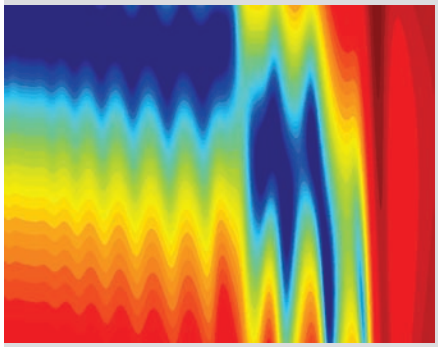
METAMATERIALS

Lay it on thin



Nature Mater. doi:10.1038/nmat2033 (2007)

As light passes from air into a liquid, it slows down and changes direction (refracts), explaining why objects appear bent when partially immersed in water. The refractive index — a measure of how much slower light travels in a medium compared with air — of most substances is positive, but in the 1960s, Veselago proposed the idea of materials with negative refractive indices that could, in theory, bend light to the same side of the normal as the incident light.

This prediction has been experimentally verified using 'metamaterials' — artificial structures whose constituents are much smaller than the wavelength of the interacting radiation. However, metamaterials reported to date are difficult to make and show high optical losses. Now, Anthony Hoffman and colleagues from Princeton University, Oregon State University and Alcatel-Lucent, New Jersey, USA report on the fabrication of an all semiconductor metamaterial exhibiting negative refraction for all incident angles in the long-wave infrared region of the spectrum.

The samples consisted of alternating layers of n-type InGaAs and undoped AlInAs, each 80 nm thick and grown onto InP substrates by molecular-beam epitaxy. The total thickness of the layers was ~8.1 micrometres. It was found that the wavelength for the onset of negative refraction depended on the free carrier density of the InGaAs layer. These materials, which are relatively simple to make, may prove useful for applications such as waveguiding and imaging.

PROTEIN FOLDING

Get into shape

Nano Lett. **7,** 3438–3442 (2007)

Proteins often fold in confined spaces such as virus capsids or pores. Experiments and theoretical studies both show that they tend to be more stable and less likely to denature when constrained in small volumes. Understanding how the shape of such a nanocontainer influences protein folding would provide an additional way to control biomaterials.

Shao-Qing Zhang and Margaret Cheung at the University of Houston in the US have therefore developed a systematic strategy to explore how the geometry of a nanocontainer affects the dynamics of biopolymers. They used molecular simulations to investigate changes in the shape of a particular protein (the B1 domain of Streptococcal G) over time when it is confined in a spherical, ellipsoidal or pancake-like container that is a few nanometres in size. The calculations show that the flat pancake-like containers lead to the greatest enhancement in the rate of folding. It is suggested that this particular shape closely follows the intermediate configuration of the proteins as they transition from unfolded to their most-favoured folded state.

The team believes that these studies will lead to drugs that are expressly designed to manipulate how proteins bind with one another or fold and configure in cells, with wide applications in nanobiotechnology.

GIANT FULLERENES

Ever decreasing circles

Phys. Rev. Lett. **99,** 175503 (2007)

Fullerenes, which are usually made from carbon, are hollow cage-like molecules roughly spherical in shape. Despite being discovered over 20 years ago, the remarkable self-assembly process giving rise to their well-known 'soccer-ball' structure from hot carbon vapour is still not fully understood. In particular, the 'shrink-wrapping' hypothesis, in which single layers of carbon sheets are wrapped into giant spheres that cast off carbon atoms until stable structures such as C_{60} are formed, has not been experimentally verified.

Now, a team of researchers have reported the first direct experimental evidence to support this mechanism. Jianyu Huang from Sandia National Laboratories, New Mexico and Boris Yakobson and colleagues from Rice University, Texas, US show that giant fullerenes formed inside multiwalled carbon nanotubes evaporate to produce smaller buckyball structures with their carbon shells remaining intact. Nanotubes containing giant fullerenes were heated to above 2,000 °C by passing an electric current through them, and the resulting thermodynamically induced changes were monitored in real time with a high-resolution transmission electron microscope.

