28]. On the other hand, in the downstream oxygen plasma technique, the samples are placed downstream from the plasma source so that generated ions are relaxed upon arrival at the graphene surface and functionalize it in a controllable way [29].

The carbon–oxygen bonds in GO are sp² hybridized and the substantial sp³ fraction in GO renders it a wide bandgap semiconductor. Thus as-prepared GO is typically insulating and exhibits sheet resistance values of around $10^{12}$ Ω/sq or higher [30]. However, the conductivity of GO can be tuned by reducing the oxygen groups through various processes and changing the hybridization of carbon atoms from sp³ to sp² bonding. A variety of methods for the reduction of GO have been studied [18, 31–39], ranging from reaction with hydrazine [18, 31, 32], high-temperature pyrolysis [30, 40, 41] and plasma-assisted reduction [42–44] to bacterial treatment [34]. The reduction of GO results in the creation of clusters of sp² carbon atoms which are visible in HRTEM studies (see figure 3(c)). The presence of sp² clusters leads to the decrease of GO sheet resistance by several orders of magnitude [45] as shown in figure 3(d) and in the increase of its optical transparency (figure 3(e)). However, due to the complications arising from the structural disorder in GO, only a few studies have been devoted to the understanding of the electronic structure of GO. Thus, the fundamental electronic properties such as the bandgap values for GO and reduced GO are yet not well understood. For instance theoretical studies predict a bandgap in GO to be in the range of 1.7–2.4 eV depending on the degree of oxidation [46–48], but experimental studies have yielded lower values of around 0.25 eV [49].

One of the attractive properties of GO is that its oxygen functional groups render it hydrophilic and make it soluble in water [51] and many other solvents [52]. This solubility allows GO to be uniformly deposited onto any substrate using cost-effective methods such as drop-casting [18, 17], spin coating [30] or inkjet printing [53]. Thus, due to such inexpensive methods of production and the availability of large quantities, GO and its reduced version are commercially available at reasonable prices, which makes these materials of tremendous interest for a wide range of applications. Below we give an overview of the application of GO and reduced GO which have been demonstrated in different fields.

The readily tunable electrical and optical properties over a wide range via chemical engineering, together with the simple, low-temperature deposition onto a wide variety of substrates make GO attractive for electronics and optoelectronics [15]. The major areas where GO can be expected to have potential is in the production of transparent conductive electrodes, as well as in its use as an active part of devices such as semiconducting channel or memory material. Any type of substrate can be coated with solution processed GO thin films, which can be subsequently converted into a conductor using different reduction treatments. Several groups have evaluated reduced GO films as transparent and conducting materials [54, 55, 30, 41]. It has been shown that thin films of reduced GO can be made transparent and conducting by optimizing the thickness and reducing at high temperatures. Various oxidation, exfoliation, dispersion, deposition, and reduction procedures have been employed, which resulted in a range of transmittance and sheet resistance values that have been reported in the literature [15]. The highest degree of reduction was achieved using high-temperature pyrolysis (1100°C) which yielding films with sheet resistances of a few kΩ/sq and 90% transmittance [30, 40, 41] (see figure 3(d)). Such coatings have been used as electrodes for photovoltaic [41, 56–58] and light-emitting [59] devices. However, in all of these applications the devices employing electrodes based on reduced GO have lower performance than devices based on commonly used transparent electrodes such as fluorine tin oxide (FTO) and indium tin oxide (ITO) (see figures 4(a) and (b)). For example, Wang et al compared the performance of solar cells based on reduced GO electrode and on fluorine tin oxide (FTO) electrode [41]. The cell based on reduced GO electrode has a short-circuit photocurrent density ($I_{sc}$) of 1.01 mA cm⁻² with an open-circuit voltage ($V_{oc}$) of 0.7 V, filling factor (FF) of 0.36, and overall power conversion efficiency of 0.26%. The cell based on FTO electrode (which is commonly used in organic solar cells) has $I_{sc}$ of 3.02 mA cm⁻², $V_{oc}$ of 0.76 V, FF of 0.36, and an efficiency of 0.84%. In this case the lower $I_{sc}$ and efficiency of the cell based on reduced GO film was attributed to the series resistance of the device, the relatively lower transmittance of the electrode, as well as the electronic interfacial change.
Another area where GO has been employed is its use as channel material for field effect transistors (see figure 4(c)). Thin films of reduced GO exhibit ambipolar field effect [60], with on/off ratio of typically lower than 10 and mobility values ranging between 0.001 and 10 cm$^2$ V$^{-1}$ s$^{-1}$, depending on film thickness and reduction conditions [60]. Individual sheets of reduced GO have also been investigated as semiconducting channel [61, 55, 62–66]. Their ambipolar characteristics and mobilities are similar to those of the thin films, suggesting that sheet junctions in films play a minor role in carrier transport.

Perhaps one of the electronics areas where GO is most suited is in resistive switching memory applications [67–73] (see figure 4(d)). For these applications a metal GO/metal sandwich structure is fabricated and the conductivity of GO is electrically switched from its high resistance state to a low resistance state by applying a voltage between the two metal electrodes. Reversible and reproducible resistive switching behaviours have been observed in GO thin films with different type of metal electrodes, but the mechanisms driving the switching process have not been un-ambiguously determined. Several mechanisms have been proposed such as creating and breaking metal filaments [67], oxygen migration to/from an insulating interface layer between the electrode and GO film [68] or the formation of sp$^2$ graphene clusters in an sp$^3$ insulating graphene oxide layer [69]. Observations of reversible resistive switching in GO films has been reported by several groups [67–73]. In all these cases the switching was ambipolar and recent studies [73] have demonstrated reasonable on/off ratios (∼300), practical high and low resistance values (∼300 and 1 kΩ), reasonable switching voltages (∼2 V) and some cyclability (up to 100 cycles).
The heterogeneous electronic structure of GO translates into unique optical properties which make GO a chemically tunable platform for optical applications [74]. Thus, in contrast to pristine graphene, GO is fluorescent over a broad range of wavelengths such as near-infrared (NIR), visible and ultraviolet (UV), with a maximum intensity located between 500 and 800 nm [74–79]. The tunability of the emission spectrum of GO has also been demonstrated by means of progressive reduction of the oxygen content [76, 75] (see figure 5(a)). Thus for reduced GO, blueshift [75, 80–82] and redshift [76] of the fluorescence from UV to NIR have been reported. Although considerable progress in the studies of GO has been achieved, the origin of the fluorescence of GO is still a controversial issue with several mechanisms proposed in the literature. In early studies, it was suggested that the fluorescence arises from the recombination of electron–hole pairs in localized electronic states originating from the heterogeneous electronic structure of GO [74]. For reduced GO it has been proposed that the fluorescence is due to the disorder-induced states and the sp² clusters formed during the reduction reaction [75, 80]. At the same time, Luo et al [76] proposed that the bond distortions also give contributions to the fluorescence of GO and reduced GO. Studies of pH-dependent fluorescence of GO suggested that the emission of quasi-molecular fluorophores give rise to the fluorescence [83]. Recent time-resolved fluorescence measurements of GO in water, complemented by theoretical analysis, suggest that the GO fluorescence is due to electron–hole recombination from the bottom of the conduction band and nearby localized states to wide-range valance band [84]. In particular it has been found that electronic transitions between the non-oxidized carbon regions and the boundary of oxidized carbon atom regions give the predominant emission from GO. Finally, similar photoluminescence features have been observed in GO produced by oxygen plasma treatment of graphene, which was assigned to correlated localized electronic states of oxidation sites [24]. Such unique optical properties of GO over a wide range of wavelengths are promising for devices such as light-emitting diodes, white light emission for solid-state lighting and flexible display applications.

