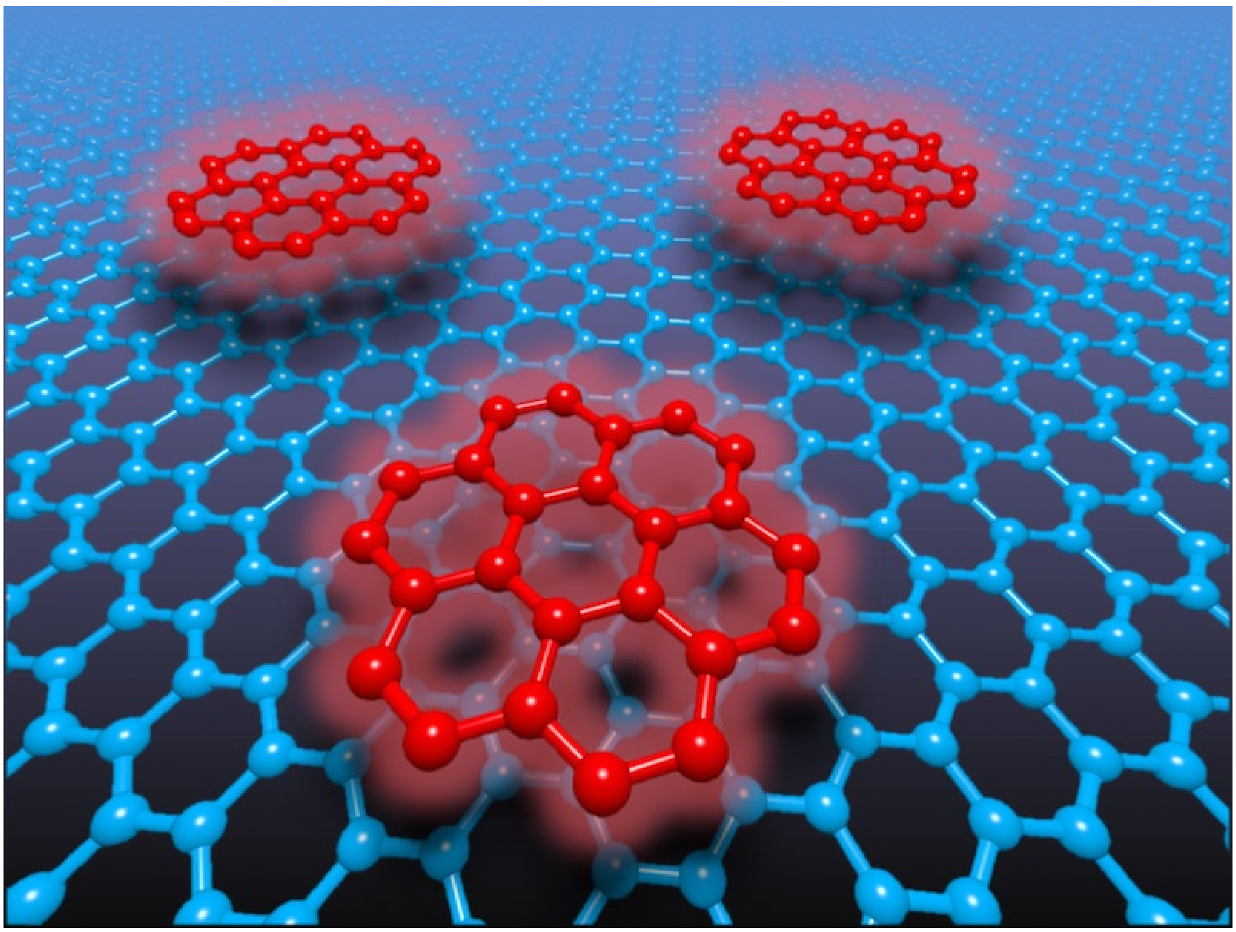
New insights into graphene and organic composites in electronics

April 10 2015



Schematic representing organic molecules attached to graphene, weakly interacting with the 2d material through supramolecular interactions. Credit: © 2015 Vincenzo Palermo/CNR-ISOF

Chemists from Europe's Graphene Flagship review the potential for graphene-organic composite materials in electronics. The researchers show how organic semiconductors can be used to better process graphene, and to tune its properties for particular applications.

The best known of all two-dimensional materials, graphene has properties that make it attractive for a whole range of mechanical, optical and electronics applications. Graphene is a challenge to produce on an industrial scale, however, and it can be difficult to tune its properties to suit specific functions. In the hope of solving these two problems simultaneously, research interest is turning to the interaction of graphene with tailor-made organic semiconductors.

Chemists have long been interested in organic molecules for nanotechnology applications. Smaller organic molecules can enable the molecular assembly of carbon nanomaterials into highly ordered architectures such as nano-fibres, crystals and monolayers. The backbone of carbon atoms in polymers, on the other hand, can lead to more disordered large-scale assemblies, but the elongated and flexible shapes of polymers make for high solubility and an efficient transport of electric charge.

