

RESEARCH/RESEARCHERS

Organometallic Zinc Cages Open New Possibilities for Semiconductors

Spurred by the increasing use of nitride semiconductors such as GaN, AlN, and InGaN in optoelectronic, high-frequency, and high-power devices, there has been a lot of recent interest in finding single-source precursors to make these materials. Group 13 hydrazides are particularly attractive candidates for cleanly fabricating these important materials. However, not much is known about main-group hydrazides. In the February issue of *Chemical Communications* (DOI: 10.1039/b516431a; p. 523), C. Redshaw from the University of East Anglia (Norwich, U.K.) and M.R.J. Elsegood from Loughborough University (Loughborough, U.K.) reported the preparation of novel tetrametallic zinc cages, which are good starting materials for the synthesis of other interesting architectures.

By reacting 1,1'-dimethylhydrazine with diethylzinc, the researchers were able to obtain a Zn_4N_8 cage complex with two six-membered rings linked together by four five-membered rings. The lack of hydrogen bonding in these networks is expected to lead to improved conductivity for these materials. On reaction with *tert*-butyllithium, the cage-like structure of this novel hydrazide complex is disrupted, yielding a chain of Zn_4N_7 clusters bridged together by lithium. The structure of the lithiated compound was determined using high-intensity x-rays generated by the synchrotron at Daresbury Laboratory.

The researchers said that the Zn_4N_8 organometallic "cube" can potentially be used to prepare many other interesting structural motifs that have not been seen before. These hydrazide complexes are expected to be useful precursors for the improved fabrication of semiconductors.

SARBAJIT BANERJEE

Flexible Carbon Nanotube-Polymer Composites Display Excellent Electromechanical Properties

Carbon nanotubes are known to exhibit exceptional electrical and mechanical properties. To tap these qualities for useful applications, nanotube structures need to be organized into stable device architectures. In the March 8 issue of *Nano Letters* (DOI: 10.1021/nl052238x; p. 413), Y.J. Jung of Northeastern University, S. Kar of Rensselaer Polytechnic Institute, A. Avadhanula of New Mexico State University, and their colleagues have presented a method to obtain aligned and patterned multiwalled carbon nanotubes (MWNTs) embedded in a soft poly (dimethylsiloxane) (PDMS) matrix. The resulting composite is an extremely flexible thin film with valuable electromechanical properties.

An array of cylindrical pillars (diameter, ~500 μm ; height, ~100 μm) comprising vertically aligned MWNTs was grown on prepatterned SiO_2/Si substrates using thermal chemical vapor deposition (CVD) of ferrocene and xylene at 800°C. After pouring a prepolymer solution of PDMS on the substrate and curing at 100°C for 1 h, self-standing nanotube-PDMS composite thin films were peeled off from the substrate. By varying the CVD growth conditions and changing the quantity of PDMS backbone, the shape and size of these composites can be easily controlled. Because of good wettability of MWNTs by PDMS, the films are relatively defect-free.

For systematic measurements of resistance, titanium wires were embedded into the matrix while it was being cured. It was observed that the resistance of these films increases linearly with both tensile and compressive strain, making them suitable for strain and pressure sensors. Also, since the conducting nature of the composite is retained under strain, the composites can be readily used in flexible electronic devices. This was demonstrated by field-emission measurements of a composite cathode fabricated by coating the thin film with Ti/Au. A field-enhancement factor of $\beta \sim 19,100$ was obtained, with a current density of 1 mA/cm^2 for a threshold field of 0.76 $\text{V}/\mu\text{m}$, which is extremely desirable for flexible field-emission devices.

TUSHAR PRASAD

Symposium

Active Nanophotonic Devices

Photonic Crystals, Ferroelectrics, Optofluidics, Plasmonics, Spintronics, and Quantum Dots

Sunday, May 21, 2006

Beckman Institute Auditorium
California Institute of Technology
Pasadena, California

Nanophotonics is rapidly developing as an integrated device technology, and is impacting applications in high speed communication systems, chemical sensing, pathogen detection, cancer research, genomics and proteomics. The significant progress in nanophotonics is related to the development of active devices whose sizes are at or below the scale of the optical wavelength. This Symposium at Caltech brings leading academic researchers in this field together with industrial scientists and investors. The day-long program will feature lectures, panel discussion and substantial opportunities for informal interactions with Symposium participants.