Owing to its fluorescence, GO has found applications in biology and medicine, such as bio-sensing, early disease detection, and even assisting in carrying cures for cancer, as well as other drugs and gene delivery. Thus, GO has been successfully used in fluorescent-based biosensors for the detection of DNA and proteins, with a promise of better diagnostics of HIV. Furthermore, GO was tested as a drug carrier and it has been shown that it has a unique ability in the attachment and delivery of aromatic, water insoluble drugs [85]. It has also been shown that GO is superior to many other anticancer drugs because it does not target healthy cells, only tumours, and has a low toxicity [86]. The intrinsic photoluminescence of GO has been used for live cell imaging in the near-infrared [85] and it was also demonstrated that GO is a robust candidate for DNA and protein analysis, and intracellular tracking [87]. GO has even been used as antibacterial material as it was shown to have superior antibacterial effects. Thus the growth of E. coli bacteria has been effectively inhibited by GO with minimal cytotoxicity [88]. This finding is of great potential for developing antibacterial materials that may assist in healing...
Figure 6. (a) Schematic structure of graphene (top) and its characteristic flat structure with sp$^2$ hybridized electronic orbitals (bottom left) which is opposed to the crumpled structure of graphane in the chair conformation with the hydrogen atoms alternating on both sides of the plane and characterized by sp$^3$ hybridized electronic orbitals (bottom right). The carbon atoms are shown in blue and red while the hydrogen atoms are in grey. (b) Predicted band structure for the fully hydrogenated chair conformer. Reproduced with permission from [104]. Copyright 2007 American Physical Society.

wounds by killing bacteria or that can be used for more sanitary packaging than current materials.

GO can mix readily with a wide range of organic and inorganic materials by interacting in non-covalent, covalent and/or ionic way to form functional hybrids, composites and paper-like materials. Graphene-based composite materials [90, 91] have been proposed as a possible route to harness the properties of graphene such as thermal conductivity, mechanical stiffness, fracture strength and electronic transport properties. Such composites have been suggested as a radical alternative to conventional polymers in the fields of transportation and electronics. Incorporation of graphene sheets in composites requires the graphene sheets to be produced on a sufficient scale and to be incorporated, and homogeneously distributed, into various matrices. Due to its solubility, GO allows the preparation of graphene-polymer composites and molecular-level dispersion of individual reduced graphene oxide sheets within polymer hosts. Thus graphene composites with styrenic polymers such as polystyrene, acrylonitrile–butadiene–styrene and styrene–butadiene rubbers have been shown to exhibit the lowest reported value of room temperature electrical conductivity for any carbon-based composite except carbon nanotubes (at only 1 vol%, the polystyrene–graphene composite has a conductivity of $0.1 \text{ S m}^{-1}$). In its solid form, GO platelets tend to stack one to another, forming thin and extremely stable paper-like structures that can be folded, wrinkled, and stretched [16, 92]. The GO paper is a free-standing carbon-based membrane material with a unique interlocking-tile arrangement of the nanoscale GO sheets. This new material has been shown to have a combination of macroscopic flexibility, stiffness and strength which outperforms many other paper-like materials (see figure 5(b)). Such free-standing GO films are considered for applications including protective layers, chemical filters, components of electrical batteries or supercapacitors, adhesive layers, electronic or optoelectronic components, ion conductors, nanofiltration membranes and molecular storage.

GO and its reduced forms have an extremely large surface area and therefore have been considered as potential materials in energy-related applications such as electrodes in rechargeable lithium-ion batteries [93, 89] and supercapacitors [94–96], as well as fuel cells [97, 98]. For instance, it was demonstrated that nanocomposite anchored on conducting graphene as anode material for lithium-ion batteries displays superior battery performance with large reversible capacity, excellent cyclic performance, and good rate capability [93, 89]. Several groups have demonstrated both types of supercapacitors based on GO: (1) electrochemical double-layer capacitors that store energy through the accumulation of charges at the interface of a high surface area electrode and an electrolyte [94, 95] and (2) redox capacitors that store energy Faradically by battery-type oxidation reduction reactions [99].

2.2. Hydrogenated graphene

Adsorbed chemical elements such as hydrogen or fluorine on the surface of graphene can form covalent bonds with the carbon atoms and create graphane (hydrogenated graphene) or fluorographene (fluorinated graphene). This process is known as chemisorption and it is accompanied by a change in the hybridization of the electronic orbitals of graphene from sp$^2$ to sp$^3$. Consequently, the planar two-dimensional crystal structure of graphene planes characterized by sp$^2$ bonds is transformed into a three-dimensional structure with sp$^3$ bonds whereby the C atoms are pulled out of the graphene plane [100–103] (see figure 6(a)). The first theoretical study predicting that hydrogenated single-layer graphene is a stable material was presented by Sofo et al [104] using density functional theory and presenting first-principles total-energy calculations. In contrast to the case of adsorbed oxygen which is randomly adsorbed on graphene [16, 17, 15], the adsorption of hydrogen [105–107] and similarly of fluorine [108–114] only takes place in a highly ordered way. More specifically,
the hydrogen (or fluorine) atoms are covalently bonded to both sides of the carbon sheet in an alternating manner, see figure 3.

Density functional theory calculations predict that the functionalization of graphene with hydrogen modifies the energy dispersion of graphene in a radical way, leading to the opening of a wide energy gap (3.5 eV for fully hydrogenated graphene [104, 115]), see figure 6(b). Uniquely to functionalized graphene, the value of the energy gap is theoretically expected to scale with the hydrogen coverage [116]. Engineering an energy gap in graphene materials is a first necessary step for the development of graphene-based digital electronics which would enable novel flexible electronic applications in the offing.

