## Magnetic Nanoparticles Assembled by Micromanipulation of Magnetotactic Bacteria

A variety of methods have been developed to pattern nanocrystals and assemble them into desired nanostructures. Examples include the formation of singleelectron devices by trapping semiconducting nanoparticles between electrodes and the use of biomineralization by genetically engineered viruses to construct ordered nanostructures. Magnetic nanoparticles can function as singledomain magnets and have applications in spintronics, magnetic memory, and drug delivery. Previously, magnetic nanowires were self-assembled by taking advantage of their large aspect ratios. In addition, magnetic properties have been used to assemble magnetic microstructures. H. Lee, R.M. Westervelt, and coworkers from Harvard University have used microelectromagnets and microfluidics to control the motion of magnetotactic bacteria, which grow intracellular magnetic nanoparticles through a biomineralization process, and have thereby assembled magnetic nanoparticles into ordered structures.

As they reported recently in *Nano* Letters (Web release date, April 8), Westervelt and co-workers selected the magnetotactic bacteria Magnetospirillum magnetotacticum, which grow intracellular, spherical, magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles contained within a phospholipid membrane. The 50 nm nanoparticles, which have a narrow size distribution and act as single-domain permanent magnets, are typically assembled into single or multiple chains that are anchored within the cell. Using either optical or electron-beam lithography, the researchers fabricated two types of microelectromagnets on a Si/SiO<sub>2</sub> substrate: a ring trap, which consists of a wire following a circular path and an insulating layer; and a matrix, which consists of two perpendicular arrays of straight conducting wires that are separated and capped with insulating layers.

The researchers used soft lithography to fabricate the microfluidic chamber from poly(dimethylsiloxane) with dimensions chosen to minimize viscous drag on the bacteria. After treating both the electromagnets and the chamber with O<sub>2</sub> plasma to render the surfaces hydrophilic, the researchers conformally sealed the chamber on top of the microelectromagnets. Currents were chosen such that the magnitude of the magnetic field was about 0.1 T, which enabled stable trapping of the bacterium, each of which have a magnetic moment of about 10<sup>-15</sup> A m<sup>2</sup>,

## **Carbon Nanotubes Used as Nanoscale Mass Conveyors**

The very concept of nanotechnology necessitates nanofabrication, including the manipulation and transport of atoms and molecules. Scanning probe techniques have already been used to manipulate atoms and molecules on surfaces, but they cannot efficiently move atoms from a distant reservoir to a work area. Carbon nanotubes have been proposed as conduits for transporting nanoscale volumes of materials because of their hollow cores and large aspect ratios. B.C. Regan, A. Zettl, and their co-workers at the University of California, Berkeley, and Lawrence Berkeley National Laboratory have demonstrated controllable mass transport along carbon nanotubes using indium as the mass transport species. Controllable mass transport of gold, platinum, tin, and tin indium alloy was also demonstrated.

As reported in the April 29 issue of *Nature* (p. 924), indium metal was thermally evaporated onto a boule of arc-grown multiwalled carbon nanotubes (MWNTs) decorating them with isolated In nanocrystals. The boule was then placed in a transmission electron microscope (TEM) that included a nanomanipulator. An individual nanotube was approached using a tungsten tip mounted on the nanomanipulator, and a contact was established with the free end of the nanotube (see Figure). An electric current was induced in the nanotube by applying voltage between the tip and the sample holder, resulting in Joule heating. The temperature could be manipulated by varying voltage. TEM video imaging was used to monitor the indium nanoparticles on the nanotube. Passing current through the nanotube resulted in the transport of In toward the cathode with a near unity correlation for mass transfer. This was observed as shrinkage of particles on the anode side accompanied by growth of particles on the cathode side.

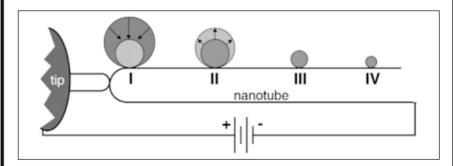


Figure. Schematic illustration of the experimental setup. Four indium particles (labeled I–IV) distributed on a nanotube substrate grow and shrink as current is passed from the tungsten tip through the nanotube.

The transfer of In was demonstrated over a nanotube length of more than 2  $\mu m$ . In addition, reversal of the voltage resulted in a reversal of the mass transport direction, with depleted particles reforming. The voltage gradient rather than the thermal gradient was seen to dictate the direction of the mass transport. The application of a square-wave function to the voltage was shown to precisely control the transport of In. According to the research team, this approach has the potential for mass delivery on an atom-by-atom basis for the tailored formation of a final preselected particle size, which has significant implications for nanoscale applications including the use of a nanotube as a "nano-soldering iron."

The researchers have developed a quantitative model for the observed nanoscale mass transfer phenomenon, using the analogy of mass conveyor belts for the transport and mass reservoirs. Plots of mass versus time for various particles along a nanotube were shown to agree well with experimental data points. The mass change rates were found to be linear, indicating that surface energies, which change with particle size, do not play a significant role in driving the transport process down to at least the femtogram level. The exact nature of the driving mechanism, however, has yet to be determined. A comparison was made to indium electromigration toward the cathode on silicon surfaces. The study demonstrates that it is possible to precisely control mass transport at the nanoscale; this bodes well for future nanotechnology applications.

