MATERIALS SCIENCE

Carbon sheet solutions

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When carbon fibres just won't do, but nanotubes are too expensive, where can cost-conscious materials scientists go to find a practical conductive composite? The answer could lie with graphene sheets.

Carbon nanotubes have revolutionized materials science, with their combination of exceptional mechanical strength and unique electrical properties. The media has added to the hype, by enthusing over the way this new form of carbon will transform the transport and electronics industries[1]. Yet many problems still need to be solved before carbon nanotubes can be successfully incorporated into composite materials. The three biggest issues are the fact that nanotubes tend to clump together during processing, the difficulty of controlling their diameter and the way the carbon sheet is rolled, and the high cost of their production[2].

With all the excitement about nanotubes, an alternative option has been overlooked. Single layers of graphite — known as graphene sheets — also have excellent electrical properties, but are cheap to make and require no helicity control. Yet graphene sheets have problems of their own, to do with their poor mechanical properties. Graphite is soft and flaky, and cannot be used in load-bearing structures. This problem could be solved by making a composite material of graphene sheets and polymers. But until recently, preparing such composites was extremely difficult, because the strong surface–surface attraction between the sheets prevents them from dispersing in a polymer solution or melt. In this respect, graphene sheets are even harder to deal with than carbon nanotubes. On page 282 of this issue[3], however, Stankovich et al. describe a method that overcomes the difficulties of making graphene–polymer composites.

The challenge was to find a process that yielded a uniform distribution of graphene in a polymer matrix. The authors[3] began by converting graphite into graphite oxide in an aqueous medium. This well-known process adds oxygen-based chemical groups to the graphite surface, and results in the bulk graphite being completely separated into single sheets. The oxygen-based chemical groups tend to have excess negative charge, so the sheets repel each other, producing stable dispersions. To restore graphene's unique properties, the oxygen-containing groups must be removed; however, without the negative charges the sheets immediately coalesce.

Stankovich et al.[3] struck on the idea of chemically modifying the surface of graphite oxide. They did this by treating the material with phenyl isocyanate, which adds hydrophobic chemical groups to the surface. The resulting material forms separated sheets that can be mixed with solutions of many commercial polymers in polar organic solvents. One may speculate that the hydrophobic groups attached to the graphite oxide sheets are attracted to similar groups in the polymers, so that the sheets prefer mixing with the polymer rather than stacking up with each other. The resulting composite material was an insulator. So, to restore the conductivity of the graphite, a small amount of a reducing agent was added to the composite solution. This did not make the graphene sheets coalesce, because hydrophobic groups remain attached to their surfaces, holding them within the polymer.

In this way, the authors obtained a composite with excellent structural characteristics: all the sheets were individually and uniformly distributed throughout the volume of the polymer. The composites were also easy to process using standard industrial technologies such as moulding and hot-pressing. This might sound trivial, but such matters are crucial if nanotechnology is to be applied in

MICROFLUIDICS

Clicks and chips

The words 'organic chemistry' tend to conjure up images of large bubbling flasks, brightly coloured test tubes and explosive reagents. Although most chemists still use flasks for their reactions, a growing number of them make their molecules using miniaturized devices. These 'labs on chips' require only tiny quantities of reagents, thus reducing cost, producing less waste and cutting down the time needed to perform a reaction and to analyse its products.

Although it is quite easy to perform a single reaction on a chip, it is much harder to carry out multiple reactions in the same device, making several different molecules. But now Hartmuth C. Kolb, Hsian-Rong Tseng and their colleagues have developed a device (pictured) that can perform 32 reactions at the same time. The group reports its results in Angewandte Chemie (doi:10.1002/anie.200601677).

The authors miniaturized a

technique known as 'in situ click chemistry', which can be used to identify high-affinity inhibitors for enzymes. These inhibitors can then be used in other biological experiments: for example, the molecules can be used to block the enzyme's 'active site' to see how it works, or to elucidate its cellular role.

Two compounds — one containing an azide group, and another containing an acetylene group — are combined in a reaction vessel with the target enzyme. Molecules of both compounds may enter the enzyme's active site, and orient themselves so that the azide group and the acetylene group fit comfortably inside. If the two groups align favourably, then 'click', they react to form a five-membered ring. Because this click reaction occurs in the active site of the enzyme, the product usually binds very tightly to that enzyme.