The change in hybridization of the electronic orbitals from \( \text{sp}^2 \) to \( \text{sp}^3 \) is expected to induce a radical modification also in other physical properties of these new materials such as a large spin–orbit interaction [117–120], which was recently experimentally measured [121]. Furthermore, even magnetic properties are expected to originate from the induced change in the hybridization of electronic orbitals which would widen considerably the range of potential applications of functionalized graphene. At the same time, the ability to bind and reversibly release hydrogen from graphene suggests the possibility to use this material for high-density hydrogen storage [104], which is of interest for example for the automotive industry [122].

To date, the successful hydrogenation of graphene has been demonstrated by several groups using various techniques such as exposure to hydrogen plasma [106, 105, 123–125], atomic hydrogen beams [107, 126–129], electron-induced dissociation of hydrogen silsesquioxane [130, 121] and more recently also with the Birch reduction process [131]. Each method presents some advantages as well as some disadvantages, making the resulting material suitable for different specific applications.

2.2.2.1. Remote hydrogen plasma. In the remote plasma technique, molecular hydrogen is dissociated in the hydrogen plasma and free to bond to the carbon of pristine graphene. To minimize the creation of atomic defects due to the highly energetic ions in the plasma, the graphene substrate is typically placed in a remote side of the chamber away from the discharge zone [106, 105, 76, 124]. In this method it is difficult to control the degree of induced atomic defects as well as the stoichiometry of the functionalization. The remote plasma makes it possible to obtain a large hydrogen coverage although when the graphene flakes are laying on a substrate the hydrogenation process takes place only on the exposed side of graphene, limiting the coverage of adatoms. Also in this one-sided hydrogenated graphene, it is energetically favourable for the hydrogen atoms to bond with different sublattices [132, 133].

2.2.2.2. Atomic hydrogen beam. Another method of hydrogenation relies on the use of an atomic hydrogen beam [107, 126–129]. To reach hydrogen saturation usually the source is operated at high temperatures (2200 K) and in a very low hydrogen gas partial pressure (\( 10^{-7} \) mbar) [126].

The opening of a bandgap in the energy dispersion of graphene through functionalization with an atomic hydrogen beam was directly measured by angle-resolved photoemission spectroscopy [107, 126–129]. These experiments also pointed out that to accomplish large hydrogen absorption on graphene, previously grown on oriented transition metal substrates, a reactive substrate is needed. Similarly to the plasma technology, also with this method it is difficult to control the coverage of hydrogen atoms and the amount of atomic defects induced in graphene.

2.2.2.3. Electron-induced dissociation of hydrogen silsesquioxane. The future development of whole-graphene electronics is reliant on the ability to pattern conductive and semiconductive graphene structures in a circuit, and the local control of the functionalization is a cornerstone for the full exploitation of the potential of functionalized graphene in electronic applications. The local hydrogenation of graphene by breaking Si–H bonds of spin-on-graphene hydrogen silsesquioxane (HSQ) upon irradiation with 30 keV electron beam at various doses (0.5–8 mC cm\(^{-2}\)) is an original solution to the spatial control of functionalization [130, 121]. This method reliably delivers hydrogenated graphene which is stable only up to moderate temperatures, since it reduces to pristine graphene at temperatures in the range of 100–200°C. However, the ability to pattern hydrogenated graphene structures in a sheet of pristine graphene might enable the birth of a new generation of flexible graphene-only electronic circuits. The challenge posed by this method is the considerable disorder-induced states with sub-gap energies which make it difficult to directly measure the bandgap in transistor structures.

2.2.2.4. Birch reduction. All the aforementioned methods for hydrogenating graphene are of interest for engineering an energy gap in the gapless energy dispersion of graphene, however they generally use specialized conditions of vacuum and low hydrogen pressure to ignite a plasma of hydrogen, reduce defects, and control locally the functionalization. Therefore, these methods are not suitable for applications in hydrogen storage where a low-temperature regeneration process is preferred [122]. Indeed, the most desirable hydrogen storage device should be light, compact and should have an efficient regeneration cycle. This implies that the materials forming this ideal device should have a high hydrogen volumetric and gravimetric density [122, 134]. Graphene has a high density weight percentage of hydrogen stored as compared to the total weight of the system (i.e. high hydrogen gravimetric density) as well as a high stored hydrogen mass per unit volume of the system (i.e. high hydrogen volumetric density). However, whether hydrogenated graphene will have a considerable impact on the hydrogen storage industry—for instance for automotive applications—will be heavily determined by the regeneration process [122]. To date, the ability to regenerate large quantities of hydrogen storage by using low pressure and low temperature represents one of the major challenges for hydrogenated graphene which is typically obtained by highly
energetic processes [106, 105, 76, 124, 107, 126–129]. The recently demonstrated hydrogenation of graphene based on the Birch reduction process [135] represents a promising solution to this problem.

Birch reduction [135] is commonly used to change the sp² hybridization of carbon-based materials into sp³ by introducing a covalent C–H bond and this is a method which is of great interest for hydrogen storage devices for it is easy to implement. In particular, a change of weight up to \( \approx 5 \) wt% has been demonstrated when conducting the Birch reduction of FLG with lithium in liquid ammonia [131]. The functionalization of graphene obtained by this method is stable to heating up to 500 °C, and the C–H bond can decompose also by exposure to UV light or laser radiation, paving the way to whole-graphene electronics where conductive and semiconducting parts of a circuit are simply drawn on a sheet of graphene by locally reducing graphene to graphene. So far, little is known on the electrical properties of hydrogenated graphene obtained by the Birch reduction, limiting the full exploitation of this method for electronic applications.

While the low values of binding energy (0.7 eV) and low chemisorption barrier (0.3 eV) characterizing atomic hydrogen chemisorption on graphene [136, 103, 104, 137–139] make it easy to functionalize graphene with atomic hydrogen, it also causes the desorption of hydrogen at moderate temperatures, limiting the range of potential applications. The chemisorption with fluorine is a valid alternative when there is the need for a graphene-based wide gap semiconductor stable to temperatures >500 °C [140].

2.2.5. Electrical transport versus spectroscopy measurements. Interestingly, the direct observation of a large energy gap in hydrogenated graphene with photoemission spectroscopy [107] is contrasted by the lack of a direct observation of this energy gap in electrical transport experiments, see figure 7. The opening of the energy gap due to the hydrogenation process leads to a strong temperature dependence of the electrical resistance in functionalized graphene. However, experiments consistently show that the resistance in these devices usually increases exponentially when reducing the temperature [105] with a characteristic functional dependence intrinsic of hopping conduction mechanisms.

