Optical Limiting Displayed by Polymer Films with Ag Nanoparticles Grown *In Situ*

Assemblies of metal nanoparticles within polymer or sol-gel films have nonlinear optical applications such as optical limiting. Typically, such films are cast from a mixture containing preformed nanoparticles, but with current concerns about the health hazards of inhalable nanoparticles, the growth of nanoparticles in thin films *in situ* is preferable. T.P. Radhakrishnan of the University of Hyderabad, S. Singh of the Centre for Cellular and Molecular Biology in India, and their colleagues have developed such a method that uses chemical reduction to form metal nanoparticles within a polymer matrix.

As reported in the January 11 issue of *Chemistry of Materials* (p. 1; doi: 10.1021/cm0485963), the researchers fabricated a poly(vinyl alcohol) (PVA) film with silver nanoparticles grown *in situ*. The simple fabrication process, which uses environmentally friendly materials, has three steps. First, an aqueous mixture of silver nitrate and PVA is spin-coated to a thickness of 400–500 nm onto quartz substrates or glass slides previously coated with polystyrene (PS). In the second step, silver nanoparticles are generated by heating the silver nitrate/PVA films in ambient atmosphere at temperatures ranging from 50°C to 110°C for 5–60 min. PVA acts as both the reducing agent for the silver nitrate and the matrix for homogeneous distribution and immobilization of the silver nanoparticles. In the third step, freestanding films are peeled off the PS substrate. The films are transparent and colorless, but increasing amounts of silver nanoparticles result in a yellow color.

Radhakrishnan and co-researchers performed optical absorption studies (on films formed on glass substrates) to show that nanoparticle production increases with heating times up to a saturation point of ~1 h. The researchers said that a decrease in particle size is shown by a steady but slow blueshift in the absorption maxima with increasing heating time. In addition, the decrease in linewidth observed with heating time demonstrates that particle size becomes more monodisperse with heating. Transmission electron micrographs (with electron diffraction) revealed that films heated for 60 min at 90°C have small particles (with a mean diameter of 2.6 nm) and a tight distribution (estimated standard deviation of 0.2 nm). The researchers said that the particle size can be fine-tuned with temperature and that the average diameter and size distribution of the particles both increase as the silver nitrate concentration increases.

Z-scan measurements at 532 nm demonstrated that the films show strong reverse-saturable absorption at high laser intensities. The researchers also observed appreciable optical limiting with a threshold (defined as the input fluence at which the transmittance reduces to half of the linear transmittance) of 0.83 J cm^{-2} and output clamped at 0.35 J cm^{-2}. The researchers said their method can be easily extended to other metal–polymer and semiconductor–polymer systems that will facilitate device development for optical limiting and other nonlinear optical and sensor applications.

STEVEN TROHALAKI

Nanotubes Fluoresce within Biological Cells

In work documenting the uptake of carbon nanotubes by living cells, a team of chemists and life scientists from Rice University and the University of Texas Health Science Center at Houston, and the Texas Heart Institute have selectively detected low concentrations of nanotubes in laboratory cell cultures. The research suggests that white blood cells incubated in dilute solutions of nanotubes treat the nanotubes as they would other extracellular particles—actively ingesting them and sealing them off inside chambers known as phagosomes.

"Our goal in doing the experiment was both to learn how the biological function of the cells was affected by the nanotubes and to see if the fluorescent properties of the nanotubes would change inside a living cell," said lead researcher B. Weisman, professor of chemistry at Rice. "On the first point, we found no adverse effects on the cells, and on the second, we found that the nanotubes retained their unique

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optical properties, which allowed us to use a specialized microscope tuned to the near-infrared to pinpoint their locations within the cells."

Weisman, Paul Cherukuri of the Texas Heart Institute, and their colleagues reported their research in the December 8, 2004, issue of the *Journal of the American Chemical Society* (p. 15638; doi: 10.1021/ja0466311). The researchers cultured mouse macrophage cells in solutions containing between 0 ppm and 7 ppm single-walled carbon nanotubes (SWNTs) for periods of up to 96 h. They found that the amount of SWNTs taken up by the cells increased smoothly as the concentration or the time of exposure increased. In addition, some cells cultured at cooler temperatures showed a slower rate of uptake, a finding that suggested that the nanotubes were being ingested through normal phagocytosis.

The samples were studied using a spectrofluorometer and a fluorescence microscope that was modified for near-infrared imaging by the addition of a digital camera containing InGaAs detector elements.

Not only did the nanotubes retain their optical signatures after entering the white blood cells, but the introduction of nanotubes caused no measurable change in cell properties like shape, rate of growth, or the ability to adhere to surfaces.

The new findings demonstrate that SWNTs might be valuable biological imaging agents, in part because SWNTs fluoresce in the near-infrared portion of the spectrum, at wavelengths not normally emitted by biological tissues. This may allow light from even a handful of nanotubes to be selectively detected from within the body. This option may prove particularly beneficial in cases where the bleaching, toxicity, and degradation of more traditional markers are problematic.

