

Bandgap Fluorescence of Carbon Nanotubes Observed

Members of the fullerene family of materials have been the subject of intense research due to their novel physical and chemical properties. Optical studies of carbon nanotubes have been hampered by the tendency of these materials to aggregate into bundles. Richard Smalley, R. Bruce Weisman, and their co-workers in the Department of Chemistry at Rice University have reported a separation methodology that produced aqueous suspensions of single nanotubes encased in a nonperturbing layer of sodium dodecyl sulfate (SDS) surfactant, allowing the optical properties of single nanotubes to be studied (see figure). These isolated single-walled carbon nanotubes were found to exhibit structured absorption and photoluminescence (PL) in the near-IR region. Both the absorbance and PL were affected by reversible protonation of the nanotubes in solution. According to Smalley, "optical activity in the near-IR [spectrum] implies potential applications in the fiberoptic communications and bio-imaging technologies."

The synthesis and purification of the individual nanotubes were described in the July 26 issue of *Science*. The researchers synthesized the nanotubes in a high-pressure CO reactor. The raw nanotube product was sonicated in an aqueous dispersion of SDS to break up the nanotube bundles. The single nanotubes were then separated from the remaining bundles by centrifugation and dispersed in deuterium oxide for spectroscopic studies. Atomic force microscopy showed that the sonicated nanotubes varied in length from 80 nm to 200 nm with an average length of 130 nm, an expected distribution for heavily sonicated nanotubes. The absence of damage to the nanotube walls was confirmed by Raman spectroscopy.

The absorption spectra of the isolated single nanotubes showed spectral structure that was enhanced and blueshifted compared with those of nanotube bundles. The nanotubes were also found to display bright, structured photoluminescence with a quantum yield of 0.1%. The PL peaks closely matched the absorbance peaks, indicating that the PL comes from the nanotubes. It was found that protonation of the nanotube side walls at pH <5 resulted in the broadening of absorption spectral structure and the loss of PL. Absorption spectral structure and PL intensity were restored following removal of the adsorbed species by adjusting the pH to >7, or irradiating the suspension with UV light to induce photo-

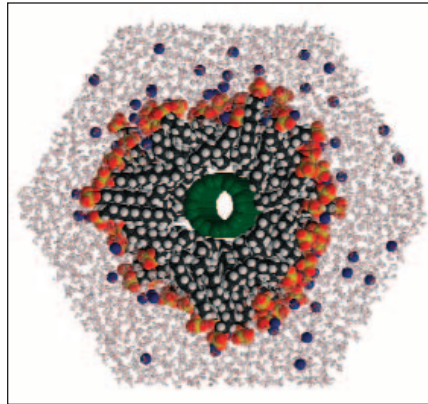


Figure. Molecular dynamics simulation of a single nanotube encased in a micelle of sodium dodecyl sulfate in water. Such nanotubes were found to exhibit photoluminescence at near-IR wavelengths.

desorption. As part of a continuing effort to understand fullerene-based materials, the Smalley and Weisman groups are currently investigating the electronic structure of isolated single-walled nanotubes through detailed spectroscopic analysis.

GREG KHITROV

Alternative Fabrication Process for Nanostructured Alloys Promises Dramatic Cost Reduction

The improvement in mechanical properties achieved by materials with ultra-fine-sized grains represents an advantage for many advanced applications. One of the typical properties of these materials is superplasticity: Although superplasticity is observed at half of the melting temperature in materials with micrometer-sized grains, it is observed at lower temperatures in materials with nanometer-sized grains. Fabrication of these materials is usually accomplished using vapor-phase condensation, high-energy ball milling, or severe plastic deformation. The first two methods are used mainly to produce fine powders and the last to produce bulk material. However, these processes are costly, and plastic deformation in particular is still in development for large-scale production. An alternative fabrication method has now been proposed by a group of scientists from Purdue University in a rapid communication in the October issue of the *Journal of Materials Research*. It is based on the large shear strains experienced by a material forming chips during machining, which makes the chips nanocrystalline. In order to demonstrate this, the scientists performed electron microscopy observations

in chips from a wide range of metals and alloys: oxygen-free high-conductivity (OFHC) copper, iron, low-carbon steel (1018), stainless steel (316L), martensite steel (AISI 52100), and nickel.

The shear plane formed between the machining tool and the surface of the bulk material defines the area where deformation occurs. The machining parameters chosen by the researchers minimized the increase in temperature in the shear plane in all cases. Chips thus produced were 100–3000 μm wide, 100–1000 μm thick, and no less than 5 mm long. Observations in the transmission electron microscope (TEM) of OFHC copper samples showed elongated grains with an average width of 175 ± 100 nm and an average length of 685 ± 190 nm. All grains had sizes of <1000 nm. Observations also revealed a high density of dislocations and both small- and large-angle grain boundaries. These features are characteristic of severely deformed nanocrystalline microstructures. Chips made from iron and different types of steel also showed similar microstructures.

Hardness values of the chips show significant increases compared with those of the bulk materials—150% in stainless steel, 200% in OFHC copper and iron, and 225% in nickel—typical for nanocrystalline microstructures. Chip hardness values rose to levels comparable to those of the similar nanocrystalline materials obtained using traditional fabrication methods. Furthermore, after conducting a special "quick-stop" test, the researchers were able to measure the increase in hardness in an OFHC copper chip while it was still attached to the bulk material. The researchers detected a sudden increase in Vickers hardness across the shear plane section, from 57 kg/mm² in the bulk to 150 kg/mm² in the chip. At the magnification where bulk grains were resolved using TEM, the researchers were not able to observe any grain structure in the attached chip.

The researchers also demonstrated that the cost involved in fabricating nanocrystalline chips from machining bulk materials is of the order of a few dollars per pound on top of the cost of the bulk material, which represents a tremendous reduction from traditional processes that can cost more than \$100 per pound. Bulk materials could be synthesized from chips thus obtained by means of powder metallurgy, ball attrition, or jet milling. Different methods to fabricate metal-matrix and polymer-matrix composites could also take advantage of these inexpensive nanocrystalline chips.

SIARI S. SOSA