The discrepancy between optical spectroscopy and transport experiments can be understood when considering the presence of disorder-induced states with sub-gap energies. In this case, when the Fermi level of graphene lies in the energy range corresponding to the energy gap, hopping of charge carriers between disorder-induced sub-gap energy states dominates the electrical conduction. This process of conduction hinders the direct observation of the energy gap in electrical transport measurements. However, optical spectroscopy is a technique mostly sensitive to the valence-to-conduction band transitions rather than transitions from the impurity states to the conduction band. The full exploitation of the semiconducting properties of graphene for transistor applications requires a clean energy gap with no disorder-induced states. Obtaining a clean-gap hydrogenated graphene in which the energy gap is the only energy dominating both the electrical and optical transport properties is currently an open quest.

2.3. Fluorinated graphene

Similarly to hydrogenated graphene, the chemisorption of fluorine atoms onto graphene modifies the hybridization of the electronic orbitals of graphene from sp² to sp³. Consequently, fluorinated graphene is also a semiconducting material with a wide bandgap in the energy dispersion. When full fluorine coverage is attained, this material is called fluoro-graphene. Theoretical calculations of the fluoro-graphene bandgap by the generalized gradient approximation and density functional theory provide values around 3.1 eV [139, 141, 142] which are similar to the value for the bulk graphite fluoride [143, 144]. Compared to hydrogenated graphene, fluorinated graphene is more stable to higher temperatures (that is >400 °C). This is mainly due to a stronger binding energy between fluorine and carbon as compared to the binding energy between...
hydrogen and carbon. Therefore, fluorinated graphene is a few-atoms-thick semiconductor suitable for a different niche of applications to those potentially targeted by hydrogenated graphene. This diversity in material properties and potential applications constitutes the true richness of chemically functionalized graphene.

The fluorination of graphene has been successfully demonstrated with various techniques which often exploit previously developed methods for the fluorination of carbon nanotubes [145–148] or bulk graphite [149]. More specifically, these methods include the reaction of graphite with fluorine gas at moderate temperatures (400–600°C) [150, 112], exposure to F-based plasma [109, 151, 114], exposure to XeF$_2$ [111, 110, 113] and the fluorination mediated by laser irradiation of a fluoropolymer covering graphene [152]. Different approaches have been used to isolate a single layer of fluorinated graphene. More specifically, it is possible to conduct directly the fluorination of single layer pristine graphene [110] or alternatively it is possible to simply isolate a single layer of fluorinated graphene from bulk fluorinated graphite by exfoliation [153, 154]. In the latter process, the exfoliation of the bulk fluorinated graphite can take place by mechanical cleavage [153, 154] or by dispersion and exfoliation in organic solvents [113]. While the mechanical exfoliation is a reliable method to fabricate devices for fundamental research, the liquid phase exfoliation is perhaps one of the most promising methods for manufacturing large area fluorinated graphene at low costs.

2.3.1. Exposure to F$_2$ gas. The fluorination of graphite by exposure to F$_2$ gas at moderate temperatures, in the range of 400–600°C, is a well-established process [149, 150] in which covalent C–F bonds are formed. This process of fluorination is easy to control, for example by controlling the temperature and the pressure of the reactant gases, leading reproducibly to the same C/F stoichiometries [112]. Fluorinated graphite obtained by this method is commonly used as a lubricant and in the cathodes of primary lithium batteries [155]. Single- and few-layer fluorinated graphene were mechanically exfoliated from fluoro-graphite grains, and their electrical properties characterized in transistor devices [153, 154]. It was found that the electrical resistance of fluorinated graphene varies significantly with the temperature, as expected for a semiconducting material. However, similarly to the case of graphene, also in fluorinated graphene the presence of a finite disorder-induced density of states with sub-gap energies hinders the direct observation of the true energy gap (corresponding to the band-to-band transition from valence-to-conduction band). Indeed, in the presence of disorder-induced states the electrical conduction for sub-gap energies is dominated by the signal due to hopping through these states. Despite the presence of disorder, fluorinated graphene remains a very attractive material system for applications as well as fundamental science. For example, recent experiments demonstrated that the electronic transport properties in fluorinated graphene can be tuned by adjusting the fluorine coverage, so that different transport regimes can be accessed, such as Mott variable range hopping (VRH) in two dimensions, Efros–Shklovskii VRH and nearest-neighbour hopping transport [112, 154].

2.3.2. Remote plasma of a fluorinating agent. The chemical functionalization of graphene with fluorine can also be carried out by using a remote plasma. It was shown that the plasma-assisted decomposition of CF$_4$ employing a radiofrequency plasma source at room temperature can induce the chemisorption of fluorine onto graphene [109, 151, 114]. The formation of covalent C–F bonds was confirmed by infrared spectroscopy. Furthermore, it is also possible to fluorinate graphene using the plasma-assisted decomposition of CHF$_3$, however a comparative study of the Raman spectra of fluorinated graphene obtained from CF$_4$ and CHF$_3$ has shown that the fluorination by CF$_4$ plasma treatment induces the lowest magnitude of lattice defects although a higher magnitude of hole-doping to graphene was observed. The electrical transport properties of F-based plasma fluorinated graphene are also dramatically affected by the presence of disorder-induced states with sub-gap energies which are also at the origin of the observed colossal anisotropic magnetoresistance [114].

2.3.3. Exposure to XeF$_2$. An alternative method to fluorinate graphene which avoids ion bombardment consists in exposing graphene to xenon difluoride (XeF$_2$) at 30°C [111] or at 70°C [110] and 350°C [113] for a faster reaction. XeF$_2$ is a well known etchant for silicon and it was also used to functionalize carbon nanotubes with fluorine [147, 148]. This processing has been successfully transferred to graphene where optical spectroscopy studies reported a bandgap >3 eV [110]. Photoluminescence measurements of fluorographene produced with this method and subsequently dispersed in acetone have also identified an emission peak at 3.8 eV as the band-to-band recombination of free electrons and holes [113]. However, this bandgap has not been directly measured in electrical transport experiments, since this process of functionalization also introduces a considerable density of states with sub-gap energies responsible of hopping conduction mechanisms which hinder the observation of activated transport over the true energy gap.