Theoretical modelling suggests that carbon atoms are removed preferentially from higher-energy pentagon sites and the number of pentagons (12) remains constant as the fullerene shrinks. These results not only represent the first experimental evidence for a 'shrink-wrapping' formation mechanism, but also open up the possibility of making fullerenes tailored for specific applications, such as for storing hydrogen in fuel cells.

GRAPHENE

The oxide route

Nano Lett. **7,** 3394–3398 (2007)
Nano Lett. **7,** 3499–3503 (2007)

Individual sheets of carbon atoms, called graphene, are the building blocks of crystalline graphite, and are extremely useful materials for building nanoscale transistors and sensors. However, current methods of acquiring them, by directly scraping them off graphite, are laborious and yield small amounts of material.

Now, two groups of researchers, one led by Richard Kaner at the University of California, Los Angeles in the US and the other a collaboration between Marko Burghard and colleagues at the Max-Planck Institute and the University of Siegen in Germany and the EPFL in Switzerland, are exploring a new high-yield method for making graphene. They start with graphite oxide, which has weaker bonds than graphite and naturally separates into single-layered flakes in water. They deposit the flakes onto a silicon oxide substrate and use chemical reduction to remove the oxygen, leaving graphene. The reduction process creates several carbon–carbon double bonds, leaving free electrons to conduct electricity. Furthermore, the resistance of the sheets increases with applied voltage, and decreases with increased temperature, implying that the sheets are p-type semiconductors.

The new method is fast and does not require high temperatures, making it more practical than recent attempts to produce graphene by reducing silicon carbide. It could lead to the first large-scale production of graphene sheets for use in electronic devices.

BIOACTIVE NANOSTRUCTURES

Branching out

Angew. Chem. Int. Edn
doi:10.1002/anie.200702732 (2007)

The self-assembly of molecules into large ordered arrays is an efficient and versatile strategy for making functional nanostructures. Incorporating bioactive

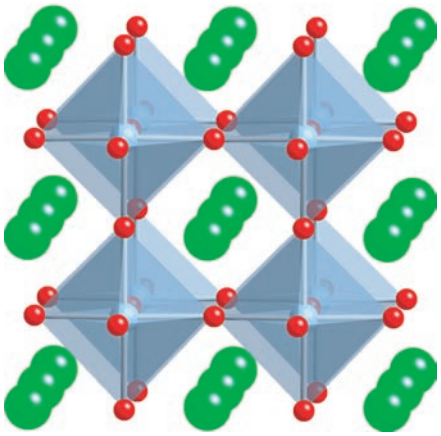
components into such structures enables them to interact with specific biological targets, which could prove useful for therapeutic and diagnostic medical applications. Peptides — small chains of amino acids — are promising candidates to impart bioactivity as they are known to mediate a range of biological events.

Now, Myongsoo Lee and co-workers from Yonsei University in Seoul, Korea report a general approach for the self-assembly of bioactive nanostructures with good control over their shape and size. A range of molecular building blocks, with a hydrophobic lipid chain grafted to the end of a peptide known to penetrate cells, were made. Depending on the size and degree of branching of the lipid, these compounds assembled into either spherical structures (11 nm in diameter) or short cylinders (12 nm in diameter and 100 nm long) with a hydrophobic lipid core and a hydrophilic peptide shell. Longer cyclindrical nanostructures could be made using branched lipids with modified chain ends.

When cells were incubated with short nanocylinders loaded with red-dye molecules, it was found that the dye was transferred to the cytoplasm and the nucleus, suggesting that these self-assembled materials are promising candidates for drug-delivery applications.

MICROSCOPY

Better and better



Nature **450,** 85–88 (2007)
Nature doi:10.1038/nature06352 (2007)

Electron microscopes have supplied data for countless papers. However, researchers are always looking for ways to improve the performance of these scientific workhorses, as demonstrated by two recent papers in *Nature* from independent groups in Japan and the US.

