research highlights

Molecular shuttles

Angew. Chem. Int. Ed. doi:10.1002/ anie.200903311 (2009)

Controlling molecular motion could lead to molecular machines that can be used in applications such as information storage. One class of compounds that have played a promising part in this area of research is rotaxanes. These consist of a dumbbellshaped molecule threaded through a macrocycle; this ring can act as a molecular shuttle if the correct chelating groups are placed at either end of the central molecule. Now Jean-Pierre Sauvage and colleagues show that by including an extra chelating group between the terminals of the central axis, fast electrochemically driven motion of the ring can be achieved over long distances. The macrocycle in the system is a copper complex incorporating an 8,8'-diphenyl-3,3'-biisoquinoline bidentate ligand with molecular motion driven by oxidation or reduction of the copper centre. The axis in the new rotaxane is roughly 23 Å long, and the team achieved speeds equivalent to those seen in a related 'two station' system of 10 Å. The work provides a basis for devices requiring fast long-distance linear motion.

Super aluminium

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Materials with a negative refractive index are known to make perfect lenses, where there is no fundamental limit as to how detailed the imaged object can be resolved. However, as a negative refractive index is difficult to obtain, researchers are studying superlenses, which have a more relaxed requirement — for light of certain polarization, negative permittivity is sufficient for lensing beyond the diffraction limit. Conveniently, at certain frequencies above their plasmon resonance metals fulfil this criterion. The first superlenses were made from silver, although these operate only in the visible region of the spectrum. Aluminium on the other hand

has its plasma frequency in the ultraviolet region, thus offering a broader range of operation as well as better resolution. Alina Schilling and colleagues from Queen's University in Belfast have now realized an aluminium lens in the ultraviolet that is capable of resolving objects only 70 nm apart. With a theoretical resolution limit of 29 nm, aluminium superlenses lenses can be used not only to image nanostructures, but also for advanced photolithography of electronic circuits.

Preferential growth

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Although the electronic properties (metallic or semiconducting) of singlewalled carbon nanotubes depend on the nanotube configuration (chirality), there is still limited understanding of what governs chirality during synthesis. Avertik Harutyunyan and colleagues have now managed to selectively grow singlewall nanotubes with a maximum of 91% of the tubes showing metallic conductivity. This has been achieved by using iron nanocatalysts deposited onto a SiO₂/Si support and varying the type of ambient noble gas during thermal annealing of the catalyst while combining reductive and oxidative species. Electron microscopy demonstrates that changing the gas resulted in morphological and coarsening differences in the nanoparticles used to nucleate the nanotubes. It seems that the addition of water not only helps the growth by etching the amorphous carbon and controls the particle diameter, but also serves to alter its shape. These results indicate that, in combination with a carbon source, other adsorbates, such as oxygen and carbon monoxide, could lead to chiral-selective growth capable of directly controlling the nanotube structure.

A beneficial swap

Delivery valves

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Mesoporous silicon nanoparticles offer the potential to deliver drugs in vivo, and when the particles also have a hollow core, it allows greater loading capacity for cargo. As with all drug-delivery systems, the challenge is to encapsulate the drugs within the particles until they reach the point of delivery, and release them in a controlled way. Jeffrey Zink and colleagues report a rotaxane-based 'nanovalve' to control the escape of drugs from the pores of hollow silica nanoparticles. The valves are based on anilinoalkane group linkers, which are covalently bonded over the pores in the silica. The linkers contain a nitrogen atom that is bare at neutral pH, so an α-cyclodextrin macrocycle can thread onto the linker and hydrogen bond to the bare nitrogen, blocking the pore. As the pH is reduced, the nitrogen becomes protonated, weakening the hydrogen bond and releasing the cyclodextrin. This opens the pore allowing the cargo out. The valves open in response to pH changes in a physiologically relevant range, and can be tailored to respond to different pH changes by using different linkers.

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It was recently shown that by applying a high enough voltage on a single atom adsorbed on a surface through a scanning tunnelling microscope, the atom can be pushed within the surface. Young Jae Song and colleagues have now investigated the details of such a process for Mn atoms adsorbed on an InAs layer. By comparing the topography images before and after the voltage application they concluded that the Mn atoms replace In atoms, which end up sitting on the surface. The substitution occurs when the voltage reaches a value of about 0.3 V, as revealed by a sudden jump in the current measured through the scanning tunnelling microscope as the voltage is ramped. Interestingly, subsequent voltage ramps do not show any current jump, implying that the substitution is irreversible and the In atoms remain on the surface. Numerical calculations confirm that the configuration in which the Mn atoms are incorporated is more stable. Details of such a substitution technique could prove to be essential for realizing nanostructures with controlled inclusions of single impurities.