

## X-ray diffraction strikes gold

### CHARACTERIZATION

Total structure determination by X-ray diffraction can be a real headache when applied to nanostructures, mostly because of variations in structure between individual particles.

But in a tour de force of structure determination, researchers at Stanford University have determined the structure of thiol monolayer-protected Au nanoparticles to 1.1 Å resolution, and found some surprising results [Jadzinsky *et al.*, *Science* (2007) **318**, 430].

Such nanoparticles have long been a subject of study, but obtaining a monodisperse sample has proven difficult – so definitive structural information has remained elusive. In the present work, Au particles are coated with *p*-mercaptobenzoic acid and crystallized from a solution containing methanol, NaCl, and sodium acetate. Further recrystallization and purification leads to samples sufficiently monodisperse to perform X-ray diffraction.

The nanoparticles contain clusters of 102 Au atoms and 44 thiolates in the monolayer shell. The researchers find that 79 of the 102 Au atoms form a 'grand core', a truncated decahedral cluster with bond lengths and atomic arrangement consistent with a bulk metal.

Studying the interaction of the remaining Au atoms, reveals that they are involved in Au thiolate complexes that interact weakly with the core atoms.

The materials properties of the clusters can now be rationalized in terms of the atomic order. The results have implications for many other self-assembled monolayers on Au substrates, which are employed in studies ranging from sensing to biophysics.

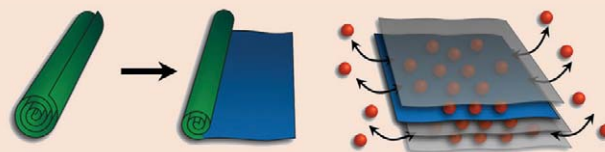
**D. Jason Palmer**

## Nanosheets unfurl to reveal 2D nature

### NANOTECHNOLOGY

Graphene has come strongly to the fore in recent times because of the unique properties afforded by its genuinely two-dimensional nature. But below dimensions of ~100 nm, graphene and other such two-dimensional structures tend to roll up into 'onions' and nanotubes, forsaking their interesting properties.

A clever new method to unfurl two-dimensional sheets has been demonstrated by researchers at Yonsei University, Seoul National University, and the Korea Basic Science Institute [Seo *et al.*, *Angew. Chem. Int. Ed.* (2007) doi: 10.1002/anie.200703175]. Transition metal chalcogenides are known to form two-dimensional structures. The researchers created WS<sub>2</sub> nanocrystals starting with tungsten oxide nanorods of diameter ~5 nm and length 30 nm. In the presence of CS<sub>2</sub> in a hot hexadecylamine solution, sulfidation of the nanorods occurs, and the strain between the heterogeneous phases causes the rods to unroll. Capping ligands bind at the edges, stabilizing the sheets as they form. The result is square WS<sub>2</sub> sheets, ~40 nm along each side. These sheets gradually stack up in groups of about six.



'Rolling-out' process for formation of a nanosheet and assembled multisheet stacks with enhanced Li<sup>+</sup> intercalation. (Courtesy of Jinwoo Cheon.)

"It took us almost two years to figure out real structures and also the mechanism behind the shape transformation from precursor rods to sheets," says Jinwoo Cheon of Yonsei University.

The as-prepared structures show high intercalation of host molecules and could be used as solid-state lubricants, biomolecule 'containers', or as the basis for nanoscale batteries.

The method lends itself to many other two-dimensional materials too, and Cheon says his group will be exploring them, and testing their hosting capabilities and diffusion kinetics.

Kostya Novoselov of the University of Manchester, UK, thinks it is a cunning approach. "I can certainly see the crystals obtained being used for research and applications, but I'm mostly excited with the way they are produced – unrolling nanoscrolls. I'm sure there is some very exciting physics in that process as well."

D. Jason Palmer

## Nanotube designs for printing flexible batteries

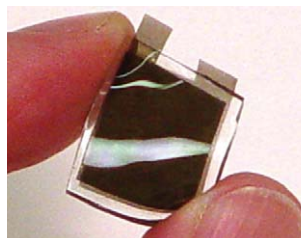
### NANOTECHNOLOGY

Industrial-scale printing processes could deposit electronics onto a variety of flexible substrates cheaply and speedily. But printed electronics need printed power.

Following on from a demonstration of flexible carbon nanotube (CNT)-based supercapacitors [Kaempgen *et al.*, *Appl. Phys. Lett.* (2007) **90**, 264104], George Grüner's group at the University of California has now fabricated a CNT-based

battery architecture from solution with cheap materials and high scalability [Kiebele and Grüner, *Appl. Phys. Lett.* (2007) **91**, 144104].

The proof-of-concept devices are deposited layer-by-layer in an all solution-phase approach amenable to large-scale production like roll-to-roll printing. The anode is Zn foil, which also acts as a charge collector. This is followed by a separator soaked in a solution of NH<sub>4</sub>Cl and ZnCl<sub>2</sub> electrolytes. The cathode is then added, made from a paste of MnO<sub>2</sub>, CNTs, and the same electrolyte mixture. A random CNT network



A flexible battery based on a CNT architecture. (Courtesy of George Grüner.)

on top serves as the charge collector, although any conducting nanowire could serve the same purpose.

The resulting devices show an open-circuit voltage of ~1.45 V, with a total capacity between 15 mA h and 25 mA h.

Besides the clear benefits of the solution-phase, room-temperature process, there is better news for future devices. The process lends itself to future one-layer-per-electrode designs; the anode and

cathode could be just two nanowire-based mixtures as in the proof-of-principle devices – a major advantage for simplicity in industrial scaling of the process.

As Grüner says, "Eventually we will be able to print batteries just like we print newspapers, and maybe one day we can even print our own batteries at home using an inkjet printer."

For now, the team is optimizing their first devices before attempting to demonstrate industrial-scale production.

**D. Jason Palmer**