8:00–9:00 a.m. Registration

Amnon Yariv (Caltech)
21st Century Photonics

Axel Scherer (Caltech)
Nanophotonics and Fluidics Integration

Kaushik Bhattacharya (Caltech)
Ferroelectric Nanophotonic Devices

10:45–11:00 a.m. Coffee Break

11:00–12:00 p.m. Industrial Panel
Dwight Streit (Northrop-Grumman)

12:00–1:30 p.m. Lunch and Poster Session

Eli Yablonovitch (UCLA)
What is the Limit of Focusing Light?

Harry Atwater (Caltech)
Plasmonics: A Route to Nanoscale Optical Devices

Oskar Painter (Caltech)
Photonic Crystal Devices

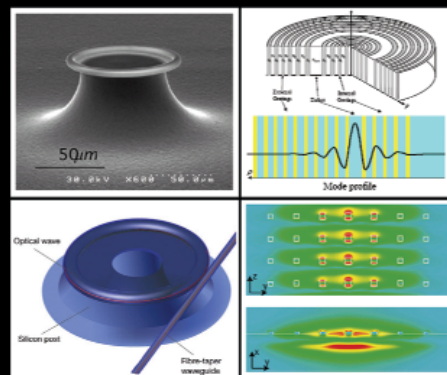
3:15–3:45 p.m. Coffee Break

Stan Williams (Hewlett Packard)
Nanophotonics Research at HP Labs

Nai-Chang Yeh (Caltech)
Novel Organic Heterostructures for Spintronic and Optoelectronic Applications

Kerry Vahala (Caltech)
Ultra High-Q Micro-Toroid Resonators

6:00–8:00 p.m. Dinner with Special Guest Speaker
Join us for an opportunity to network with the speakers and attendees



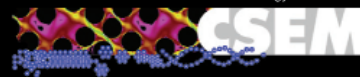
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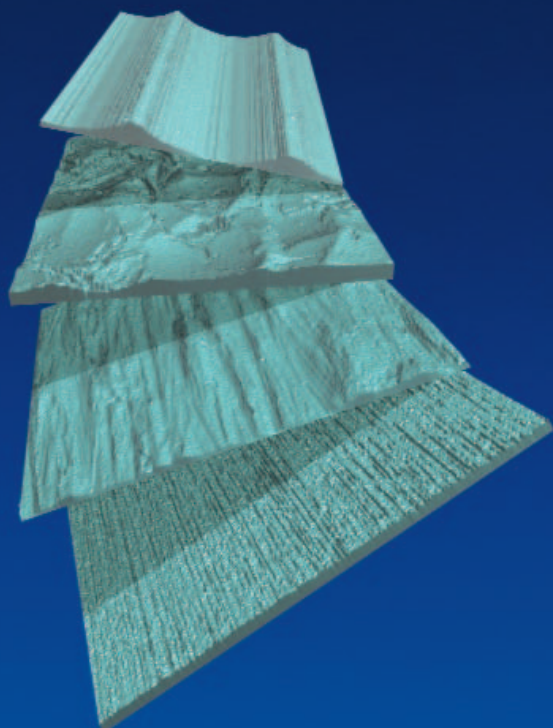
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Foldamer Made Photoswitchable

Foldamers are molecules that reversibly switch between folded and unfolded conformations in response to changes in temperature or solvent composition. The dynamic nature of this reversible conformational change makes foldamers suitable for responsive materials in biological and nanoscience applications. Foldamers that respond to light are desirable because the stimulus is noninvasive and its location, intensity, and timing can be controlled. Toward this end, researchers from Max-Planck Institut für Kohlenforschung in Germany have developed the first example of a photoswitchable foldamer (see Figure 1).

