Graphene–organic composites for electronics: optical and electronic interactions in vacuum, liquids and thin solid films

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Graphene exhibits exceptional mechanical, optical and electrical properties that are unfortunately accompanied by poor processability and tunability of its properties. The controlled interaction of graphene with tailor-made organic semiconductors (OSs) can offer a solution to solve these two problems simultaneously. The use of well-chosen organic semiconducting molecules interacting with graphene enables optimal control over the molecular self-assembly process forming low-dimensional graphene–organic architectures. Moreover, OSs allow modulation of numerous physical and chemical properties of graphene, including controlled electrical doping, ultimately making it possible to boost the performance of conventional organic electronic devices. Significantly, the interaction of organic molecules with graphene is strong not only at short distances but it is relevant also at longer distances, up to 30 nm. This feature article reviews some of the most enlightening results in the field, giving an overview of the interaction between graphene and organic molecules, starting from the simplest systems at the molecular scale, single molecules on single layer graphene in UHV, up to mesoscopic, more complex systems i.e., thick interpenetrated layers of graphene–organic composites embedded in working electronic or photovoltaic devices.

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1. Introduction

Carbon-based systems such as small molecules, polymers, nanotubes and graphene are active components for many materials for opto-electronics applications. Their physical and chemical properties are tunable and strictly depend on their precise chemical structure and size. All these carbon-based systems possess an extended $\pi$-conjugated scaffold that can be decorated with functional groups. Their functionalization can be optimized in order to programme their self-assembly into highly ordered supramolecular architectures, as driven by non-covalent interactions such as $\pi$-$\pi$ stacking, hydrogen-bonding, etc.

Small $\pi$-conjugated molecules (pyrenes, pentacenes, coronenes, polythiophenes, etc.) possess a well-defined electronic bandgap and a mono-dispersed nanometric size, the latter enabling molecular self-assembly into highly ordered low-dimensional architectures such as fibers, nano-crystals or uniform monolayers (Fig. 1a and b). Polymers, conversely, feature a larger linear backbone of $sp^2$ carbons, ranging between a few to hundreds of nm in length; unlike small aromatic molecules, they tend to form more disordered assemblies (Fig. 1c and d), but can have an elongated and highly flexible shape that allows high solubility and efficient transport of electric charge.

Carbon nanotubes (CNTs) and graphene are based on an aromatic honeycomb network reaching sizes up to a few tens of microns (Fig. 1e and f). This exceptional molecular structure leads to extraordinary optical, electronic and mechanical properties that have triggered research activities in various fields and resulted in the Nobel Prize in physics. However, two of the greatest challenges that remain to be addressed in the research of carbon nanotubes and graphene are: (1) process them using up-scalable approaches and (2) obtaining an ad-hoc chemical functionalization to control their physical and chemical properties. CNT samples are usually a mixture of semiconducting and metallic tubes; graphene, while having very high charge mobility, is a semi-metal, a zero-bandgap semiconductor, thus giving electrical devices with very poor $I_{on}/I_{off}$ ratio.

While many OSs, thanks to their small size and flexible side chains, are easily sublimed in vacuum or processed from solution, pristine graphene sheets have a strong tendency to undergo aggregation, in solvents or in polymer matrices, to give graphitic clusters. Composites merging together the excellent properties of graphene with the high tunability and processability of organic molecules are in great demand in different research fields. For example, graphene could improve the mechanical and electrical properties of commercial polymers, but the interaction between graphene and the polymer matrix is often poor, and the graphene sheets tend to aggregate when processed with polymers. Graphene is also an interesting substrate for biomedical applications, but its interaction with biomolecules, as well as its biological activity, is still controversial.1

In particular, many of the possible applications of graphene are in electronics, but its zero-bandgap and poor processability on insulating substrates are major issues hindering this potential technological development. Many groups are trying to open a bandgap in graphene, for example by using graphene nanoribbons3-5 or stacked bilayers,4 to combine high charge carrier mobility with high $I_{on}/I_{off}$ ratios in transistors. Organic semiconductors (OSs) already have a well-defined and tunable bandgap. By merging together their properties with those of graphene one may obtain a “dream material” for the semiconductor industry, optimal for flexible electronics applications. However, even if small polyaromatics, conjugated polymers and graphene or nanotubes exhibit an $sp^2$ carbon based backbone, these different classes of materials cannot
always be blended together effectively enough to yield beneficial effects on the materials’ properties.

The co-processing of graphene and organic semiconductor molecules remains a challenge and a very active field of research, with a particular aim to control and optimize the process of intermolecular charge transport, and exploit this to fabricate high-performance devices. This requires structural and energetic tuning of the interfaces between the two components to ensure efficient fundamental processes such as charge exchange or exciton splitting in the final material. A high number of published results are available, giving in some cases conflicting outcomes. In light of this, an overview of this field is timely and needed.

In the following sections, we will provide an extensive overview of possible ways that graphene and organic semiconductors can interact. To obtain a clear and useful picture of the state-of-the-art, we will use a “bottom up” approach describing the interaction of graphene with organic molecules starting from the simplest systems at the molecular scale, i.e. single molecules on single layer graphene in UHV, to the mesoscopic, most complex materials, i.e. thick layers of graphene–organic composites embedded in working electronic devices.

For each section, we will first briefly describe the structure and the production techniques of the graphene–organic system, and then provide details on how the interaction changes the properties of graphene and/or of the interacting organic molecules. Given the wide extent of the field considered and the high number of papers published on graphene every single week, this feature article is not intended to be exhaustive; we thus apologize to the authors whose work is not cited herein.