By miniaturizing this process on a chip, the authors were able to run 32
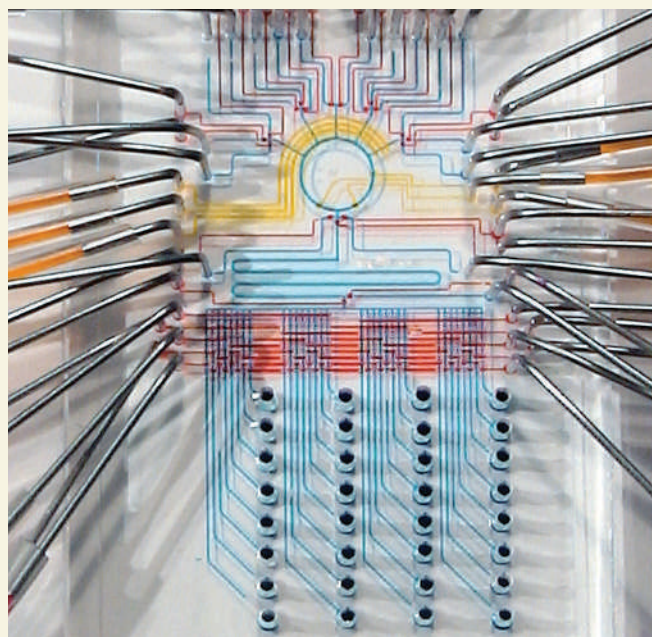
reactions at the same time to find inhibitors for a well-known target enzyme (bovine carbonic anhydrase II) using much less of the protein than would have been needed in a traditional, microtitre-based procedure.

Many interesting proteins are

notoriously difficult to obtain in large quantities, preventing their use in biochemical assays for inhibitors. This chip enables such proteins to be screened at last, and may open up many areas for biological and medicinal study.

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the real world. Previous work using a similar process of surface modification to produce thin films of graphite did not have this advantage[4]. Thin films, and other kinds of graphite sheet, could be used for specialized applications, in electronic devices or for certain high-performance nanocomposites[5].

Stankovich and colleagues' efforts[3] resulted in composites with intriguing properties. Only 0.1% by volume of graphene in the composite is required for electrical conduction — this is the lowest threshold observed for conductive polymer composite materials, except for those using carbon nanotubes. The conductivity rapidly increases by incorporating more graphene, reaching 1 siemen per metre at a loading of 2.5% by volume; conductivities in the range of 0.1 S m^{-1} are sufficient for many applications.

The graphene composites could be very useful: for example, in the manufacture of fuselages for aircraft, which must combine low weight, high strength and electrical conductivity. This last property is necessary for protection against lightning strikes while in flight. Nevertheless, the conductivities of these composites[3] are still several orders of magnitude lower than those of the best examples of nanotube mats (which are made entirely of nanotubes). They are also lower than the conductivity of graphite itself, or that of other nanotube composites[6-8]. The positive trade-offs for graphene-sheet composites are low cost and the plentiful supply of graphite.

The small amount of graphene required in the composite[3] for conductivity results from a high probability of sheet-to-sheet contact even at relatively low graphene loading, and from the conductive highway formed by the over-lapping electron clouds of adjacent carbon atoms. However, high conductivities, rivalling those of individual nanotubes or thin nanotube

films, will not be achieved with these composites. This is because of the limited degree to which the phenyl-isocyanate-modified sheets mix in the polymer solution; the large number of defects in the carbon layers; and the slow rate of electron tunnelling through gaps between the sheets.

The technology described by Stankovich and colleagues has two main advantages. The first is its ease of use for large-scale industrial applications where the conductivity of carbon fibres is insufficient, but where carbon nanotubes would be too expensive. The second is its applicability to a variety of polymers. The modification of graphite oxide by phenyl isocyanate should be considered as a proof-of-concept demonstration. The phenyl group could be replaced by other groups compatible with different polymers. This opens up a wide area of research that could lead to a large family of composites with differing properties. Clearly, the next step is to determine the mechanical properties of the graphene composites, and to see whether they can compete with nanotube-based materials. ■

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STRUCTURAL BIOLOGY

Proteins downhill all the way

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The hundreds of hydrogen atoms in a protein can be used as reporters to describe how the protein folds into and out of shape. The results challenge the dogma that this is always an all-or-nothing process.

The three-dimensional structures of proteins govern their activity, yet we know far less than we would like to about how these molecules fold into shape. Proteins use an intricate network of weak, non-covalent interactions to acquire the folded state[1]. Conventional wisdom states that protein folding is a highly cooperative process — proteins are either completely folded or completely unfolded. This all-or-nothing model is convenient because it enables spectroscopic data to be

converted into thermodynamic data, simply by measuring the distribution of folded and unfolded molecules at equilibrium. But is this model always correct? Muñoz and colleagues (page 317 of this issue)[2] use nuclear magnetic resonance (NMR) spectroscopy to follow the unfolding of an all-helical protein known as BBL.

BBL folds in a 'downhill' fashion — that is, the process is characterized by very low energy barriers between the folded and unfolded