Koji Kimoto and co-workers at the National Institute for Materials Science in Tsukuba, Japan report how scanning transmission electron microscopy can be combined with electron energy-loss spectroscopy to perform element-selective imaging of atomic columns in a layered manganite crystal. Although these two techniques have been combined before, various technical difficulties have made it impossible to perform two-dimensional imaging of atomic columns. Using advances in both equipment (such as improved electron sources) and software enabled Kimoto and co-workers to image the columns of lanthanum, manganese and oxygen atoms in their sample.

Meanwhile Kamil Ekinci and colleagues at Boston and Cornell Universities in the US have developed a souped-up scanning tunnelling microscope (STM) with a frequency response (bandwidth) that extends up to 10 MHz — 100 times better than the previous state of the art. Although the basic idea behind the STM is quite simple — a sharp tip is scanned over a conducting surface, moving up or down to keep the tunnelling current constant — complex read-out electronics are needed to achieve atomic resolution. By improving the impedance matching in the read-out circuitry, the group was able to increase the bandwidth, and hence the temporal resolution, of the STM.

ENZYMES

All wired up

Nano Lett. doi:10.1021/nl072319o (2007)

Hydrogenase enzymes, which are found in various microbes, can catalyse the reversible oxidation of molecular hydrogen, providing a biological alternative to expensive precious-metal catalysts. There has, therefore, been great interest in their potential for use in biofuel cells and hydrogen production. However, it is difficult to incorporate them into electrical devices without compromising their catalytic activity.

Now, a group from the National Renewable Energy Laboratory in Colorado in the US have made biohybrids from hydrogenases and single-walled carbon nanotubes (SWNTs) in which the nanotube acts as a molecular wire and forms an electrical connection to the catalytic region of the hydrogenase. Michael Heben and colleagues used an iron-based hydrogenase from the bacterium *Clostridium acetobutylicum* and simply mixed it with a suspension of SWNTs in a surfactant. The enzyme spontaneously displaced the surfactant and adsorbed onto the SWNT surfaces.

Photoluminescence excitation and Raman spectroscopy studies were used to evaluate electron transfer in the hybrid material. Under anaerobic conditions and with an appropriate H_2 partial pressure, the hydrogenase remained catalytically active and could mediate the injection of electrons into the nanotube.

TOP DOWN BOTTOM UP

Collective memory

Researchers on opposite sides of the Atlantic are working together on a new approach to making silicon-based memory devices.

Michael Kozicki and Rainer Waser had known about each other's work for a number of years before they met for the first time at the Euromat conference in Prague in 2005. Kozicki, who is director of the Center for Applied Nanoionics at Arizona State University (ASU), agreed to write a chapter for a book that Waser, a physicist at the Jülich Research Centre in Germany, was editing, and they also started a collaboration to make better non-volatile memory devices with copper-doped silicon oxide.

Work started in earnest in 2006 when Maria Mitkova of ASU visited Jülich. One of Waser's students, Christina Schindler, then went to ASU to work on the fabrication and characterization of the devices, which can be switched between a high-resistance OFF state and a low-resistance ON state with relatively low voltages and currents (*IEEE Trans. Elect. Dev.* **54**, 2762–2768).

The low voltages and currents required for switching should translate into devices that are smaller and consume less power than other memory technologies. And being based on silicon, the new approach should be compatible with existing approaches to device fabrication.

Kozicki admits that it is never easy to collaborate between facilities separated by thousands of miles. "But having a physical presence, in the form of Ms Schindler certainly helped overcome this", he says. "Once there is an ongoing relationship, it is easier to maintain the collaboration by exchanging data and samples even when people are back in their home institutions."

The project was originally funded by Axon Technologies Corporation, a spin-out company co-founded by Kozicki, and the exchange of personnel between ASU and Jülich was supported by a grant from the US National Science Foundation held by Himanshu Jain, a materials scientist at Lehigh University.

The definitive versions of these Research Highlights first appeared on the *Nature Nanotechnology* website, along with other articles that will not appear in print. If citing these articles, please refer to the web version.