GOPAL RAO

MRS BULLETIN/JUNE 2004 365

given the other experimental variables employed. By staining the bacteria with a fluorescent dye, the researchers were able to monitor the manipulation of the bacteria with a fluorescence microscope.

By controlling the current in each wire of the matrix, versatile manipulation of the bacteria could be achieved. For example, the researchers transported multiple groups of bacteria independently along different paths and oriented individual bacterium. The assembled magnetic nanostructures, which were exposed when the researchers lysed the cells and removed the cellular membranes and other debris, were viewed with scanning electron microscopy. Examples of the nanoassemblies include a long chain of spherical nanomagnets and a ring of magnetic nanoparticles, resembling a pearl necklace, formed by trapping two bacteria.

The researchers said, "Using an electric field for manipulation, [our] method... can be extended to assemble other types of biogenic nanoparticles, for example, silver or gold nanocrystals in bacteria, or cadmium sulfide nanocrystals in yeast." They said that biomineralization and micromanipulation can be combined to grow and assemble nanoparticles into customized structures.

STEVEN TROHALAKI

## Organic-Inorganic Hybrid **Electrolyte Membrane Achieves** Thermal Stability above 100°C

Proton conductors are attractive materials because of their application in fuel cells, proton sensors, and ion-exchange membranes. However, currently available materials suffer from a decrease in conductivity at temperatures above 80°C and are unstable above 100°C. A group of researchers in Japan from the Himeji Institute of Technology, the New Glass Forum Osaka Research Laboratory, the Kobe University of Mercantile Marine, the National Institute of Advanced Industrial Science and Technology, and Kyoto University has developed an organic-inorganic hybrid ionic conductive material with chemical resistance and thermal stability above 100°C.

As reported in the March issue of the Journal of the American Ceramic Society (p. 504), T. Yazawa of the Himeji Institute of Technology and co-workers fabricated a porous glass by phase separation and later modified its surface by attaching thiol groups. The modification was performed by the reaction of the glass with (3-mercaptopropyl)trimethoxysilane. The thiol groups were later oxidized in concentrated HNO<sub>3</sub> to obtain sulfonic acid groups, which are effective donors of protons. The

pore size and pore volume of the samples were measured by nitrogen absorption isotherms; the researchers also studied their surface acidity and conductivity.

The conversion of the thiol groups on the surface upon oxidation to sulfonic acid produced an increase in the surface acidity. The intrinsic acidity constant  $pK_a$ 

## Circular Photonic Crystals Allow Formation of an Isotropic Photonic Bandgap

One of the main advantages of photonic crystals is their ability to inhibit spontaneous emission of light. An isotropic photonic bandgap has been previously proposed to suppress spontaneous emission in all directions. To date, two vehicles used to obtain an isotropic bandgap are quasi-crystals and amorphous (i.e., disordered) photonic materials. In the May 15 issue of Optics Letters (p. 1084), N. Horiuchi of RIKEN, T. Nozokido of Tohoku University, and their colleagues have reported that circular photonic crystals (CPC) are yet another route to the formation of an isotropic photonic gap. Disordered materials are inherently difficult to design for specific bandgaps due to their random nature. The advantage of the CPC over disordered materials is that the CPC has a very structured design that allows a priori determination of the bandgap.

The CPC was fabricated by carefully arranging 30 mm alumina rods (with a refractive index of 3.1) in concentric circles, similar to microstructured optical fiber. The number of circles was varied between 10 and 108. While no translational symmetry exists in such a structure, triangular and square-like lattices appeared within different regions of the structure. In order to minimize this, a random phase shift from 0 to  $\pi/3$  of the sixfold symmetry for each circle was employed, as shown in the Figure. In this way, the distance between rods within a concentric circle is constant. Despite the phase shift, the nearest-neighbor distance also remains unchanged.

The transmission of a millimeter wave into the CPC was measured by irradiating the CPC with a transverse magneticpolarized wave incident from a direction orthogonal to the longitudinal axis of the rods. The signal strength inside the CPC was measured by placing a probe antenna within it. Multiple measurements were made, and the resulting transmission spectra showed a bandgap between 9.1 GHz and 14.0 GHz. Theoretical calculations were in close agreement with the experimental findings. Angle-resolved measurements showed no significant change in the bandgap, indicating an isotropic photonic bandgap. It was found that an exterior part of CPC with a large number of concentric circles (108) yielded a 1 GHz shift upwards in the lower band edge, but the bandgap was otherwise unaffected.

The researchers said that the

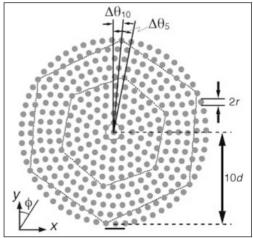


Figure. A circular photonic crystal composed of 10 concentric circles with a small phase shift ( $\Delta\theta$ ) to reduce the appearance of ordered regions. The bar at the bottom indicates the position of the probe antenna, d is the radial distance, and r is the radius of the rods. The angle of the incidence of the millimeter wave o is zero when parallel to the v axis.

isotropic bandgap is found not only at the axis of the concentric circles, but throughout the structure. This suggests, they said, that the isotropic photonic bandgap is the result of the short-range order of the CPC. The research team said that a practical application of this technology, beyond that of suppressing spontaneous emission, is the ability to create two-dimensional waveguides by line defects with arbitrary bend, since the technology is not restricted to the photonic crystal lattice.

JEFFREY DIMAIO