2.3.4. Laser irradiation of a fluoropolymer coating graphene. Finally, the laser-assisted fluorination of graphene was demonstrated by creating fluorine radicals upon laser irradiation of a fluoropolymer (Cytop, CTL-809 M from Asahi Glass Co.) which coats graphene. This method offers a straightforward way to locally control the fluorination of graphene, enabling a new concept of whole-graphene electronics whereby conductive and semiconductive parts of a circuit are all made from graphene but with different degrees of functionalization—i.e. different coverage of adatoms [152].

3. Patterning of graphene circuits by local functionalization

Engineering the electrical and optical properties of graphene by chemical functionalization with molecules or adatoms
widens considerably the potential range of applications for this novel material. In particular, the possibility to control locally the functionalization of graphene would enable a whole new concept of electronic applications whereby the current electronic printed circuit boards would be replaced by whole graphene-based boards where devices are simply patterned on a graphene matrix by functionalization. This idea was theoretically studied in [156–158] and tunable electronic and magnetic properties depending on the edge geometry (zigzag or armchair orientation) and edge adsorbed atoms have been predicted. Recent experimental advances in the local control of fluorination have shown that these graphene circuit boards are a closer reality than initially anticipated [153, 152]. To date two complementary approaches to fabricate whole-graphene circuit boards with functionalization have been experimentally demonstrated: (1) start off from functionalized graphene sheet and reduce the functionalization in specific regions [153]; (2) start off from pristine graphene sheet and functionalize only specific regions [152].

3.1. Electron-assisted defluorination

In the first method, the starting material was a sheet of functionalized graphene obtained by mechanical exfoliation from fluorinated graphite by exposure to F₂ gas at 450°C, resulting in a fluorine content of 28%. Subsequently, the irradiation of the functionalized graphene with an electron beam with appropriate energy was used to dissociate the C–F bonds and reduce the fluorinated graphene. In this way, conductive channels as narrow as 40 nm have been drawn by electron beam defluorination in the hosting insulating sheet of fluorographene [153], see figure 8.

This innovative technique offers a simple and direct way to change the coverage of fluorine adatoms, and it has enabled the experimental demonstration that the energy dispersions of fluorinated graphene has an energy gap with a value dependent on the degree of functionalization—i.e. coverage of adatoms [159]. More specifically, a semiconductor-to-metal transition was experimentally observed upon changing in situ the F-coverage from 28% to <1% with electron beam irradiation. This transition is accompanied by a significant change of the resistivity of the diluted fluorinated graphene (see figure 9(a)). At the same time, the energy gap between the impurity band and the top of the valence band changes by 500%, while the spreading in energy of the localized states only changes by 30% (see figures 9(b) and (c)).

3.2. Laser-assisted fluorination

An alternative route to control locally the covalent functionalization of graphene with fluorine consists in coating the pristine graphene with a fluoropolymer (Cytop, CTL-809 M from Asahi Glass Co.). Subsequently, the CYTOP-polymer is decomposed by means of a laser (wavelength 488 nm and spot size 500 nm) and active fluorine radicals are produced boosting the formation of the fluorinated graphene. Due to the small laser spot size, this process naturally offers a good control over the spatial resolution of the fluorination process, and fluorinated circuits were indeed demonstrated on a pristine graphene sheet [152]. The possibility to tune in situ the optical and electrical properties of graphene from a fully metallic state all the way to a wide gap semiconductor simply by controlling the coverage of fluorine adatoms enables a new class of potential applications in flexible and wearable electronics.

3.3. Electron-assisted hydrogenation

As discussed in the previous section, spatial control of hydrogenation in graphene has been demonstrated by electron beam irradiation of an HSQ layer deposited on graphene [130, 121]. Furthermore, AFM lithography has also been used to locally hydrogenate graphene [160]. However, as opposed to patterned fluorinated graphene, the hydrogenated graphene produced by patterning is not stable at above 100°C and reduces to pristine graphene at temperatures in the range of 100–200°C.

3.4. AFM assisted thermochemical reduction of GO

Finally, nanoscale patterning of conductive reduced GO within an insulating GO sheet has also been reported using an AFM tip-based thermochemical nanolithography method to control the extent of reduction of GO [161]. In this method, reduced GO features can reliably be obtained by scanning...
a heated AFM tip over isolated GO flakes deposited on a SiO$_2$/Si substrate. In a related method, a metallic AFM tip was used to locally reduce GO through electrochemical conversion, which generated micrometre-scale features with tunable conductance [162]. Similarly to hydrogenation, AFM lithography was employed to oxidize locally graphene and create pattern nanoscale GO [160].

4. Two-dimensional intercalated graphitic materials

Another way to functionalize FLG is by introducing molecular and/or atomic species between the planes of the FLG. This intercalation process has been extensively studied in bulk graphite and has granted access to an overwhelming variety of novel properties such as an intrinsic superconducting state as well as magnetic properties [163]. To date, few experiments have been conducted on few-layer graphene systems on insulating, metallic or carbide substrates [164]. These substrates initially serve as a host material to produce graphene by means of chemical vapour deposition (CVD) or epitaxial growth. In this case monolayer or multilayer graphene used as a starting material for intercalation is not free-standing but electronically coupled to the substrate. It is therefore traditionally called two-dimensional graphitic film (2DGF) [165]. 2DGFs can be formed on many metals such as Pt, Ir, Rh, Ru, Ni, Pd, Re, silicon carbide SiC and metal carbides (for example, MoC, ZrC, NbC, TaC, TiC).

One of the first successful attempts to intercalate guest atoms between a monolayer 2DGF and Ir substrate was carried out using Ni as intercalant [164]. More specifically, Ni atoms were deposited on top of graphene in UHV and the intercalation process was boosted by heating at temperatures higher than 1000 K. The phenomenon is similar to that of intercalation into bulk graphite (resulting in graphite intercalation compounds, GIC) when guest atoms or molecules penetrate into the interlayer space while graphene planes remain unchanged and only move apart to accommodate the intercalated molecules. This topic is still thriving with more new molecules and/or atoms intercalated recently, for example hydrogen between monolayer and bilayer graphene and SiC [166], Eu between graphene and Ir [167], Al between graphene and Ni [168], HF between graphene and Ir [169], oxygen between graphene and Ir [170], oxygen between graphene and Ru [171] and finally Cs between graphene and Ni(111) substrate [172].