2. Graphene–organic interactions in vacuum: single molecules on single sheets

The simplest graphene–organic interaction one can imagine is that of a single molecule adsorbed on a graphene sheet, in vacuum, i.e. not surrounded by neither gas nor solvent molecules. Such systems can be routinely obtained in ultra-high-vacuum (UHV) chambers, by thermal evaporation of different small molecules on graphene produced by chemical vapour deposition (CVD) or by epitaxial growth on silicon carbide. A main advantage of molecules deposited on graphene is that the spatial arrangement and electronic properties of the molecule–graphene interaction can be studied simultaneously with high resolution by means of Scanning Tunneling Microscopy (STM, Fig. 2a).

It is well known that small conjugated molecules can adsorb on solid and flat sp²-carbon surfaces forming highly ordered nanostructures, similar to 2-dimensional crystals. This approach is thus very useful to create a periodic electronic modulation of the graphene surface through self-assembly of aromatic molecules. Many different classes of molecules can form robust, stable physisorbed self-assembled monolayers on graphite or graphene, from simple alkanes to phthalocyanine, benzenes, anthracene, pyrenes and perylenes, to larger polycyclic aromatic hydrocarbons such as coronene derivatives.

Generally, the morphology of the self-assembled architecture is driven by a complex interplay between non-covalent intermolecular and molecule–substrate interactions. In the case of polyaromatic molecules such as most organic semiconductors, π–π interactions play of course a significant role in governing the molecular orientation and packing. Polyaromatic molecules can be also considered as “nanographenes”, given that their aromatic core is like a small 2D fragment of graphene, and thus have a strong tendency to stack over each other and over graphene with a stacking distance of ca. 3.3 Å, i.e. similar to the interlayer distance in graphite.

Overall, several results indicate that nucleation, orientation, and packing of OSs on graphene are different compared to those grown on conventional substrates such as silicon or even graphite. A detailed theoretical analysis of the adsorption of neutral molecules on graphene was performed by Mat Persson’s group applying density functional theory. It revealed that for neutral (poly)-aromatic, antiaromatic, and more generally for π-conjugated systems, purely dispersive forces drive the docking of adsorbates on graphene, whereas short-range electrostatic interactions ultimately stabilize the complex.

However, if the aromatic backbone of a molecule is decorated by side groups exposing well defined functionalities, the latter can work in synergy or in opposition to the π–π interactions between the adsorbed molecules and graphene, leading to more complex self-assembly pathways. Functionalization of the
aromatic core gives rise to strong medium-range interactions involving the substituents: e.g., ab initio simulations revealed that derivatives of benzoic acids serve as sub-units for the controlled formation of ordered nanopatterns on graphitic surfaces. Three types of molecule–molecule or molecule–substrate interactions control the nature of the ultimate assembly: (1) long-range repulsive π–π interactions (0.10–0.30 eV), (2) medium-range attractive π–π* interactions (0.30–0.60 eV), and (3) short-range hydrogen bonding (0.60–0.80 eV), the latter giving strong directional intermolecular interactions that position adjacent molecules in predictable ways.\(^{16}\)

These strong intermolecular interactions on graphene have been observed experimentally in continuous uniform layers of perylenes bearing carboxyl groups (perylene-3,4,9,10-tetra-carboxylic dianhydride).\(^{14,17,18}\) An extensive study by STM, X-ray reflectivity and modelling indicates that such molecules form a highly uniform and coherently layered structure, parallel to the graphene surface but weakly interacting with it, held together by hydrogen bonds. Perylene layers adsorb on the graphene surface with characteristic π–π stacking bond lengths, thus indicating weak interaction with the graphene surface.

One can expect molecules with a greater electron acceptor or donor character to interact more effectively with graphene; in fact, another example of directed, self-assembled layers on graphene describes the epitaxial growth of perfluoropentacene yielding a π-stacked arrangement of coplanar molecules with an exceedingly low π-stacking distance of 3.07 Å, among the lowest π-stacking distance ever reported for organic semiconductor crystal lattices, likely due to the effect of fluorine side-groups. This low stacking distance gives rise to significant electronic band dispersion along the π-stacking direction.\(^{19}\)

Interfacial dipole interactions induced by charge transfer between copper phthalocyanine (CuPc) molecules and graphene are shown to epitaxially align the CuPc molecules in a face-on orientation in a series of ordered superstructures on CVD graphene.\(^{20}\) Furthermore, the assembled structure can be used as a molecular probe to visualize graphene’s domain boundaries as Ogawa et al. demonstrated for chloro-aluminum phthalocyanine on CVD graphene.\(^{21}\) In another example, Gao’s group demonstrated that monolayer graphene can act as a template for fabrication of unique nanoarchitectures. A molecular layer of magnetic iron(II)phthalocyanine was deposited on a single crystal, monolayer graphene grown via chemical vapour deposition. The iron(II)phthalocyanine arranged in regular Kagome lattices on the surface, following the lattice of the graphene moiré pattern. A monolayer of graphene is thus sufficient to direct the self-assembly of molecules and to decouple the adsorption process of the phthalocyanine derivative from the underlying metal surface.\(^{22}\)

Slightly different results have been obtained on graphene and graphite\(^{23}\) indicating that, while graphene can template effectively molecule adsorption, it does not shield completely the molecules from the underlying substrate, which shall anyhow influence the final structure.

The influence of the substrate underlying graphene was in fact demonstrated for cobalt phthalocyanine (CoPc) on graphene\(^{24}\) (Fig. 2b and c) transferred onto silicon dioxide (SiO\(_2\)) or hexagonal boron nitride (BN). With both underlying substrates, CoPc molecules formed a square lattice on the graphene layer. However, with graphene on SiO\(_2\), the domain size was limited by the surface corrugation due to SiO\(_2\) atomic roughness and chemical inhomogeneity, and there was a degree of disorder in the molecular ordering within the domains which was not observed for graphene on BN. Additionally, Scanning Tunneling Spectroscopy (STS) measurements revealed that the energy of the orbitals shifted from one molecule to another, and that this effect was stronger on graphene/SiO\(_2\) than on graphene/BN hybrids.