Copper Oxide Nanotube Arrays Produced by MOCVD Process with Template

Because of the tremendous improvement in chemical properties resulting from the incorporation of nanostructured materials, inorganic nanostructures have been extensively studied for applications such as electrical contacts, catalytic gas-sensing devices, and solar cells. Various techniques, including metalorganic chemical vapor deposition (MOCVD), have been attempted for synthesizing inorganic (metal, oxide, halide, and chalcogenide) nanotubes or nanowires. Researchers are now trying to achieve the synthesis of CuO nanotubes by a simple and reproducible method using a so-called "template" to help create well-aligned nanostructures, which may have applications in devices containing copper oxide thin films or as cathode materials in lithium copper oxide electrochemical cells. In the December 28, 2004, issue of *Chemistry of Materials* (p. 5559; doi: 10.1021/cm048685f), researchers from Università di Catania in Italy announced that they have grown homogeneous CuO nanotube arrays on a template by MOCVD.

G. Malandrino of Università di Catania and colleagues used anodic aluminum oxide membranes as a template. The 60-µm-thick template consists of a precise, non-deformable structure, with pores 200 nm in diameter arranged in a hexagonal array. The membrane was positioned vertically in a hot-wall reactor and maintained at 400°C. Oxygen and argon were used as the reaction gas and carrier gas, respectively. The $Cu(tmhd)_2$ (Htmhd = 2,6,6,6-tetramethyl-3,5-heptandione) source was sublimed at 100°C. The deposition was carried out for 3 h at a total pressure of 2 Torr.

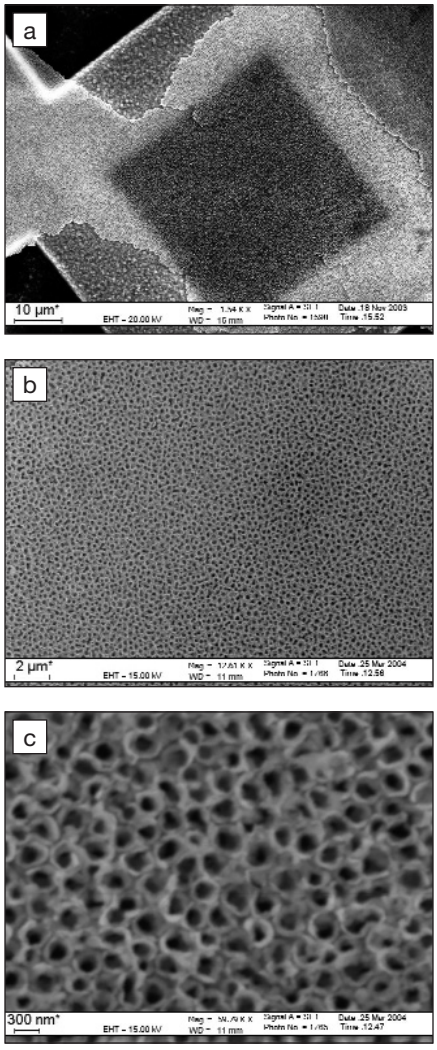

Figure 1. Freestanding CuO nanotube arrays: (a), (b) low-magnification plan-view scanning electron microscopy images of the CuO nanotube sheet; and (c) high-magnification plan view of the nanotube sheet. Reprinted with permission from Chemistry of Materials ***16*** *(26) (2004) p. 5559. © 2004 American Chemical Society.*

Scanning electron micrographs show that the outer diameters of the CuO nanotubes are ~250 nm and the wall thicknesses are ~40 nm. The nanotubes are ~1 µm long. The researchers said that the characteristic pore dimensions of the template membrane influence the diameters of the nanotubes, whereas the length of the nanotubes depends on the process conditions. Furthermore, according to the researchers, the template can be completely removed by dissolving it in a NaOH solution, resulting in freestanding CuO nanotube arrays (see Figure 1).

"To our knowledge, this is the first example of a regularly packed CuO nanotube array made through a rather straightforward process," said the researchers. The "transfer" of a well-assessed MOCVD procedure for the deposition of CuO films to analogue nanotubes, they assert, could open viable routes to the fabrication of nanotube arrays of various oxides.

SHIMING WU

Silicalite-1 Self-Supported Micromembrane Separates Propane/Nitrogen Gas Mixture

Zeolite membranes are used industrially as an aid during the pervaporation process for the dehydration of solvents. They are currently under development for applications such as the separation of certain gas/hydrocarbon mixtures, membrane reactors, and sensors, and heading toward applications in silicon-based microdevices. Among several constraints to take into consideration are the loss of separation selectivity at high temperatures and the high cost of the membranes, at more than \$2600 per m^2. Efforts are concentrated on developing small-scale membranes, which could potentially be single crystals with improved stability during fabrication and thermal cycling. Following this direction, E. Mateo and colleagues from the University of Zaragoza, Spain, have created arrays of micromembranes of silicalite-1 on a stainless steel sheet, which they reported in the November 30, 2004, issue of *Chemistry of Materials* (p. 4847; doi: 10.1021/cm048504+).

The investigators fabricated the silicalite-1 powders for seeding, starting from a solution of tetrapropylammonium hydroxide (TPAOH), tetraethyl orthosili-