Intercalation of 2DGFs was a strategy to obtain graphene free of electronic coupling to the substrate (quasi-free-standing graphene) before the method of mechanical exfoliation was put forward, although in several cases the electronic properties of pristine graphene are modified by the presence of the intercalant specie. For example, a site-dependent periodic variation of the local effective spin polarization in cobalt-intercalated graphene on Ir(111) was observed by means of spin-polarized scanning tunnelling microscopy [173]. Modelling based on density functional theory shows that the origin of this variation is a site-dependent magnetization of the graphene, where graphene is coupled to the cobalt underneath either ferromagnetically or antiferromagnetically. Such a surface may be utilized in the future to inject spin currents with different spin signs energy-selectively, by choosing appropriate adsorption sites for spin-active adsorbates. For example, a giant (up to 100 meV) spin–orbit splitting of π-states in Au-intercalated graphene was observed with the help of angle- and spin-resolved photoemission spectroscopy [174, 175], making functionalized graphene a promising material for applications in spintronics.

Another intercalant of FLG which has been recently shown to decouple electrically graphene layers from the substrates and from each other is methane [176]. Upon intercalation, each graphene layer was found to behave as quasi-free-standing high-quality monolayer graphene. Furthermore, it has been theoretically predicted that an external electric field applied perpendicular to the plane of this methane intercalated few-layer graphene should open a controllable bandgap [177], widening considerably the range of potential applications targeted by this functionalized graphene.

Finally, intercalated compounds are of great interest also for energy storage devices. For example, the intercalation of
bilayer graphene on SiC by Li not only decouples electrically the bilayer from the SiC substrate [178], but it also intercalates in the bilayer leading to a well-ordered structure as in C$_6$Li. Since lithium is traditionally widely used as an anode material in rechargeable batteries, these findings are of potential interest for nanoscale Li-ion battery. Furthermore, theoretical investigations show that bilayer graphene with structural defects and isolated C atom vacancies will store more Li ions between two graphene sheets than bulk graphite [179]. This defect-full FLG is also expected to have shorter charging/discharging times [178].

Apart from the use for energy storage devices, Li intercalation is expected to grant access to new states such as the superconducting state. First-principles density functional theory calculations predict phonon-mediated superconductivity of monolayer graphene with adjacent layer of lithium [180]. Although later studies based on the cluster expansion method and density functional theory calculations [181] suggest that Li cannot reside on the surface of defect-free graphene, the quest for an intrinsic superconducting state in intercalated few-layer graphene is still open. Another attractive property of Li-FLG arises when narrow strips of FLG (nanoribbons) are used. In this case the possibility of antiferromagnetic coupling between the edge states of adjacent nanoribbon layers arises [182]. These nanostructures with spin magnetic edge states are of great interest for spintronics. Finally, a large enhancement of the charge carrier density can be achieved by Li intercalation into quasi-free bilayer graphene, as can be seen by means of density functional theory [183]. Therefore, Li intercalation could be used to improve significantly the electrical conductivity of graphene and replace existent transparent electrodes such as indium tin oxide. However, issues related to the air stability of Li-FLG will need to be addressed.

The thrilling possibility to induce an intrinsic superconducting state in atomically thin systems by doping is of great fundamental relevance [184]. It is well established that graphite becomes superconducting after intercalation with alkali metals and alkaline-earth metals, therefore intercalation is probably one of the most promising fabrication techniques to search for intrinsic superconductivity in few-layer graphene. For example, Ca-intercalated graphene bilayer was considered theoretically [185], and substantial similarities between Ca-intercalated bilayer and bulk graphite compound CaC$_6$ were predicted. In particular, the nearly free electron band in intercalated bilayer is expected to cross the chemical potential, which is an essential ingredient for superconductivity in intercalated graphites. Furthermore, the calculated properties of zone-centre phonons for intercalated bilayer are very similar to those of bulk CaC$_6$. Experimentally, Ca intercalation was recently successfully demonstrated in bilayer graphene grown on silicon carbide [186]. The structure and electronic states of this material was studied by scanning tunneling microscopy and angle-resolved photoemission spectroscopy. The free-electron-like interlayer band at the Brillouin-zone centre was observed. However, direct observation of the superconducting state has not yet been reported. Similarly, a parabolic metallic band at the Brillouin-zone centre of Rb-intercalated bilayer graphene on 6H-SiC(0001) was observed [187], making Rb-intercalation potentially interesting for inducing a superconducting state in FLGs. Finally, potassium doped FLG is the only system in which intrinsic superconductivity has been experimentally observed. In this case, the FLGs were prepared in a solution with K/Na alloy and 1,2-dimethoxyethane as the impregnant and subsequently a sheet containing mainly doped four graphene layers was found to have a critical temperature of 4.5 K [188].

5. Intercalated quasi-free few-layer graphene

Unlike CVD graphene on metals or epitaxial graphene on SiC, graphene deposited on SiO$_2$, Si$_3$N$_4$, glass or graphene in liquid suspension has pristine electronic spectrum and we refer to this as quasi-free single- and few-layer graphene. Various molecules and particles can be intercalated in this quasi-free FLG, and it has also been demonstrated that it is possible to wrap nanocrystals by graphene. More specifically, Fe$_2$O$_3$, Co$_2$O$_4$, and SnO$_2$ nanocrystals were inserted into bilayer graphene through a mechanism analogous to colloidal coagulation [189]. Similarly, a 3D nanostructure was achieved with nano-sized TiO$_2$ intercalated between graphene layers as pillars [190]. The obtained composites can be used as an anode material for Li-ion batteries with improved lithium storage capabilities.

Intercalated FLG is expected to grant access to a large variety of unique properties. For example, bilayer graphene intercalated with Br and Br$_2$ has been predicted to be characterized by a significant charge transfer from graphene to Br/Br$_2$ which can result in a significant enhancement of the electrical conductivity of graphene work [191]. The intercalation of C, N or O atoms is expected to open a bandgap in bilayer graphene since these atoms are preferentially absorbed by one of the graphene layers as opposed to the case when they are being placed in the middle between graphene layers, leading to a potential difference between the outer layers and the opening of a bandgap [192]. Furthermore, intercalation of C and N atoms is also expected to originate magnetic properties of interest in spintronics [192]. At the same time, the intercalation of Ni into bilayer graphene is expected to make bilayer a nonmagnetic semiconductor with bandgap of 0.64 eV, whereas incorporation of Fe and Co should result in ferromagnetic two-dimensional metals [193]. Finally, the band structure and electron–phonon coupling of quasi-free K-intercalated bilayer graphene calculated using density functional theory also suggests that K-intercalated bilayer graphene is a good candidate to search for intrinsic superconductivity [194].