In graphene/SiO\(_2\) the substrate underlying the graphene layer does not only govern disorder in the self-assembled cobalt centred phthalocyanine layer, but also influences the system’s electronic properties.

Interestingly, the molecule–graphene interaction could be dramatically enhanced by introducing metal atoms obtaining molecule/metal/graphene sandwich structures.\(^{25}\)

3. Graphene–organic interactions in liquids: supramolecular self-assembly, stabilization and processing

Graphene processability is key for large-scale exploitation of graphene’s unique properties. To this end, soluble graphene–organic hybrid systems have a clear advantage over CVD or epitaxial graphene because of the tunability of their properties and low cost.\(^{26}\)

Graphene–organic suspensions can be processed with large area deposition techniques in coatings, screen or ink-jet printed electronic devices\(^{22,23}\) allowing embedment of graphene into functional composite materials.\(^{24}\)

Graphene suspensions are typically obtained by liquid-phase exfoliation (LPE) in a suitable organic solvent, frequently assisted by ultrasonication treatment.\(^{25–27}\) Aromatic cores based on anthracene,\(^{28}\) pyrene,\(^{29–31}\) perylene\(^{32,33}\) and coronene\(^{44}\) have side functionalization to tailor solubility and electronic properties have also been employed as agents to promote graphene liquid phase exfoliation and stabilize the exfoliated sheets. Table 1 shows some examples of how the strong interaction of graphene with organic molecules has been used to exfoliate and stabilize graphene in solution. The surfactant effect of aromatics was first demonstrated for aqueous dispersions of reduced graphene oxide (RGO); by means of non-covalent interactions water soluble, sulphonated derivatives of pyrene and perylenedimide can efficiently stabilize the RGO sheets in aqueous suspension, while aqueous suspensions of RGO undergo heavy agglomeration and precipitation.\(^{32,33}\)

More interestingly, the approach of non-covalent functionalization works also for pristine, non-oxidized graphene; graphite is directly transferred into a solution of a small aromatic exfoliant agent in a process assisted by ultra-sonication (Fig. 3). Dong et al. showed that the aromatic molecule tetrasodium 1,3,6,8-pyrenetetrasulfonic acid (TPA) can effectively exfoliate graphite into graphene monolayers by sonication in aqueous solutions, yielding up to 90% of graphene single
layers.\textsuperscript{35} Besides sulphonated pyrene and perylene diimide derivatives, stabilization of graphene in aqueous suspension was successfully demonstrated with carboxyl functionalized coronene\textsuperscript{34} and a cationic aza-pyrene and aza-perylene derivative.\textsuperscript{36}

Direct exfoliation of graphite to graphene in aqueous media with organic dyes involves a complex process that requires not only a strong graphene–molecule interaction, but also well-defined kinetics of the adsorption process and solvent choice. In particular, the adsorption of molecules on graphene proceeds by a "sliding" mechanism through the solvent media (Fig. 3c); a key step to increase interaction is to displace the last layer of solvent molecules from the graphene surface, as we demonstrated combining experimental exfoliation data with modelling (see our studies\textsuperscript{31,37} and references therein).

The choice of suitable aromatic systems that non-covalently interact with graphene has a triple bonus: (i) improves the yield of exfoliation in liquid-phase exfoliated graphene, (ii) stabilizes the graphene suspension, and (iii) confers new physical and chemical properties to graphene.

### Table 1 Examples of published studies reporting graphene–organic interactions to exfoliate or stabilize graphene in solution

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Molecule</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>Sulphonated and hydroxylated pyrene</td>
<td>Water</td>
<td>30,31,37 and 55</td>
</tr>
<tr>
<td></td>
<td>1,3,6,8-Pyrene-tetrasulfonic acid tetrasodium salt [Py(SO$_3$)$_4$]</td>
<td>Water</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>1-Pyrene carboxylic acid</td>
<td>MeOH/water</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Perylene-based bolaamphiphiles</td>
<td>Water</td>
<td>86 and 87</td>
</tr>
<tr>
<td></td>
<td>7,7,8,8-Tetracyanoquinodimethane (TCNQ)</td>
<td>Water</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>9-Anthracene carboxylic acid (ACA)</td>
<td>Water</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Sodium cholate (SC)</td>
<td>Water</td>
<td>89 and 90</td>
</tr>
<tr>
<td></td>
<td>Sodium dodecylbenzene sulfonate (SDBS)</td>
<td>Water</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>Ethyl cellulose</td>
<td>ETOH</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Ionic and non-ionic surfactants</td>
<td>Water</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>N,N-Dimethyl-2,9-diazaperopyrenium dication (MP$^2^+$)</td>
<td>Water</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>N,N-Dimethyl-2,7-diazapyrene (DAP-2Cl)</td>
<td>Water</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Hexadecyltrimethylammonium bromide (CTAB)</td>
<td>DMF</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>5,10,15,20-Tetraphenyl-(4,11-acetylthiounde-cyl-oxyphenyl)-21H,23H-porphine (TATPP)</td>
<td>NMP (with org. Ammonium ions)</td>
<td>93</td>
</tr>
<tr>
<td>Expandable graphite</td>
<td>Tetrabutylammonium hydroxide + oleum + 1,2-distearyl-sn-glycero-3-phosphoethanolamine-N-(methoxy(poly-ethyleneglycol)-5000) (DSPE-mPEG)</td>
<td>DMF</td>
<td>94</td>
</tr>
<tr>
<td>Thermally exfoliated graphite oxide</td>
<td>Coronene tetracarboxylic acid tetrapotassium salt</td>
<td>Water</td>
<td>34</td>
</tr>
<tr>
<td>Arc evaporation of graphite</td>
<td>Coronene tetracarboxylic acid tetrapotassium salt</td>
<td>Water</td>
<td>34</td>
</tr>
<tr>
<td>Reduced graphene oxide</td>
<td>3,4,9,10-Perylenetetra-carboxylic diimide-bis-benzesulfonic acid (PDI)</td>
<td>Water</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Pyrene-1-sulfonic acid sodium salt (PyS)</td>
<td>Water</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Pyrene-block copolymer polyPA-b-polyPEG-A</td>
<td>Water or DMF</td>
<td>38</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>Bolaamphiphilic or amphiphilic perylene bisimides</td>
<td>Water</td>
<td>33</td>
</tr>
</tbody>
</table>
systematic fine-tuning of the electronic properties of graphene. As an additional advantage, the exceptional optical properties of these organic molecules (strong and well-defined absorption spectra in the visible spectrum, efficient light-emission, etc.) make it possible to use optical spectroscopy as an easy method to investigate the interactions between aromatic molecules and graphene (Fig. 3b).