As reported in the March 13 issue of *Angewandte Chemie International Edition* (DOI: 10.1002/anie.200503849; p. 1878), MPI researchers A. Kahn, C. Kaiser, and S. Hecht incorporated a photoisomerizable core connecting two strands of a foldamer—amphiphilic oligo(*meta*-phenylene ethynylene)—previously developed and reported in the literature. The *trans*-azobenzene core mimics a dimer repeat unit of the foldamers. Irradiation at 365 nm converts the azobenzene core conformation from *trans* to *cis*. The researchers deliberately chose foldamer chain lengths that are not long enough to individually fold into helices or with the core in a *cis* conformation but that will form a helix when connected, that is, by the core in a *trans* conformation (see Scheme 1). The researchers also introduced enantiomerically pure (*S*)- α -methyl(ethylene glycol) side chains to bias the sense of the helix and thereby allow them to monitor the conformational transition with circular dichroism spectroscopy. While the photochemical helix-coil unfolding transition occurs in seconds, thermal reversion at room temperature takes place over several hours.

The researchers said that the light-triggered foldamer system they developed not only “can provide fundamental insight into the folding and unfolding mechanisms by enabling time-resolved measurements but promises applications in smart delivery devices based on photoresponsive dynamic receptors.”

STEVEN TROHALAKI

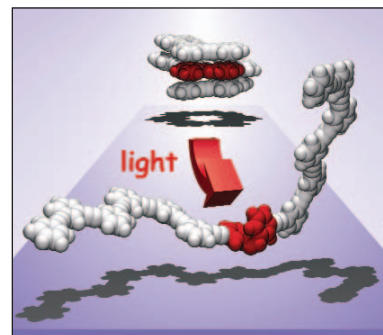
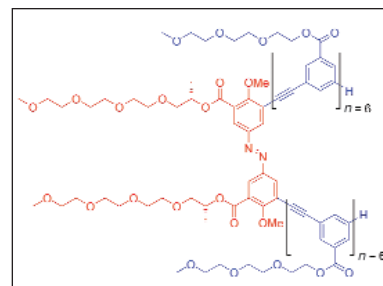


Figure 1. Irradiation of the photoisomerizable core (red) in the center of a helically folded backbone (blue) induces a reversible helix-coil transition. (Courtesy of S. Hecht and R.S. Stoll.)



Scheme 1. Molecular structure of the photoswitchable foldamer includes the azobenzene core (red) and the two foldamer strands, amphiphilic oligo(*meta*-phenylene ethynylene) (blue).

Layer-by-Layer Assembly Technique Used to Study Fluorescence Quenching by Gold Nanoparticles

Functionalized metal nanoparticles are of great interest for fluorescence-based sensing and biomedical diagnosis and treat-

ment. In the case of metal-polymer core-shell structures, the fluorescence of the organic dye may be quenched because of complex interactions with the metal core. To study the effect of separation distance on fluorescence quenching, G. Schneider and G. Decher of Institut Charles Sadron and Université Louis Pasteur, along with N. Nerambourg, R. Praho, M. Werts, and M. Blanchard-Desce of Université de Rennes, have described an approach in which up to 20 polyelectrolyte layers (the last layer being fluorescently labeled) were coated on gold nanoparticles. The core-shell distance was altered by tailoring the thickness of adsorbed, non-fluorescent polymers, which were used as spacer layers in the core-shell structure.

As reported in the March 8 issue of *Nano Letters* (10.1021/nl052441s; p. 530), gold particles (diameter, 13 nm) were synthesized by the reduction of tetrachloroauric acid with trisodium citrate. Spacer layers of polyallylamine hydrochloride (PAH) and polystyrene sulfonate (PSS) were adsorbed consecutively using electrostatic layer-by-layer assembly to obtain gold nanoparticles coated with 2, 10, and 20 layers of Au(PAH/PSS)_n. Fluorescein

isothiocyanate (FITC) and lissamine rhodamine B sulfonyl chloride (LISS) were covalently attached to PAH to obtain PAH-FITC and PAH-LISS, which were then adsorbed onto the Au(PAH/PSS)_n core-shell particles, followed by the adsorption of a final PSS layer. After each coating step, the particles were washed thoroughly by successive centrifugation/re-suspension cycles. Transmission electron microscopy and *in situ* UV-visible absorption spectra were used to characterize the structural and photophysical properties of the nanoparticle dispersions.

