

Self-Assembly at a Liquid-Liquid Interface Yields High-Quality Photonic Crystals

Photonic crystals, a key component in optical devices, can be fabricated using colloidal particles with diameters on the order of the wavelength of light. In the November 28, 2006, issue of *Chemistry of Materials* (p. 5643; DOI: 10.1021/cm0615525), S. Takeda and P. Wiltzius of the University of Illinois at Urbana-Champaign demonstrated a method for fabricating colloidal polystyrene (PS) photonic crystals using self-assembly at the interface of water and a fluorinated solvent. This method is more robust than existing dip-coating methods and produces crystals with fewer defects.

In this method, a droplet of water containing PS microspheres (~466 nm diameter) was added to the surface of a fluorinated solvent bath. The solvent was chosen so

that it had density lower than water and surface tension higher than water. Consequently, the two liquids remained separated and the colloidal particles self-assembled into close-packed structures at the interface between them. After the water droplet and the ordered microspheres were transferred to a glass slide and allowed to dry, scanning electron micrographs and optical reflectance measurements revealed highly ordered crystals covering large areas of the substrate. Because of the high mobility at a liquid-liquid interface, the degree of ordering achieved using this method surpassed that of standard dip-coating methods in which the self-assembly occurs at a liquid-solid interface. Furthermore, using separate droplets containing PS microspheres of two different sizes (i.e., one droplet with 466 nm diameter microspheres and one

droplet with 240 nm diameter microspheres), the researchers coated both sides of a glass slide with crystals of different periodicities. The reflectance spectrum at visible and near-infrared wavelengths of this photonic crystal depends upon which side the light is initially incident. When light was incident on the side coated with the smaller microspheres, strong reflectance peaks were observed near 580 nm and 980 nm in wavelength. However, when the light was incident on the side coated with the larger microspheres, the shorter wavelength reflectance peak vanished. The researchers said that this asymmetry is due to the stronger scattering of the short-wavelength region by the 466 nm diameter microspheres. They also said that this structure could form the basis of an optical switch in which the switching is obtained by simply rotating the photonic

crystal device to present the different faces to the incident light.

This technique offers a new, potentially easier, and more effective approach for the fabrication of highly ordered photonic crystals than currently used. According to the researchers, further refinement of this method may yield even greater advantages by shortening fabrication time and further reducing defects.

KRISTA NIECE

New Coating Method Produces Arrays of Orthogonally Tilted Nanopores in Ceramic Films

Surfactant-templated thin mesoporous ceramic films with hexagonally close-packed (hcp) cylindrical nanopores aligned perpendicular to the substrate attract more interest than films with pores aligned parallel to the substrate surface in fields such as membrane separations, sensors, and catalysis, because their channels are accessible to larger solutes. V.R. Koganti and S.E. Rankin from the University of Kentucky, D. Dunphy of Sandia National Laboratories, V. Gowrishankar and M.D. McGehee from Stanford University, and X. Li and J. Wang from Argonne National Laboratory have demonstrated that a chemically neutral sacrificial copolymer layer directed the orientation of orthogonally tilted hcp pores in surfactant-templated silica and titania films.

As reported in the November 8, 2006, issue of *Nano Letters* (p.2567; DOI:10.1021/nl061992v), chemically neutral layers were formed by coating clean glass substrates with PEO-*r*-PPO copolymer (PEO—poly (ethylene oxide); PPO—poly (propylene oxide)) and cross-linking the films by an isocyanate hydroxyl reaction at 120°C overnight. Then, a film of silica sol was dip-coated onto the substrates, with P123 (PEO-co-PPO-co-PEO) as a surfactant pore template and tetraethyl-orthosilicate as a silica precursor. The films were aged and dried at 40°C for 24 h and 100°C for 24 h, and calcined in air at 500°C. The researchers controlled the thickness of the silica films by diluting the original sol in ethanol. Similarly, surfactant-templated titania films were produced by dip-coating titania sols, prepared by adding a solution of P123 in ethanol to a mixture of titanium(IV) ethoxide and concentrated HCl, onto PEO-*r*-PPO copolymer-modified surfaces. Titania films were aged in a highly humid environment at 4°C for 2 h and calcined at 400°C.