4. Effect of graphene–organic interactions on electronic, optical and magnetic properties

Before describing the most complex systems used in devices, we detail a bit more the different possible effects of OSs on graphene. As mentioned in the introduction, organic molecules can be used to modify, in certain cases significantly, the properties of graphene, and vice versa. Table 2 reports a list of different molecules that have been employed to interact with/modify graphene along with the underlying mechanism and the effects obtained.

Doping

The adsorption of molecules such as anthracene, naphthalene and pyrene on graphene has a noteworthy effect on graphene electronic properties, inducing p- or n-type doping as demonstrated indirectly by Raman spectroscopy.\(^ {39}\) G-band splitting was observed in these systems, and explained by lifting of the two-fold degeneracy of the optical phonons at the \( \Gamma \) point.\(^ {15}\)

Larger aromatic rings such as anthracene and pyrene produce wider G-band splitting (\( \approx 23 \) cm\(^{-1}\)) than smaller rings such as naphthalene (\( \approx 20 \) cm\(^{-1}\)). This kind of doping was observed also monitoring charge transport in transistors,\(^ {7,39}\) as will be described in the following section.

From a theoretical point of view, Yong Peng’s group addressed the binding of organic donor, acceptor and metal atoms on graphene sheets, and revealed the effects of different non-covalent functionalizations on the electronic structure and transport properties of graphene.\(^ {28}\) Their simulations suggest that strong hybridization between the molecular levels and the graphene valence bands can be achieved through adsorption of particular OSs such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetrathiafulvalene (TTF).

p-Doping and n-doping were monitored by combined Raman and X-ray photoelectron spectroscopy (XPS) on an oxidized few layer thick graphene combined with tetracyanoethylene (TCNE) and tetrathiafulvalene (TTF) molecules, observing shifts in S 2p and N 1s XPS peaks for the two molecules.\(^ {40}\) This kind of dopant layer can be very stable, and be preserved in air up to 200°C.\(^ {41}\)

Fluorescence quenching by charge or energy transfer

The interaction between a light-emitting dye and graphene is interesting from a fundamental point of view (because it can be considered as the interaction between a 0D small emitter and a 2D semi-infinite quencher), and from a technological point of view (for applications in LEDs, photovoltaics, sensors, etc.).

Fluorescence quenching and excited energy transfer from dyes to graphene have been demonstrated with reduced graphene oxide, carbon nanotubes, and pristine graphene\(^ {33,42-44}\) (Fig. 4).

The interaction between fluorescent emitters and graphene is associated with local dipole-induced electromagnetic fields that are strongly enhanced due to the unique properties of graphene: graphene is an extraordinary energy sink with great potential for prospective application in photo-detection, nanophotonic and photovoltaic devices.
Quenching of pyrene emission through energy transfer to graphene is proportional to graphene–pyrene distance $d$. The rate of energy transfer proportional to $d^{-4}$ has been calculated, suggesting that quenching should be observable for distances up to 30 nm, much larger than what observed for any other surface.\textsuperscript{45,46} The $d^{-4}$ distance dependence on the quenching of emitters with monolayer graphene was confirmed experimentally with rhodamine molecules by Koppens et al.\textsuperscript{47} (Fig. 4d). In this work the emitter lifetimes were also measured as a function of emitter–graphene distance $d$, revealing agreement with a universal scaling law governed by the fine-structure constant. On graphene, the emitter decay rate exhibited a 90-fold enhancement (corresponding to an energy transfer efficiency of 99%) with respect to the decay in vacuum at distance $d = 5$ nm. The high energy transfer rate was associated mainly with the two-dimensionality and gapless character of monolayer graphene, with the control sample.

Hirsch and co-workers demonstrated the binding and electronic interactions of pristine single- and few-layer thick graphene with an organic dye molecule in homogeneous solutions.\textsuperscript{48} Electronic cross-talk with dendronized perylenebisimides and graphene suspended in NMP was confirmed spectroscopically by photoluminescence and Raman measurements, confirming experimentally an efficient fluorescence quenching with graphene. The emission quenching by energy or electron-transfer mechanisms provides clear evidence for the non-covalent binding of the two π-systems.
Quenching with graphene in liquid phase has been explained with the occurrence of both energy and electron transfer, according to the system under study. Investigations on the fluorescence quenching of graphene with two organic donor molecules, pyrene butanoic acid succinimidyl ester (PyBS) and oligo(2-phenylenevinylene)methylester (OPV-ester) have been carried out by Matte and co-workers. They did not use pristine graphene, but amide-functionalized graphene soluble in chloroform (CHCl₃) and dimethylformamide (DMF). For the two molecules selected, the absorption and photoluminescence spectra were recorded in mixtures with graphene at increasing concentration of the latter component. The emission spectra of the molecules in a solution with graphene did not show any additional bands that could be ascribed to a charge-transfer complex. Unlike the absorption spectra, the emission markedly changes with the increasing graphene concentration, resulting in a dramatic loss in emission intensity. Given that no change was observed in absorption, Matte et al. attributed the strong emission quenching to photo-induced electron transfer, an excited state phenomenon. The ability of graphene to quench the fluorescence of these aromatic molecules was attributed to photo-induced electron transfer on the basis of fluorescence decay and time-resolved transient absorption spectroscopic measurements. The occurrence of energy transfer could not be entirely excluded, but the main effect is attributed to photo-generated, charge-separated species in which graphene acts as an acceptor. These charge-separated species are long-lived and thus interesting for the design of photovoltaics.