The researchers said that the addition of dye-functionalized polyelectrolytes does not perturb layer growth or the aggregation state of the solution. For $n > 5$ layers, the surface plasmon resonance from the gold particles reaches a fixed position and intensity, 534 nm in the case of PAH-FITC and 533 nm for PAH-LISS, and obscures the dye-related absorption bands. The surface-plasmon band was removed by slow dissolution of the gold core by adding cyanide ions to the solution. Dissolution of the gold core is accompanied by a strong increase in fluorescence, and reveals the weak dye-related absorption band.

Fluorescence quenching is distance-dependent and remained significant 8 nm from the metal core. The fluorescence quenching seems to be caused by a decrease in radiative transition probabilities induced by the gold core. The researchers said that despite quenching, dye fluorescence remains sufficiently bright for diagnostic and sensing applications.

JEREMIAH T. ABIADÉ

Highly Porous Inorganic Thin Films Formed Using Polymer Microsphere Templates

The use of colloidal templates as self-assembled building blocks for fabricating ordered submicrometer structures of various materials has been explored in recent years. These templates have been used to fabricate photonic crystals and synthesize catalysts and sensors. However, synthesis of compounds with complex compositions using this method has been difficult due to the wet chemical techniques used and the ability of the chemicals to infiltrate the voids between the colloids with the precursors. A study done at the Massachusetts Institute of Technology has now demonstrated the successful application of



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microsphere templating for fabricating macroporous $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) thin films using pulsed laser deposition (PLD) on poly(methyl methacrylate) (PMMA) templated substrates. The polymer microspheres are removed by thermal decomposition, and the residual inorganic films have unique morphologies comprising hollow hemispheres of the inorganic material with large surface areas and surface-to-volume ratios. I.-D. Kim, A. Rothschild, and co-workers reported the preparation of the CCTO thin films, as well as gas-sensitivity measurements for possible sensor applications, in the February issue of *Nano Letters* (DOI: 10.1021/nl051965p; p. 193).

Given its extraordinarily high dielectric constant and nonlinear I - V characteristics, CCTO was expected to make an excellent sensor when interacting with reactive gases. To prepare the CCTO films, an aqueous solution of 800-nm diameter PMMA microspheres was dripped onto Al_2O_3 substrates which had interdigitated Pt electrode arrays and then dried overnight. CCTO films were then deposited onto the microsphere-templated substrate using PLD. The samples were calcined in air at 800°C for several hours to remove the PMMA microspheres. The resultant intact films were 80–90 nm thick and consisted of a monolayer of hollow CCTO hemispheres with ~800-nm diameters, as shown in Figure 1. Good chemical bonding between the film and substrate was observed. X-ray diffraction measurements showed that the films were single-phase polycrystalline CCTO.

A network of voids between the film and substrate allowed easy gas access to the internal surfaces of the hemispheres. The specific surface area was twice as large and the surface area four times as large as films on untreated substrates due to the hemispherical morphology and the voids—very favorable for gas sensor applications. Electrical property measurements demonstrated highly nonlinear I - V characteristics with strong thermal activation. The macroporous CCTO films were tested for sensitivity to H_2 , CO, and CH_4 gases between 200 – 400°C and were found to be very sensitive to H_2 . In contrast, the sensitivity of films deposited on untreated substrates to H_2 was negligible. The large surface area clearly promoted interactions with the gas while the relatively smaller interfacial area reduced the adverse effects of the interface between the film and the substrate. The limit of detection was determined to be about 55 ppm at a temperature of 300°C , comparable to the detection limit of commonly used commercial Taguchi H_2 sensors. The responsivity of

