

Extending their Monte Carlo simulation to three dimensions, the researchers said it elucidates the process and the mechanism of the nanoporosity evolution in selective dissolution.

HAILONG HUANG

Molecular Random-Access Memory Cell Demonstrated

As a result of the common computer user's demands, both the software and hardware industries are struggling to push technological resources to the farthest limits possible. However, the traditional limits appear to be not that far away, so research focuses on faster and smaller microprocessors, faster and larger memory, and larger data-storage capabilities, for example. Researchers at Yale and Rice Universities have developed and demonstrated devices that exhibit electronically programmable and erasable memory bits compatible with conventional threshold levels, but at a molecular monolayer level. They reported their work in the May 28 issue of *Applied Physics Letters*.

Electronic memories that operate at the charge limit (single electron effects) have been previously demonstrated by other research teams, but without addressing yet the dimensional limit of a single molecule, which this team now believes is achievable. They have observed a charge storage in a self-assembled nanoscale molecular device that is operated as a random-access memory with practical thresholds and output under natural ambient operation, and with a bit retention time of 15 min. They said that their device can potentially be scaled to the single-molecule level.

The molecular systems investigated were Au-(1)-Au (1: 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiolate); Au-(2)-Au (2: 4-ethynylphenyl-4'-ethynylphenyl-2'-nitro-1-benzenethiolate); Au-(3)-Au (3: 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-1-benzenethiolate); and Au-(4)-Au (4: 4-ethynylphenyl-4'-ethynylphenyl-1-benzenethiolate). The first two combinations were observed to change conductivity state upon application of a voltage pulse, indicating the responsible molecular moiety. Although the size of the nanoscale structures built was determined by the limitations of the lithographic technique used for defining the contacts, there are no indications in the observed characteristics that limitations exist in scaling down to one the number of molecules in the active region of the device, assuming that an appropriate fabrication scheme can be identified.

CLAUDIU MUNTELE

Use of Area Array Detector for X-Ray Fluorescence Holography Allows Simultaneous Recording of the Full Hologram without Sacrificing Angular Accuracy

Holography has traditionally, as in the case of lasers, been limited by the radiation wavelength, the source size, and the detector resolving power. X-ray fluorescence holography (XFH) has recently been studied as a method for creating holograms of bulk structures with atomic-scale resolution. The primary hurdle to developing XFH into a practical investigative tool has been the difficulty associated with measuring the fluorescent radiation with an acceptable signal-to-noise ratio. While typically a solid-state detector with energy discrimination is employed, researchers at the Sincrotrone Trieste in Italy have developed a simpler method whereby an absorption filter is used in front of an area detector without energy resolution. They have increased their photon count rate by more than an order of magnitude without sacrificing angular accuracy.

As reported in the May 7 issue of *Applied Physics Letters*, the researchers performed an internal source XFH experiment using a position sensitive detector (i.e., an image plate with pixel size $150 \mu\text{m}^2 \times 150 \mu\text{m}^2$) along with an absorption filter to record the full hologram of a CoO single crystal. They employed an 8.0-keV monochromatic x-ray beam collimated to a $0.3 \text{ mm}^2 \times 0.3 \text{ mm}^2$ spot. A 50- μm -thick Fe absorber was placed between the sample and the detector in order to create an energy window. The fluorescence emitted by the Co atoms was incident on this Fe foil, causing the elastically scattered primary x-ray beam along with Co α radiation to be absorbed, so that only Co β photons along with some inelastically scattered photons reached the detector. An intensity pattern was recorded by measuring the fluorescent radiation, leaving the sample in different directions, and an image of the (001) plane of Co atoms was reconstructed.

"An important point," said researcher Andrea Lausi, "is that this setup does not require complex or dedicated instrumentation. Since both area detectors and foil filters are readily available at synchrotron facilities, this simplified setup should open up XFH experiments to a much wider community."

The scientists found that the photon flux incident on the image plate, or detector, was $\approx 5 \times 10^8$ photons/s which represents a gain of approximately three orders of magnitude over XFH experiments that employ solid-state detectors. The entire image was

recorded on the position sensitive detector with an angular resolution better than $0.1^\circ \times 0.1^\circ$. They found that the recorded image was undistorted even though the measurement was performed at only a single photon energy, and images of the third, fourth, and fifth Co neighbors were visible up to a distance of greater than 7 Å from the emitter. Furthermore, the real-space image obtained from the experimental hologram was in good agreement with simulated data.

The researchers are excited by the ability to record x-ray holograms on an area detector, and Milos Kopecky said, "The combination of fast data collection times and high angular accuracy, which has not been demonstrated before, creates the possibility of time-resolved holographic imaging. This is a promising tool for imaging the structures of small clusters or molecules."