The experimental realization of intercalation of molecular and atomic species into quasi-free FLG was recently reported for K, Rb [195], ICl and IBr [196] using the vapour-phase method. In particular, partial intercalation of K and Rb was performed by means of a two-zone vapour-phase method at 210 and 160°C, whereas the intercalation of ICl and IBr requires relatively low temperatures (just 35°C).
Similarly, the intercalation of FeCl₃ was demonstrated using temperatures of about 350°C [197]. A large upshift of the G-peak in the Raman spectra is commonly observed upon intercalation, and it signifies that a large charge transfer occurs from (to) the molecular or atomic specie to (from) graphene. Furthermore, a strong anisotropy of resistance manifested in high c-axis (perpendicular to graphene planes) resistivity is expected [196] owing to a strong localization of the \( \pi \) -electronic orbitals in the graphene layers separated by ICl or IBr. The substantial reduction of the coupling between intercalated graphene layers makes this systems promising for studying excitonic condensates.

Finally, another possible route to intercalate FLGs exploits the reduction of intercalated GO [198]. More specifically, exfoliated GO in liquid ammonia and lithium metal was reduced chemically and filtered through a polytetrafluoroethylene membrane filter of 0.2 m pore size. Partial intercalation of lithium ions in between graphene layers of the resulting structure was demonstrated, making this material a good candidate for electrochemical energy storage applications.

### 6. Making graphene the best transparent conductor

Transparent materials able to conduct electricity are nowadays embedded in many optoelectronic devices, such as displays, organic solar cells, etc. One of the most widely used transparent conductors is indium tin oxide (ITO). This is a highly conductive material (just 10 Ω/sq at room temperature) and highly transparent. However, ITO is a brittle material [199] which is therefore not suitable for future flexible electronic applications. Furthermore, organic photovoltaic devices which implement ITO anodes are known to suffer of ion diffusion from ITO into the organic films [200, 201] which limits severely the lifetime of these devices. Therefore, there is a growing need to find materials which can replace ITO and potentially display added functionalities for developing novel optoelectronic applications.

Networks of carbon nanotubes and metallic nanostructures have been at the focus of current research as potential replacement for ITO [202] and very recent advances in this research area have demonstrated transparent electrodes based on a metal nanotrough network with superior optoelectronic performances to those of ITO, with a sheet resistance of 2 Ω/sq at 90% transmission in the visible wavelength range [203]. Networks of conductive structures typically employ opaque metallic nanostructures (with transverse dimensions of \( \sim 300 \) nm [203, 202]), and one of the major drawbacks of these metallic nanostructures is hazing. Haze is an unwanted side-effect caused by light scattering [204, 202], which can be unacceptably high for displays and touch panels. Hazing can be counteracted by reducing the size of the metallic nanostructures, however lower conductivities and loss of film uniformity constitute a further limit to the size of these structures [204].

Graphene constitutes a very attractive alternative to metallic networks, owing to its unique mechanical flexibility, high optical transparency and ability to conduct electricity. However, the high values of sheet resistance of graphene in its pristine form limits the possible range of applications. The chemical functionalization of graphene is usually accompanied by the charge transfer to/from graphene and this can reduce dramatically the sheet resistance of graphene. In particular, the recent discovery that intercalation of FeCl₃ in FLG gives an air stable compound with \( 8 \) Ω/sq and optical transmittance as high as 96% in the visible wavelength range makes graphene the best known transparent conductor [197].

#### 6.1. FeCl₃-intercalated few-layer graphene

Intercalated graphitic compounds have been extensively studied in the past decades. However, very little is known on intercalated FLG compounds, and it is likely that the overwhelming variety of electrical, optical and magnetic properties which can potentially be engineered in intercalated FLG compounds will be at the focus of future fundamental and applied research.

Since the discovery in 2012 of the best known transparent conductor based on FeCl₃ intercalated FLG (FeCl₃-FLG), a material whimsically called graphExeter, it has become clear that it is possible to conduct the intercalation of large molecules between the planes of a few-layer graphene [197]. This intercalation process with FeCl₃ is typically performed in vacuum using a multi-zone furnace where anhydrous FeCl₃ and the FLG substrates are positioned in different zones inside a glass tube. At first, the tube is pumped down to 2 × 10⁻⁴ mbar at room temperature. Subsequently, the FLG and the powder are heated for 7.5 h at 360°C and 310°C, respectively. It was found that this intercalation process does not depend on the substrate even when intercalating bilayer graphene. The resulting material is a very good conductor of electricity with a sheet resistance of \( 8 \) Ω/sq and optical transmittance as high as 96% in the wavelength range from 400 to 700 nm.

The values of electrical conductivity and optical transmittance characterizing FeCl₃-FLG are far better than any other known transparent conductor, making this novel graphene-based material a valuable replacement for the widely used ITO in the display industry. Furthermore, the record high charge densities attained in FeCl₃-FLG as high as \( 9 \times 10^{14} \) cm⁻²—together with typical charge carrier mobility of 1000 cm² V⁻¹ s⁻¹—gives a mean free path for the charge carriers of almost 1 \( \mu \)m at room temperature. In contrast to pristine graphene where the electrical properties depend dramatically on the substrate, the large mean free path found in FeCl₃-FLG does not depend at all on the substrate supporting this intercalated compound—for example identical values of mean free path were demonstrated on SiO₂/Si substrate as well as on microscope glass slides. Indeed, the extremely high values of charge densities present in these intercalated compounds screen the charge defects of the substrate, making the electrical properties of these materials extremely robust and not vulnerable to the quality of the supporting substrates.

Interestingly, a comparative study of the Raman spectra and magneto-electrical measurements has shown that upon intercalation the charge carriers in each individual graphene...
layer forming the FLG are decoupled. Indeed, the Raman spectra of intercalated FLG shows a change of the 2D-band from multi- to single-Lorentzian peak structure and this has been reported using several kinds of intercalants such as potassium [195], rubidium [195] and also FeCl$_3$ [197, 205]. At the same time, from the temperature dependence of magneto-electric measurements it has been clearly demonstrated that upon intercalation the charge carriers in each graphene layer are still Dirac fermions [197].

The optoelectronic properties of intercalated graphene compounds are also superior to the doped graphene. For example, doped graphene with AuCl$_3$ can result in a 77% decrease in the sheet resistance [206]. The high work function and low sheet resistance which characterizes AuCl$_3$ and FeCl$_3$ intercalated graphene are key requirements for improving significantly the luminous efficiency of organic light-emitting diodes. Air stability is another extremely important requirement for transparent electrodes and though AuCl$_3$-FLG has an attractive combination of high electrical conductivity and high optical transmittance in the visible wavelength range, a study of the stability of this functionalization to air as a function of time and/or humidity is still an open question. It is also known that many intercalated compounds of graphite are air-unstable materials [163]. In contrast, the intercalation with FeCl$_3$ is gives air stable compounds [197]. This was demonstrated experimentally by measuring an unchanged Raman spectra measured on 10 different locations in a 5L-intercalated device after keeping the samples for three months and one year in air, see figure 10.