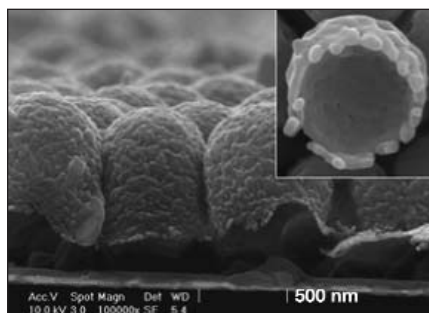


Figure 1. Scanning electron micrograph shows a cross-sectional view of the macroporous $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) film formed following calcination at 800°C . The inset shows one hollow CCTO hemisphere. (Courtesy of Avner Rothschild, MIT.)

the macroporous films to H_2 was also found to be reversible.

The researchers said that in view of the simplicity of this approach, which can be applied to a wide range of materials and deposition techniques, and the remarkable improved performance, this processing strategy holds promise for chemical sensors, fuel cells, catalysts, and other electrochemical devices for energy conversion, environmental protection, and other applications. The technique has the ability to control parameters such as porosity, composition, and film thickness as well as form multilayered structures of compounds with complex chemistries and therefore is very versatile.

The research team's future plans include extending this work to other materials commonly used for gas sensing, such as SnO_2 , TiO_2 , and ZnO , and examining the role of processing conditions on microsphere morphology and correspondingly on the sensing properties. The researchers will also investigate the negligible responsivity of the macroporous films to gaseous CO and CH_4 .

GOPAL RAO

CdSe/CdS QD-LEDs Fabricated Using a Thermally Polymerized Hole-Transport Layer

By spin-coating CdSe/CdS quantum dot solutions onto thermally cross-linkable hole-transport layers (HTLs), a team of researchers at the University of Washington fabricated multilayer nanocrystal quantum dot light-emitting diodes (QD-LEDs) with external quantum efficiencies (EQEs) of ~0.8% that exhibit spectrally pure QD emission. This method enables researchers to incorporate high-quality QD layers of varied thickness into devices

with multiple solution-processed organic hole-transport layers and no organic background emission.

In the March issue of *Nano Letters* (DOI: 10.1021/nl052417e; p. 463), the research team, led by A.K.-Y. Jen and D.S. Ginger, reported progress in the fabrication of efficient CdSe/CdS QD-LEDs. The researchers first spin-coated the cross-linkable HTL, polystyrene- N,N' -diphenyl- N,N' -bis(4- n -butylphenyl)-(1,1'-biphenyl)-4,4'-diamine-perfluorocyclobutane (PS-TPD-PFCB), onto a plasma-cleaned indium tin oxide (ITO) slide and then heated it in nitrogen to activate the cross-linking process in the HTL. After cross-linking the PS-TPD-PFCB, the researchers spin-coated a layer of CdSe/CdS QDs (average diameter, 4.6 nm) from a chloroform solution onto the HTL. They then deposited the electron transport layer, 1,3,5-tris(N -phenylbenzimidazol-2-yl)benzene (TPBI), on the QD layer by thermal evaporation. They completed the devices by thermal evaporation of the back electrode (Ca/Ag).

The thermally cross-linked HTLs possess a high glass-transition temperature (T_g ~ 150°C) and are solvent-resistant, factors which make it easy to add additional device layers such as emissive QDs by solution processing. Using atomic force microscopy (AFM), the researchers found that the surface of the polymerized PS-TPD-PFCB HTL is very smooth and provides a compatible hydrophobic surface for the formation of uniform and pinhole-free layers of QDs over comparatively large areas. The researchers compared the QD-LEDs with different CdSe/CdS QD coverage in the active region. They observed that the device efficiency increases with increasing QD coverage until one monolayer (ML) of dots has been deposited; then it decreases rapidly to 0.1% when the QD layer is more than 3 ML thick. The researchers also observed a substantial decrease in EQE with increasing current density. They attributed these phenomena to slow dot-dot charge transport and a carrier imbalance or charge-induced quenching, respectively. The researchers found they could further improve the EQE of the LEDs by using a second (cross-linkable) HTL on top of the PS-TPD-PFCB layer. The EQE of these QD-LEDs is improved to 0.8% at a brightness of 100 cd/m^2 and the maximum brightness is improved to more than 1000 cd/m^2 . The researchers suggested that optimizing the energy levels and better balancing carrier transport and injection into the QD emissive layer may further improve the performance of these QD-LEDs.