Scalable processing and functionalisation of graphene is the subject of a feature article by three Graphene Flagship scientists writing in the Royal Society of Chemistry periodical, the *Journal of Materials Chemistry C*. The Graphene Flagship is an international consortium of academic and industrial partners, part-funded by the European Commission, which focuses on the development of graphene and related 2d materials.

Andrea Schlierf, Paolo Samorì and Vincenzo Palermo look in their review at a number of commercial polymers, the mechanical and electrical properties of which could be improved with the addition of graphene. The authors also consider graphene as a substrate for biomedical applications, and the use of organic semiconductors to open up an electronic band gap in graphene. The absence of a band gap in the pure form of this highly conductive material is a major issue hindering its exploitation in electronics.

Deposit small organic molecules on a flat carbon surface such as graphene, and one can modulate that surface through the externally undirected chemical process known as self-assembly. There are many classes of molecules that can be used for this purpose, ranging from simple alkanes to larger aromatic hydrocarbons. Self-assembly is in all cases driven by a complex interplay between inter-molecular and molecule-substrate interactions.

Experimental results show that the nucleation, orientation and packing of organic semiconductors on graphene are quite different from those grown on conventional substrates such as silicon and graphite. Adding chemical side chains to the backbone of the organic molecules can also expose functionalities that work in synergy with or opposition to the core interaction between the adsorbed molecules and graphene, leading to more complex self-assembly pathways.

Coating graphene with organic molecules in a vacuum is one thing, but when it comes to functionalisation and cost, soluble graphene-organic hybrid systems have clear advantages over graphene produced by chemical vapour deposition or epitaxial growth. Graphene-organic suspensions can be processed with large-area deposition techniques such as ink-jet printing, with the graphene produced by liquid-phase exfoliation in an organic solvent. This is the kitchen sink approach to graphene manufacture, and the process is cheap, effective and highly scalable.

An example of this liquid-based approach to graphene exfoliation is provided in another recent research publication to which all three review authors contributed. In a paper published in the Institute of Physics journal 2D Materials, Schlierf and her colleagues describe the exfoliation, processing and inclusion in polymer composites of graphene nano-platelets using indanthrone blue sulphonic acid sodium salt, a common industrial dyestuff known as IBS for short.

As is common with composite nanomaterials in general, the adsorption of organic molecules on graphene can have a significant effect on the electronic properties of the latter. The influence of this material doping is confirmed by spectroscopic measurements, and includes G-band splitting in Raman spectra.

Another notable effect of graphene-organic interactions is fluorescence quenching in light-emitting dyes by charge or energy transfer. In this case, the interaction is associated with electromagnetic fields strongly enhanced as a result of the energy sink nature of graphene. It is this quality of graphene which makes it a promising material for photo-detection, nano-photonic and photovoltaic applications.

Adsorption of organic semiconductors can also confer a magnetic function on graphene, complementing its electronic, mechanical and optical properties. This could lead to the application of graphene-organic hybrid materials in spintronics, with magnetic functionalities that alter the spin polarisation of electric currents flowing in graphene.

Spintronics aside, the potential for graphene in electronics rests largely on its application in integrated circuits, and for example in the components known as field-effect transistors (FETs). The problem with graphene, at least in its pristine form, is that the high charge carrier mobility is offset by a very poor on-off current switching ratio. Doping graphene with other materials can ameliorate this to some degree, but there is another way of approaching the problem. Graphene could be incorporated into organic FETs, resulting in increased electron mobilities, and switching ratios comparable with or better than those observed in organic FETs without graphene.

The focus here is on graphene, but graphene is only one of hundreds of two-dimensional materials of interest to flagship researchers and industry. Other layered materials of note include boron nitride and molybdenum disulphide (MoS2), the semiconductor qualities of which give them an advantage over pure graphene in certain applications. Such 2d materials could for example be used in transistor gate insulators, photo-responsive components, as active materials for FETs, or in electrodes. A polymer composite of liquid-phase exfoliated MoS2and polyethylene oxide was recently demonstrated as an anode material for lithium-ion batteries. The composite displays high charge storage capacities, and long-term reversibility.

Graphene is often spoken of in contrast to silicon as the electronic material of a 'post-silicon age'. Reality is more nuanced than this idealised picture, but still, graphene can in some respects outperform silicon. It also opens up new possibilities, especially when used in combination with other materials.

"A major advantage of graphene over silicon is that is based on carbon, which forms the basis of all organic materials", says Vincenzo Palermo, who heads the functional organic materials unit at the Institute for Organic Synthesis and Photoreactivity of the Italian National Research Council in Bologna. "This affinity of graphene with organic compounds allows for a seamless integration of graphene into composite materials for flexible electronics, sensing and biomedical applications. Graphene can strongly interact with and tune the morphology of most organic molecules, and it does so in a more controlled way than is the case with other materials such as silicon or metals."

As Palermo and his co-authors state in their conclusion to their review, the possibility of combining carbon-based materials with very different properties should allow for the integration of high-speed electronics, organic electronics and composite materials science.

More information: Graphene–organic composites for electronics: optical and electronic interactions in vacuum, liquids and thin solid films, *J. Mater. Chem. C*, 2014,2, 3129-3143
DOI: 10.1039/C3TC32153C

Provided by Graphene Flagship