X-ray diffraction and grazing incidence small-angle x-ray scattering patterns confirmed that the films contained hcp chan-

nels tilted perpendicular to the substrate so long as the film thickness was below a critical value between 70 nm and 100 nm. Thicker films (up to 240 nm thick) could be completely oriented by sandwiching them between two PEO-*r*-PPO-modified substrates. Direct observation by electron microscopy corroborated these results.

Because the cross-linked PEO-PPO layer masks substrate-specific effects, the researchers said that orthogonally tilted hcp nanopore ceramic films can be deposited on substrates of any curvature and size onto or into which the PEO-PPO layer can be deposited. Other ceramic precursors may allow extension of this approach to other applications, including photovoltaics and fuel cells, with the added advantage that this is a cheap and rapid procedure that can be easily incorporated into micro-electronic fabrication processes.

JOAN J. CARVAJAL

Nanoparticles Conjugated with Tobacco Mosaic Virus Form Electronic Memory Device

The unique properties of nanostructured biomaterials make them ideal candidates for next-generation electronic nanodevices. Although electrical switching has been observed for nanoparticles incorporated into organic polymer thin films, electronic devices fabricated directly from biomaterials are largely unsuccessful due to a lack of charge transport. Recently, however, Y. Yang, C.S. Ozkan, and co-researchers from the University of California, Los Angeles, and the University of California, Riverside, have demonstrated an electronic memory effect in a device featuring inorganic-biomaterial composite nanowires.

As reported in an article recently published in the October 2006 issue of *Nature Nanotechnology* (p. 72; DOI: 10.1038/nnano.2006.55), Yang, Ozkan, and co-researchers formed nanowires by incorporating platinum nanoparticles (Pt NPs) with tobacco mosaic virus (TMV), which is rigid and tubular in shape with a length of about 300 nm, outer diameter of 18 nm, and inner diameter of 4 nm. Electroless deposition with a Pt-ion solution conjugated the NPs with TMV. Transmission electron microscopy and atomic force microscopy (AFM) showed that an average of about 16 Pt NPs per virus, with an average diameter of 10 nm, were evenly distributed over the TMV surface, although NP clustering was observed at each nanowire node. Photoelectron spectra showed that the primary binding site of the Pt NPs was the outer surface of TMV. The researchers followed a simple fabrication process: thermal

evaporation was used to deposit bottom aluminum electrodes onto a glass substrate; a thin film of Pt-TMV nanowires in an insulating poly(vinyl alcohol) (PVA) matrix was added by spin-coating; sandwiching the film with electrodes deposited onto glass completed the device. The thicknesses of the electrodes and thin films were determined with a profilometer to be 70 nm and 60 nm, respectively. The active area of the device was 0.04 mm².

Yang, Ozkan, and co-researchers showed that the nonlinear current-voltage (*I*-*V*) behavior exhibited by their device arises from bistable electrical states. An abrupt increase in current by more than three orders of magnitude (from 10⁻⁸ A to 10⁻⁵ A) was observed once a threshold bias of 3.1 V was reached. The stability of this "on," or high-conductance, state was demonstrated by a second scan. During a reverse scan from 0 to -5 V, the on-state was switched to the off, or low-conductance, state—that is, from 10⁻⁵ A to 10⁻⁷ A, at a turn-off bias of -2.4 V. Control devices, in which the PVA thin film contained either TMV or Pt NPs, did not display conductance switching.

From measurements of current and voltage as functions of temperature, the researchers deduced that the conduction mechanisms are thermionic injection in the off-state and charge tunneling in the on-state. Conductance AFM was also used to demonstrate conductance switching in a single TMV-Pt nanowire. The researchers programmed their device for repetitive write/read/erase cycles and found difficulty in returning to the off-state after about 400 cycles, which they believe was caused by degradation of the TMV-Pt interface due to Joule heating. An analysis of the temperature-dependence of the memory retention led the researchers to insights into the charge storage mechanism, which has implications on the potential of their device for commercialization. The researchers said that charge trap sites are located on the Pt NPs and that the TMV protein coating effectively acts as an energy barrier. The activation energy of the charge trap was calculated to be 0.15 eV, which the researchers noted is close to the charging energy of similarly sized NPs. Yang, Ozkan, and co-researchers said that the composition of the TMV core—RNA with aromatic rings rich with electrons—can act as charge donors; the function of the TMV is therefore not merely to provide a backbone for the organization of the NPs. The researchers said that "the retention stability and cycling endurance of the device could be further improved by introducing smaller-sized or other types of nanoparticles" and that "the concept of