A more stable, irreversible graphene–molecule interaction is obtained by direct covalent grafting of organic semiconductors such as porphyrins, fullerenes or oligothiophenes to graphene. In this case, however, the quality of the resulting material is lower, because the grafting creates a defect on the graphene sheet, or because the grafting is directly performed on already defective graphene oxide. The covalent “tethering” of a molecule to graphene anyhow gives interesting systems, because the optoelectronic properties are controlled not only by π–π or electrostatic interactions, but also by the length and flexibility of the covalent linker. For example, significant fluorescence quenching (>60%) can be observed when oligothiophene dyes are tethered to GO using short linkers (ca. 0.7 nm). Conversely, by using a long and more flexible linker, smaller quenching (<16%) is monitored, along with an absence of the perturbation of the most delicate optical properties of the dye, like pH-dependent light-emission.

Photo-induced interactions of graphene–organic hybrids can proceed as well through the transfer of phonon energy: since a phonon is a quantum mechanical description of a specific type of vibrational motion, the enhancement of the phonon energy transfer will increase the vibrational energy of a phonon acceptor. Pan and co-workers demonstrated phonon energy transfer to reduced graphene oxide with water-soluble, sulphonated pyrene derivatives in solution. Phonon transfer with water soluble systems is of particular interest as it allows for prospective medical application in photo-thermal therapy.

Magnetization

The adsorption of the OS can also confer a magnetic function to graphene, complementing its outstanding electronic, mechanical and optical properties. A charge-transfer complex character has been observed with graphene–organic structures based on magnetic functional layers adsorbed on graphene. With adsorption of TCNQ on rippled graphene/Ru(0001), each isolated molecule acquires charge from graphene, developing a localized magnetic moment and showing a prominent Kondo resonance. On completion of the TCNQ monolayer, the delocalization on a spatially extended band preserves a common orientation of the electron spins, as revealed by spin-polarized scanning tunneling microscopy. Thus, a magnetically ordered, 2D organic layer can be created by electron transfer from graphene/Ru(0001) to the strong acceptor TCNQ, similar to what is observed in intermolecular charge-transfer complexes. As organic metals and magnets rely on charge-transfer processes to create either the metallic character or the magnetic properties, these findings open a pathway towards applications of graphene–organic hybrid materials in spintronics: the TCNQ monolayer could act as a spin filter or 2D spin polarizer, adding magnetic functionalities to graphene by altering the spin polarization of a current flowing in graphene.

In another nice study, a magnetococonductivity signal as high as 20% was obtained in graphene nano-constrictions decorated with pyrene-substituted terbium(III)bis(phthalocyanine) quantum magnets (TbPc, Fig. 2d). In this approach, pyrene moieties are used to control the adsorption of the TbPc on graphene that becomes sensitive to the magnetization of the terbium-phthalocyanine molecules.

In addition, the finding that the adsorption of benzene turns the magnetic Fe/graphene into nonmagnetic Fe/graphene may help to design novel magnetic sensing or switching devices.

5. Graphene–organic interactions in solid: thin films and electronic devices

Besides fundamental studies in vacuum or solutions, graphene interaction with organic semiconductors can be exploited in bulk systems consisting of OS/graphene blends. These bulk composite systems are particularly relevant for applications in organic field-effect transistors (FETs), photovoltaics and sensing devices (Fig. 5). Table 3 shows some examples of how graphene–OS interactions have been used to produce working electronic devices.

To better evaluate the possibilities offered by graphene–organic FETs, we should also mention briefly the numerous interesting results obtained with carbon nanotubes.

Nanotube bundles can be effectively employed to template the growth of organic crystals under certain experimental conditions, resulting in the formation of organic nucleates with preferred orientations. Incorporation of an appropriate amount of random bundles of single-walled nanotubes in pentacene or sexithiophene films was observed to give 20-fold enhancement in field-effect mobility without reduction of the $I_{on}/I_{off}$ ratio.
High mobility, air-stable organic transistors have been realized from sequential deposition of high conductivity carbon nanotubes beneath an organic semiconductor (HBC); in this way the transconductance and charge carrier mobility of the semiconductor have been significantly improved. The effective mobility was increased by a factor of 6 while preserving the $I_{on}/I_{off}$ ratio above $10^4$.\(^\text{59}\)

The use of carbon nanotubes as all-carbon electrodes integrated in both nanoscale and thin-film pentacene transistors made it possible to improve the charge injection at the electrode–semiconductor interfaces, leading to increased device performances when compared to devices based on traditional noble metals as electrodes.\(^\text{60}\)

However, studies on CNTs showed that they do not act just as preferential, highly conductive additives to enhance the mobility of OSs; the electronic processes within such devices are more complex, with a key effect on charge transport characteristics of the interfaces present in the devices. Charge trapping at the dielectric/polymer (e.g. polythiophene) interfaces has been used in transistors based on carbon nanotubes for sensing applications.\(^\text{61}\) In a different study, optically gated FETs based on CNTs coated with poly(3-octylthiophene-2,5-diyl) (P3OT) have been realized in which the switching mechanism is due to trapping of photo-excited electrons at the polymer/dielectric interface. Sufficient power and selection of an eligible wavelength induces a change in conductance upon illumination, up to four orders of magnitude.\(^\text{62}\) All these approaches anyhow have to deal with the well-known negative aspects of CNTs such as the mixture of properties (semiconducting & metallic) typical in CNT batches. The same approaches can be exploited using graphene, having better processability and different dimensionality as compared to 1D nanotubes.