TAO XU

Electric-Field-Driven Jetting Phenomenon Applied to Process Living Cells

Although recent advances have made inkjet printing of biological samples possible, concentrated suspensions pose a problem: the lower limit of the droplet diameter is about twice the internal diameter of the needle orifice, resulting in blockage in needles with diameters of 30 μm or less for the production of $\sim 60 \mu\text{m}$ droplets. In practice, inkjet printing has a resolution of $\geq 100 \mu\text{m}$ due to droplet spreading.

Electrohydrodynamic jetting (EHDJ), also known as electro spraying or electrostatic atomization, however, has been shown to produce droplets in the nanometer-to-micrometer size range from concentrated suspensions. In EHDJ, a charged medium exiting a needle enters a high-intensity electric field, thereby producing jets, which then initiate droplet formation through nonlinear processes. In inkjet printing, by contrast, a current is used to flex a piezoelectric crystal within a needle, thereby promoting droplet formation or, alternatively, ultrasound is used to create waves that generate droplets. Recently, researchers from the Mechanical Engineering Department at University College London and the Randall Division of Cell and Molecular Biophysics at Kings College

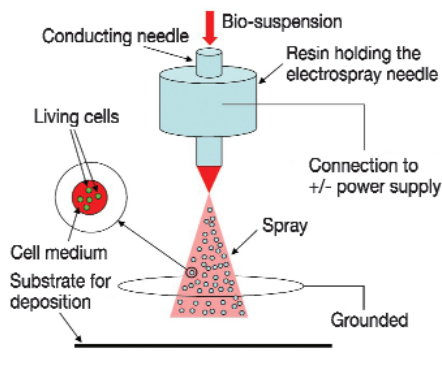


Figure 1. Schematic of the electrohydrodynamic jetting equipment.

London have demonstrated that EHDJ can be used to deposit living cells in suspension onto surfaces in droplets $< 40 \mu\text{m}$ in diameter ($< 100 \mu\text{m}$ after spreading). Moreover, the cells remain intact and viable after electro spraying.

As reported in the February issue of *Small* (DOI:10.1002/sml.200500291; p. 216), University College London researcher S.N. Jayasinghe and Kings College London researchers A.N. Qureshi and P.A.M. Eagles electro sprayed a suspension of Jurkat cells (a common cell line derived from human T-cell leukemia)

using the apparatus shown in Figure 1. The medium was charged by syringing at a flow rate of $10^{-8} \text{ m}^3 \text{ s}^{-1}$ through a needle kept at positive potential with respect to the ground electrode and was immediately dispersed upon entering the external electric field 0.85 kV mm^{-1} in strength. Sparks discharging between the needle and the ground electrode were observed periodically. The polydisperse droplet size distribution, which was measured by a laser spectrometer, showed large peaks at $\sim 17 \mu\text{m}$ and $\sim 37 \mu\text{m}$. The researchers used a $40\times$ phase objective on an inverted microscope to examine the electro sprayed sample and observed that the cells appeared normal. About 2 h after electro spraying, optical microscopy revealed no signs of cellular damage. Incubation of several samples of electro sprayed cells for 24 h showed no adverse effects on cell division. The researchers also took samples of other types of cells (including primary cells) through a similar electro spraying protocol and found no adverse effect on the cells' structure, activity, or rate of division.

The researchers said that "the electrohydrodynamic jet processing phenomenon is strongly placed for competing with inkjet technology in the race to develop biological tissues for repair."

STEVEN TROHALAKI

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