

As reported in the November 18, 2005, issue of *Angewandte Chemie International Edition* (p. 7439; DOI: 10.1002/anie.200501264), J. Lee and N. Kotov from the University of Michigan and A. Govorov

from Ohio University created a reversible nanothermometer built from two types of NPs connected by a polymer that acts as a molecular spring. The superstructure is based upon a layer of poly(ethylene gly-

col) (PEG) derivatives with *tert*-butoxycarbonyl (Boc) and *N*-hydroxysulfosuccinimide (NHS) groups at the terminal ends of the linear molecules. Au NPs of 20-nm diameter are attached to the Boc ends and 3.7-nm diameter CdTe NPs are attached to the NHS ends. The superstructure coils into a corona-like structure, with the gold core surrounded by the PEG derivatives and the CdTe NPs.

Exciting the superstructure with the He:Ne laser at 633 nm excited the CdTe NPs. The similarity of the energies of the Au NP plasmon (2.26 eV) and the CdTe NP exciton (2.18 eV) results in resonance conditions in the superstructure that have two effects on the emission of CdTe: an enhancement of the luminescence intensity of the NPs and a strong dependence of the intensity on interparticle distance. The temperature of the CdTe-PEG-Au dispersion was varied between 20°C and 60°C, and it resulted in a swelling of the PEG molecule and an increase in its diameter with increasing temperature. This alters the distance between Au and CdTe NPs and, as a consequence, changes the luminescence output. The process is reversible, with less than 10% photodegradation in each temperature cycle. The researchers applied a simplified mathematical model to perform calculations that demonstrated that the change in the PEG-controlled distance is the cause of the variation in emission intensity.

The researchers concluded the CdTe-PEG-Au system constitutes a nanoscale superstructure that undergoes a reversible structural change in response to a change in environmental conditions, with very high sensitivity of the output to the distance between CdTe NPs and Au NPs. The researchers said that these nanocolloids represent the foundation of a new family of sensing and optoelectronic devices.

MARÍA MARTA FIDALGO

### Hot-Drawing Process Aligns and Toughens Carbon Nanotube Fibers

The abundance of commercial applications for high-performance textiles and cables has driven a great deal of materials research. In the November 2005 issue of *Nano Letters* (p. 2212; DOI: 10.1021/nl051419w), P. Miaudet from the National Center for Scientific Research (Pessac, France), V. Pichot from Paris University South (Orsay, France), and their colleagues report how they wet-spun multiwalled carbon nanotubes (MWNTs) with poly(vinyl alcohol) (PVA) to form super-tough composite fibers. The researchers demonstrated that a post-synthesis, hot-drawing treatment dramatically enhanced the composite fiber's mechanical properties. The

### Metal-Oxide-Metal Heterojunction Nanowires Formed

Oxide nanowires are currently being developed and investigated for a variety of nanoelectronics applications because of their unique properties and potential opportunities for "bottom-up" assembly. Going a step further, if metal-oxide-metal (MOM) heterojunctions could be formed, sandwiching a functional oxide between two noble-metal nanowires, they could have distinct advantages over all-oxide nanowires. The synthesis of MOM nanowires using a template-based method has now been reported by J.S. Tresbeck and A.L. Vasiliev of the University of Connecticut and N.P. Padture of the Ohio State University.

As reported in the October 2005 issue of the *Journal of Materials Research* (p. 2613; DOI: 10.1557/jmr.2005.0347), the researchers examined Au-SnO<sub>2</sub>-Au systems and Au-NiO-Au systems (see Figure 1 for Au-SnO<sub>2</sub>-Au nanowires). Au-Sn-Au and Au-Ni-Au nanowires were formed inside anodic aluminum oxide (AAO) templates with 60-nm and 220-nm diameter nanoholes, respectively. First, one side of the template was sealed using 0.5- $\mu$ m-thick Ag thin film. A small 0.5- $\mu$ m Ag segment was electroplated within the nanoholes. Au was then electroplated inside the nanoholes. This was followed by Sn or Ni electroplating. Au was then again electroplated on top of the Sn or Ni. The Ag and the AAO template were then dissolved using nitric acid and NaOH, respectively, yielding Au-Sn-Au or Au-Ni-Au nanowires, which were centrifuged and rinsed. These nanowires were subjected to heat treatment to yield Au-SnO<sub>2</sub>-Au (through oxidation of Sn to SnO and then SnO to SnO<sub>2</sub>) or Au-NiO-Au nanowires, through oxidation of Ni to NiO. The nanowires were then dispersed in deionized water or ethanol. These MOM nanowires were examined in both a scanning and a transmission electron microscope.

The overall length of Au-SnO<sub>2</sub>-Au nanowires in one case was more than 2  $\mu$ m. The Au diameter was  $\sim$ 60 nm, and the SnO<sub>2</sub> segment was  $\sim$ 60 nm in diameter and  $\sim$ 70 nm in length. Grain size in the SnO<sub>2</sub> ranged from 5–10 nm. Similarly, the overall length of a Au-NiO-Au nanowire was more than 7  $\mu$ m, with a Au diameter of  $\sim$ 270 nm, a NiO diameter of  $\sim$ 300 nm, and  $\sim$ 200 nm length. These dimensions varied for different templates used.