FETs based on pristine graphene typically show very high charge mobility ($>10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), but a very poor $I_{on}/I_{off}$ ratio.\(^\text{63}\) Achieving high mobility while maintaining a high $I_{on}/I_{off}$ ratio is the greatest challenge to allow development of graphene-based (flexible) electronics; a viable approach intensively explored relies on the incorporation of graphene into solution processed organic field-effect transistors (OFET). The addition of an organic semiconductor can bring into play new physical processes like the controlled doping of graphene.

The effect of adsorbed molecules on graphene doping and related charge transport was explored by drop casting a solution of either pyrene, naphthalene or anthracene derivatives on a “scotch tape” graphene layer (as mentioned above). Shifts in threshold voltage from $-108 \text{ V}$ to $+62 \text{ V}$ could be observed in this way, together with significant changes in Raman spectra indicating significant doping.\(^\text{64}\)

Transistors based on CVD graphene were realized in a recent study with self-assembly of solution processed triethylsilylethynyl-anthrathithiophene (TES-ADT). TES-ADT displayed a standing-up molecular assembly, which facilitates lateral charge transport on graphene.\(^\text{65}\)

Blends of reduced graphene oxide microsheets and OS polymers such as poly-3-hexyl thiophene (P3HT) and poly-(p-phenylene vinylene) (PPV) have shown significant fluorescence quenching as compared to the pure OS, providing evidence for a good interaction between the two materials in the solid state.\(^\text{15,64}\) In particular, efficient charge transport across graphene and polymers has been demonstrated for simple bilayer systems composed of reduced graphene oxide (RGO) and P3HT, with a 20-fold increase of the effective mobility and $I_{on}/I_{off}$ ratios $>10^3$.\(^\text{64}\) The use of bi-component systems as active...
Table 3  Examples of published studies reporting different mechanisms of graphene–organic interactions in working devices

Graphene–organic semiconductors – applications in electronic devices

<table>
<thead>
<tr>
<th>Device</th>
<th>Effect</th>
<th>Mechanism</th>
<th>Carbon allotrope</th>
<th>Component containing G or CNTs</th>
<th>Molecule</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field effect transistor</td>
<td>Increase in conductance</td>
<td>Photoexcitation</td>
<td>Carbon nanotube</td>
<td>Bulk composite</td>
<td>P3OT (polythiophene)</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Hole injection</td>
<td>Better injection barrier</td>
<td>Carbon nanotubes</td>
<td>Electrode</td>
<td>Pentacene</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Increase in mobility, high on/off ratio</td>
<td>Electric field enhancement at CNT tips</td>
<td>“Fast lanes” for charge carriers in conduction channels</td>
<td>Bulk composite</td>
<td>Pentacene, sexithiophene</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>Increase in mobility, stable on/off ratio</td>
<td>Graphene (LPE)</td>
<td></td>
<td></td>
<td>P3HT or PQT-12 poly(3,3-didodecyl-2,2'-bipyridine-5,5'-dicarboxylic acid)</td>
<td>67</td>
</tr>
<tr>
<td>Work function tuning</td>
<td>Increase in conductivity and ambipolar mobility</td>
<td>Charge percolation</td>
<td>GO-isocyanate functionalized</td>
<td>Bulk composite</td>
<td>2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Increase in conductivity</td>
<td>Doping</td>
<td>Graphene</td>
<td>Electrode</td>
<td>Tetrathiafulvalene (TF)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Increase in conductivity n- or p-doping of graphene</td>
<td>Doping</td>
<td>Mechanically cleaved graphene</td>
<td>Electrode</td>
<td>1,5-Naphthalenediamine, dimethylanthracene, pyrene-tetrasulfonic acid</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Increase in mobility</td>
<td>“Fast lanes” for charge carriers in conduction channels</td>
<td>RGO</td>
<td>Active layer</td>
<td>P3HT</td>
<td>66</td>
</tr>
<tr>
<td>Tunable memory effect transistor</td>
<td>Increase in conductance</td>
<td>Photoexcitation</td>
<td>CNTs</td>
<td>Bulk composite</td>
<td>Polythiophene, MoS2/BN heterostructures</td>
<td>61</td>
</tr>
<tr>
<td>Tunable tunnel barrier</td>
<td>Increase in mobility and ambipolar mobility</td>
<td>Electric field enhancement at CNT tips</td>
<td>Mechanically cleaved graphene</td>
<td>Tunneling electrode</td>
<td>1-Pyrene butyric acid</td>
<td>79</td>
</tr>
<tr>
<td>Charge transport modulation</td>
<td>Increase in conductivity</td>
<td>Photoexcitation</td>
<td>Carbon nanotubes</td>
<td>Bulk composite</td>
<td>Allyl-substituted hexabenzocoronene</td>
<td>7</td>
</tr>
<tr>
<td>Enhancement in performance</td>
<td>Increase in conductivity and mobility</td>
<td>“Fast lanes” for charge carriers in conduction channels</td>
<td>Functionalized CVD graphene</td>
<td>Electrode</td>
<td>SAM of pyrene butanoic acid succidymidyl ester (PBASE)</td>
<td>73</td>
</tr>
<tr>
<td>Photovoltaic cells</td>
<td>Increase in quantum efficiency</td>
<td>Photoexcitation</td>
<td>Carbon nanotubes</td>
<td>Hole-collecting electrode</td>
<td>Poly(4-phenylphenylene vinylene) (PPV)</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>Increase in photoconversion efficiencies</td>
<td>Photoexcitation</td>
<td>MWNT</td>
<td>Single and sandwiched layers</td>
<td>Polythiophene</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>Increased short-circuit photocurrent densities and fill factors</td>
<td>High specific surface area</td>
<td>Graphene</td>
<td>Electrode</td>
<td>PEDOT–PSS</td>
<td>100</td>
</tr>
<tr>
<td>Nonvolatile electronic memory cell</td>
<td>Bistable switching, charge transfer</td>
<td>Electric field</td>
<td>GO-g-PBA polymer grafted GO</td>
<td>Sandwiched</td>
<td>P3HT</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>Bistable switching, charge transfer</td>
<td>Electric field</td>
<td>Hexadecylamine-graphene oxide (HDAGO)</td>
<td>Bulk composite</td>
<td>P3HT</td>
<td>70</td>
</tr>
<tr>
<td>Sensors</td>
<td>Non-covalent functionalization</td>
<td>n/a</td>
<td>Exfoliated graphene</td>
<td>Electrode</td>
<td>1-Pyrenecarboxylic acid</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Increase in conductivity</td>
<td>Interaction of the OS with gas</td>
<td>Exfoliated graphene</td>
<td>Electrode</td>
<td>1-Pyrenecarboxylic acid</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Molecular magnetic gate</td>
<td>Magnetic coupling</td>
<td>Mechanically cleaved graphene, patterned</td>
<td>Electrode</td>
<td>Pyrene-substituted terbium-bis(phthalocyanine) TbPc2</td>
<td>57</td>
</tr>
<tr>
<td>Super-capacitors</td>
<td>Non-covalent functionalization</td>
<td>n/a</td>
<td>Exfoliated graphene</td>
<td>Electrode</td>
<td>1-Pyrenecarboxylic acid</td>
<td>29,101</td>
</tr>
</tbody>
</table>
layers of FET has a major disadvantage: charges will have to face several injection barriers, hopping continuously from P3HT to RGO and vice versa. However, the WF values measured by Kelvin Probe Force Microscopy (KPFM) on RGO monolayers and P3HT amounted to 4.75 ± 0.02 and 4.80 ± 0.03 eV, respectively. The low WF difference favors charge transport from one material to the other.