6.2. Engineering the optoelectronic properties of graphene by functionalization with quantum dots

The gapless linear energy dispersion of graphene allows it to absorb $\sim$2.3% of the impinging light nearly independently of the wavelength from UV to THz [4–6], with a slight increase in UV absorption attributed to $\pi^*$ inter-band electronic transitions [207]. The unique absorption of far-infrared frequencies is at the core of the recently demonstrated room-temperature THz detectors [208] and this truly is another uncommon property in most semiconductor devices [209]. The low optical absorption makes graphene also an ideal material for use as flexible transparent electrode as demonstrated in photodetectors [210], solar cells [41], and LEDs [211]. Furthermore, high-speed phototransistors based on gated FLG with speeds up to 500-GHz have also been demonstrated [212] as a result of the high charge carrier mobilities [213] in FLGs. While in some cases advantageous, the lack of a well-defined bandgap in pristine graphene hampers its use in frequency-specific detection where a bandgap is required. At the same time, low light absorption can constitute a limit in applications where a high photo-gain is required. Functionalized graphene can offer unique solutions to the aforementioned limitations extending the domain of potential optoelectronic applications targeted by graphene.

The functionalization of graphene with colloidal quantum dots is a promising novel way to engineer its properties. For example, the deposition of colloidal quantum dots (QD) onto graphene has recently been shown to significantly increase the frequency-dependent absorption of graphene. Furthermore, thanks to recent advances in low-dimensional semiconductor technologies, colloidal solutions of quantum dots can be manufactured from a variety of semiconductors (e.g. PbS, ZnO, CdSe, PbSe) by chemical synthesis. In quantum dots an effective bandgap can also be tuned for specific applications simply by controlling the size of the dots [214], and their electrical transport properties can be further engineered by functionalizing the surface of the dots. Solution-processed
QDs have been used as the photoactive layers in non-graphene devices for light emission [215], photovoltaics [216] and photodetection [217–219], and have recently appeared in consumer products such as ultra-bright television screens.

The unique combination of the properties found in graphene and QDs has led to IR [220, 221] and UV graphene photodetectors [222] through functionalization with PbS and ZnO QDs respectively. These novel graphene-based photodetectors consist of a thin layer of colloidal QDs spin-coated onto a pristine graphene transistor. The photogenerated charges in the QDs are easily transferred to the graphene and extracted from the drain electrode. These QD/graphene photodetectors may also be tuned by field-effect leading to the multiple recirculation of charge carriers for a single absorbed photon and yielding frequency-dependent gains of up to $\sim 10^7$ A W$^{-1}$ for PbS QDs [221].

The application of a reverse bias back-gate pulse causes the charge carriers in the graphene to recombine as excitons in the QDs—effectively resetting the photodetector. To date most of these early examples of graphene–QD hybrid devices make use of QDs for detection of UV or IR–THz frequencies. Such devices show desirable effects such as charge carrier trapping in the QDs upon absorption of photons [223]—introducing an intrinsic gain mechanism which may be controlled by source–drain bias. A second intrinsic gain mechanism may be due to multiple exciton-generations in semiconductor QDs as reported by Sargent et al [224]. Graphene–QD hybrid structures have a great potential for future applications and their exploitation is still in its infancy. For example, heterostructures obtained by several alternating layers of graphene and CdS QDs have recently been used for photovoltaic applications with a record high incident photon-to-charge-carrier conversion efficiency (16%) as compared to previously reported carbon/QD solar cells [225].

Since the functionalization of graphene with QDs is easily scalable, fast and low-cost, it is a very promising method for device production on an industrial scale. The variety of possible applications is also helped by the stunning properties of both graphene and QDs. For example, solar powered flexible smart windows might be realized through graphene–QD heterostructures able to harvest electricity from the UV light while remaining perfectly transparent to the visible wavelength.

7. Future prospects

Intercalated FLG truly are two-dimensional systems just a few atoms thick, in which the physical properties can be engineered by chemical functionalization to fit a specific requirement for both fundamental science and future applications. For example, the superconducting state is the manifestation of the electron interactions in a material and it is expected to be suppressed in two-dimensional systems by quantum fluctuations at zero temperature. To date, experimental attempts to study the superconducting state in the extreme two-dimensional limit have been restricted to cases where the superconducting order parameter behaves as a 2D wavefunction, but the underlying electrons are still three-dimensional (such as the recently observed superconducting state at the interface between oxides [226]). This limitation was largely due to the inability to isolate stable two-dimensional atomic systems. FLG is probably the ideal material for investigating the superconducting electronic ordering in the two-dimensional limit. The superconducting state in graphene is expected to occur at high charge carrier concentrations ($>10^{13}$ electrons cm$^{-2}$ [227])—not achievable with ordinary oxide gate dielectrics. Ionic liquid gating would in principle offer the possibility to induce the required charge carrier concentration necessary for attaining intrinsic superconductivity [228], however these liquids freeze at cryogenic temperatures posing serious technical challenges. Chemical functionalization is a valid and yet largely unexplored way to explore the intrinsic superconducting state in graphene and study the evolution of this fundamental phase transition when changing the dimensionality of the system from 2D to 3D simply by changing the number of atomic layers composing the FLG. Adding superconductivity to the list of the unique properties of graphene material would stimulate the development of novel concepts in superconducting circuits where local electric fields can dynamically control the superconducting state and lead to unprecedented functionalities.

Similarly to the superconducting phase transition, magnetic ordering is a property characteristic of bulk materials which is expected to be suppressed by quantum fluctuations at zero temperature in systems with reduced dimensionality. Graphene would offer the unique opportunity to study the interplay between these collective quantum phases in the 2D limit. Magnetic ordering could be induced by chemical functionalizing of graphene with magnetic molecules such as FeCl$_3$ [197]. Making graphene magnetic would enable the development of novel flexible and transparent spintronic devices which cannot be fabricated using the conventional opaque and rigid magnetic materials.

The ability to dial up a specific physical property in graphene-based materials simply by selecting the intercalating molecule or chemical specie which functionalizes graphene extends dramatically the horizons of future electronic applications targeted by graphene. For example, the ability to engineer magnetic properties in intercalated FLG might enable a new class of graphene-based flexible and transparent memories. Intercalated compounds might also enable the development of graphene-based flexible and transparent batteries, as well as the development of all-graphene light-emitting devices.

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