The study has demonstrated the feasibility of synthesizing MOM nanowires in the Au-SnO<sub>2</sub>-Au and the Au-NiO-Au systems. This synthesis method appears to be applicable to a wide variety of metal-oxide combinations. Also, there are several potential unique advantages of this architecture. The dimensions of the functional oxide segment in the nanowires can be controlled by varying the electroplating conditions. The synthesis method described here also offers the possibility of better control over the structure and characteristics of the oxide segments. Site-specific assembly of the MOM nanowires into nanoscale circuits is a possibility. The structure of the nanowires may also enable the direct measurement of the functional properties of the oxides at the nanoscale.

GOPAL RAO

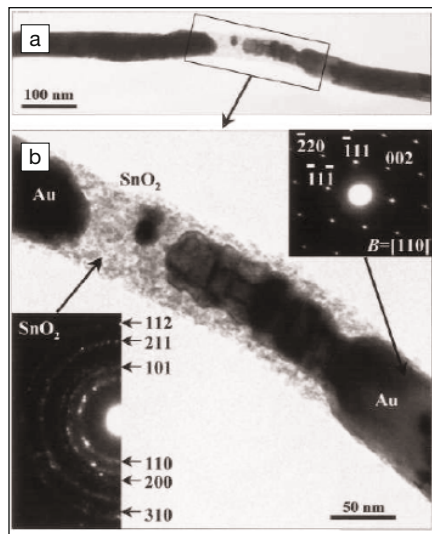


Figure 1. Transmission electron micrographs show an isolated Au-SnO<sub>2</sub>-Au nanowire synthesized inside an anodic aluminum oxide template, at (a) low and (b) high magnifications. The dark regions are Au, and the light region is SnO<sub>2</sub>. Reprinted with permission from the *Journal of Materials Research* **20** (10) (October 2005) p. 2613; © 2005 Materials Research Society.

group also compared the properties of untreated composite fibers containing MWNTs to those containing single-walled nanotubes (SWNTs).

The scientists spun their continuous fibers by injecting a homogeneous dispersion of nanotubes into a co-flowing stream of aqueous PVA. They then investigated the mechanical properties under tensile load. Toughness is measured by the specific amount of energy that is required to break a fiber and the amount of strain tolerated before failure. Their untreated SWNT fibers reached a record strain-to-failure of 430% and an unprecedented toughness of 870 J/g. Untreated MWNT/PVA fibers performed nearly as well. These composite fibers are an order of magnitude tougher than polyaramide fibers such as Kevlar.

Unfortunately, classical nanotube/PVA composite fibers swell and lose strength in humid conditions, and they absorb relatively little energy at low strain, compared with polyaramides. Miaudet and co-workers drew inspiration from textile technologies and remedied both drawbacks by hot-drawing their nanotube/PVA fibers. After drying the fibers, they pulled them to 850% within a hot air stream at 180°C, which is above the PVA glass transition.

X-ray diffraction confirms that the hot-drawing process increases the crystallinity of the PVA and further aligns the PVA chains and the nanotubes. This microstructural change enhances the stress transfer between the polymer and the nanotubes. The hot-drawn fibers are radically stronger and absorb much more energy at lower strain. Furthermore, because crystalline PVA does not dissolve in water at room temperature, the treated fibers retain their mechanical properties in humid conditions and do not become bloated, even when submerged.

Even stronger fibers are a possibility. "The nanotubes are still not as well-aligned as the PVA chains are," said Miaudet, "but this problem may be solved if we use straighter or less entangled nanotubes. It is predicted that the Young's modulus will grow by an order of magnitude during the last degrees of alignment."

RICH LOUIE

### Single Screw-Sense Cylindrical Nanoshutter Driven by Thermal and Solvent-Polarity Changes

Molecular motors are nanomachines that perform work by transforming low-input energy sources, such as thermal energy or solvent-polarity changes, into mechanical motion. Potential applications for nanomotors include data storage, optical devices, and liquid-crystalline displays. Recently, researchers from the Department of Chemistry at North Carolina State University (Raleigh, N.C.), and the Department of Chemistry at Vanderbilt University (Nashville, Tenn.) developed a new model for a nanomotor—a cylindrical shutter consisting of a thermal and solvocontrollable switching polyguanidine derivative—in which the switching phenomena does not involve inversion of the polymer backbone.

As reported in the November 11, 2005, issue of *Angewandte Chemie International Edition* (p. 7298; DOI: 10.1002/anie.200501977), North Carolina State University researcher B.M. Novak, Vanderbilt University researcher P.L. Polavarapu, and co-researchers used helix-sense-selective polymerization to synthesize the species shown in Figure 1, which is chiral because the backbone possesses a single-handed screw sense and the anthracene and imine are stereoregular. While complete racemization requires high temperatures and long periods of time (nearly 80°C and >100 h), switching of electronic circular dichroism (ECD) and UV-vis spectra occurs within seconds at moderate temperatures. At 38.5°C, the Cotton effect (i.e., the production of circular birefringence under electromagnetic radiation) at 382 nm in ECD spectra switches from positive to negative. Similarly, UV-vis spectra show a strong absorption at 382 nm at 25°C, but a weaker absorption at 60°C. Concomitant switching of the vibra-

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