It should be noted that the WF of organic semiconductors like P3HT depends significantly on molecular packing, which in turn depends on other parameters such as deposition conditions and molecular weight. The value obtained by KPFM measurements for the P3HT is in fairly good agreement with the HOMO of P3HT estimated by cyclic voltammetry measurements, i.e. 4.9 eV. The WF of P3HT is close to the RGO value thus allowing efficient charge transport across the two materials as shown in Fig. 5a, which is a schematic representation of charge transport across the RGO-P3HT blend reporting the experimental WF values as measured by KPFM.

Huang et al. showed that, when compared to pure organic semiconductor layers, graphene–organic hybrid FETs exhibit up to 20-fold increase in effective field-effect mobilities maintaining an $I_{on}/I_{off}$ ratio comparable to or better than what observed without graphene. The mobilities determined in P3HT/graphene PQT-12/graphene hybrid FETs resulted in values as high as 0.17 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.6 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. In addition, non-covalent interactions in bulk GO-P3HT hybrid assemblies were found to enhance optical absorption, charge transfer, and photocatalytic properties. With their broad absorption, excited states can be generated with sunlight, rendering GO-P3HT hybrids highly promising for potential application as efficient green photocatalysts in organic synthesis.48

Organo- and water-dispersible GO-polymer nanosheets were used also for organic electronic memory devices. Thin films of poly(ert-butyl acrylate), covalently bound to GO sheets, showed bistable electrical conductivity switching behavior and a non-volatile, rewritable memory effect in an Al/GO-g-PtBA + P3HT/ITO sandwich device.49 The non-volatile rewritable memory effect has also been demonstrated with a nanocomposite of hexadecylamine-functionalized graphene oxide (HDAGO) and poly(3-hexylthiophene) (P3HT). The device had an ITO/P3HT-HDAGO/Al sandwich structure, in which the composite film of P3HT-HDAGO was prepared by simple solution phase mixing and spin-coating. This memory device exhibited typical bistable electrical switching behavior and a non-volatile rewritable memory effect, with a turn-on voltage of about 1.5 V and an $I_{on}/I_{off}$ ratio of $10^5$. The electrical switching behavior was attributed to the electric-field-induced charge transfer between P3HT and HDAGO nanosheets.50

The full potential of graphene in integrated circuits can be accessed only with a reliable ultrathin high-k top-gate dielectric. In top-gated graphene devices an oxide layer, typically Al$_2$O$_3$ and HfO$_2$, is grown on graphene by atomic layer deposition. Even in this case, OSs can have a beneficial effect; a molecularly thin organic seeding layer of perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) has been found to beneficially direct oxide deposition, with significant improvements in dielectric performance limits for ALD-grown oxides on graphene.71

A main potential application of graphene, intensively studied worldwide, is to use it as a transparent conductor, and this application has been studied also for organic electronic devices.

Although GO is known to be insulating, when deposited as a thin coating layer it can have a beneficial effect on charge transport in organic photovoltaic devices. The incorporation of GO deposited from neutral solutions between the photovoltaic poly(3-hexylthiophene) (P3HT):phenyl-C$_6$1-butyc acid methyl ester (PCBM) layer and the transparent and conducting indium tin oxide (ITO) results in a decrease in recombination of electrons and holes and leakage currents, and a dramatic increase in the photovoltaic efficiencies to values that are comparable to those of devices fabricated with PEDOT:PSS as the hole transport layer (Fig. 5d).72 Large-area, continuous anodes composed of pristine few-layered graphene were also realized by CVD and tested in organic photovoltaic devices: non-covalent functionalization of graphene with pyrene butanoic acid succidymidyl ester (PBASE) allows for alignment of the Fermi level of graphene very close to the highest occupied molecular orbital of PEDOT:PSS for efficient hole collection. Graphene anodes modified by self-assembled PBASE exhibit excellent performance characteristics73 (Fig. 5e).

Also the work function of graphene electrodes in OFETs can be engineered by functionalizing the surface of SiO$_2$ substrates with self-assembled monolayers (SAMs). In general, the measured WF of graphene can vary significantly, as shown well in the band diagrams of Fig. 5; graphene WF depends on the production method and on the underlying substrate that can induce relevant doping. The electron-donating NH$_2$-terminated SAMs with aminotriethoxy-silane induce strong n-doping in graphene, whereas the CH$_3$-terminated SAMs neutralize the p-doping induced by SiO$_2$ substrates. Graphene doped by SAMs displays a Dirac voltage shift over 150 V in transistor application and enables graphene to have a tunable work function. The work function of graphene shifts down to 3.9 eV for NH$_2$-SAM-modified SiO$_2$, facilitating electron injection at this low work function graphene electrode74 (Fig. 5b and c).

It should be noted that the quality of the underlying CVD graphene is critical for interaction with OSs in devices; Sun et al. studied the assembly of oligothiophene derivatives on graphene and found that defect-like ripples and wrinkles significantly weaken the molecule–graphene interaction. By using two different quaterthiophene derivatives they showed that such structural irregularities in graphene hinder stable molecular adsorption.75

An original approach was also reported by Eda and Chhowalla, who managed to obtain working transistors even via blending RGO with an insulating polymer. By preparing a well dispersed mixture of RGO with polystyrene (PS), they obtained working ambipolar transistors with electron and hole mobilities of 0.2 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.7 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, although accompanied with very low $I_{on}/I_{off}$ ratios ranging between 3 and 6. In the latter case, of course, the polymer was not actively contributing to the charge transport process, the latter taking

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Feature Article  
Journal of Materials Chemistry C
place via percolation among RGO sheets dispersed in the insulating PS matrix.76 Blending an insulating polymer in the active layer of microelectronic devices is not meant to have high performance, but this result is interesting as it lies at the edge between organic electronics and research on bulk composites: nowadays, many groups are trying to use graphene in commercial polymers to increase electrical conductivity and give “functional” properties to structural materials already used in automotive and aerospace fields.

6. Beyond graphene – emerging 2D materials and inorganic heterostructures with graphene

With recent developments in large-scale production techniques such as liquid-phase exfoliation and CVD growth, new layered materials beyond graphene such as BN, NbSe2, TaS2, and MoS2 based nanosheets holding great potential in both fundamental and applied research can be made available (see ref. 77 and 78). If the electronic interaction of organic molecules with graphene (a semi-metal) is rather complex, their interaction with semiconducting 2D nanosheets will give systems even more challenging to be understood, but more versatile to be used as 2D composites79–80 as alternative gate insulators, photo-responsive components, active materials for field-effect transistors or electrode materials. A polymer nanocomposite of liquid phase exfoliated MoS2 and polyethylene oxide (PEO) has been recently demonstrated as an anode material for lithium ion batteries. MoS2/PEO electrodes exhibit high charge storage capacities and long-term reversibility.81

Composites from organic semiconductors and other non-carbon based 2D materials, such as tin sulphite or tin selenide, are particularly interesting. For instance, it has been found that the presence of 1,10-phenanthroline can govern the morphology of SnSe giving 2D nanosheets, instead of 3D SnSe nanoflowers obtained in the absence of the molecule. Single-crystalline nanosheets are obtained from the coalescence of the SnSe nucleus in an oriented attachment mechanism. Bandgap determination and optoelectronic test based on hybrid films of SnSe and poly(3-hexylthiophene) indicate the great potential of the ultrathin SnSe nanosheets in photodetection and photovoltaics.82

1. Graphene can interact in a controlled way with a very wide portfolio of organic semiconductors, driving their self-assembly towards ordered 2D crystals. Many molecules can physically adsorb on graphene. However, only some of them (for example strong acceptors and fluorinated OSs) show an interaction strong enough to perturb effectively graphene’s electronic properties.

2. The interaction of OSs with graphene is strong not only at short distances, by charge transfer or \( \pi-\pi \) interactions, but energy transfer can also be relevant at longer distances, up to 30 nm.

3. The interaction of organic molecules with graphene can also be used in solution, to foster graphene exfoliation. As compared to other exfoliation techniques based on organic solvents or non-aromatic surfactants, the use of OSs allows us to monitor effectively graphene–organic interactions by optical spectroscopy, and to obtain graphene–organic hybrids suitable for electronic applications.

4. Graphene can be used as a nano-additive or functional coating either in the active layer or contacting electrodes of many organic electronic devices, allowing the boost of the performance of conventional OSs.

Thanks to their processability and broad arsenal of derivatives that are available, organic molecules can interact with graphene in infinite ways, leading to the formation of various types of assemblies spanning from simple monolayers on single sheets to complex, bulk graphene–organic composites. The physical interaction has a dramatic effect on the optical and electronic characteristics of the hybrid system, influencing numerous properties such as processability and charge transport which can be tuned e.g., via controlled doping. Graphene can strongly interact with and tune the morphology of most organic molecules, in a more controlled way than other technologically relevant materials such as silicon or metals. The possibility to combine together carbon-based materials having very different properties shall allow a seamless integration between high-speed electronics, organic electronics and composite science.

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Notes and references