STEFFEN K. KALDOR

Dicyclopentadiene Serves as Automated Healing Agent of Cracks in Thermosetting Materials

When thermosetting polymeric materials are damaged by mechanical loading or thermal fatigue, cracks develop which may continue to grow and compromise their structural integrity. Recently, a team of researchers from the University of Illinois at Urbana-Champaign have developed a material system with the ability to autonomously heal cracks. As reported in the February 15 issue of *Nature*, the system incorporates dicyclopentadiene (DCPD) as a healing agent into an epoxy matrix. The healing agent is microencapsulated within a urea-formaldehyde shell. When the cracks in the thermosetting material reach the 50–200 μm microcapsules, they rupture and release the healing agent into the crack plane. Once in the crack plane, the healing agent contacts an embedded catalyst, triggering polymerization of the healing agent and bonding the crack faces.

A transition-metal catalyst (Grubbs' catalyst) is used to initiate the living ring-opening metathesis polymerization (ROMP) with the DCPD. The ROMP reaction satisfies the diverse requirements of the self-healing system such as long shelf life, low monomer viscosity and volatility, rapid polymerization at ambient conditions, and low shrinkage upon polymerization.

The researchers confirmed their work with a series of materials characterizations and analysis. The results of solution-state and solid-state nuclear magnetic resonance offered information on the stability and activity of the Grubbs' catalyst in the epoxy

matrix. Fracture tests were performed using double-cantilever-beam specimens. Environmental scanning electron micrographs showed a thin polymer film on the fracture surface and illustrated the rupture process of an embedded microcapsule. Infrared spectroscopy supplied chemical information confirming that the film is the polymerized healing agent. Virgin and healed load-displacement curves from fracture tests assessed the crack-healing efficiency of the composite sample, which in this case was up to 75% recovery of the virgin fracture toughness.

"Self-healing composites possess great potential for solving some of the most limiting problems of polymeric structural materials: microcracking and hidden damage," said the researchers. They said that the material cannot only "recover structural function," but also "increase the reliability and service life of thermosetting polymers used in a wide variety of applications ranging from microelectronics to aerospace."

YUE HU

Increased Lateral Electrostriction Realized in Ferroelectric Liquid-Crystalline Elastomer Films

The strain due to the external electric field of electrostrictive materials forms the basis of such micromachines as transducers, actuators, pumps, and medical micro-robots. Of the reported electrostrictive materials—including piezoelectric crystals, grafted polyglutamates, carbon nanotubes, and polycopolymers—the best performance exhibited in these materials is 4% strain at an electric field 150 MVm^{-1} . Ferroelectric liquid-crystalline elastomer (FLCE) films, however, have shown the same constriction of 4%, but require only a $100\times$ lower electric field of 1.5 MVm^{-1} .

F. Kremer, whose group studied the films at the Institute for Experimental Physics at Leipzig University, said the principle of FLCE lies in the fact that the orientation of liquid crystal (LC) molecules is influenced by an applied electric field, and that the ferroelectric LC molecules can respond to the external electric field at a very high speed.

As reported in the March 22 issue of *Nature*, the paraelectric S_A^* phase LC material organizes itself in a layered liquid-crystalline structure. In each layer, the long axes of the rodlike LC molecules are aligned perpendicular to the layer plane. Such LC polymers can be synthesized by means of attaching the LC molecules to a polysiloxane backbone perpendicularly with a flexible alkyl chain, and cross-linking of the polymer LC. In this way, the layered structure can be preserved under mechanical stress. When a lateral electric field is applied, the LC molecules will tilt

at an angle proportional to the external electric field, thus thinning the layer and the overall thickness of the film.

Mathematical analysis shows that the constriction of FLCE films is proportional to the square of the lateral electric field, and that the frequency of the effect is twice that of the applied alternating electric field, which is characteristic of electrostriction. The electrostriction of a freely suspended FLCE film was measured at continuously increasing voltages. The square dependence of the electrostriction on the external lateral electric field could be clearly seen. The electrostriction coefficient of the FLCE was also measured at different temperatures, demonstrating that the electrostriction coefficient of FLCE films varies with temperature. The maximum electrostriction coefficient was found to appear near the Curie temperature at which the phase transition of the LC material from the ferroelectric (S_C^*) to paraelectric S_A^* phase occurs.

The researchers expect the FLCEs high mechanical response to an electrical field to be useful in nanomachine applications.

SHUYAN ZHANG

Low-Temperature Synthesis of Stable, Insoluble Uranium Boride Demonstrated

Storage of plutonium presents a myriad of problems from pollution concerns to nuclear weapon proliferation risk. It has long been known that plutonium and boron could be combined to create a very stable and insoluble compound, plutonium boride. However, this could only be done at temperatures higher than 3000°C . The two elements are melted at a very high temperature, cooled, ground into a powder, then mixed and melted again. Sometimes this process must be done several times in order to achieve proper mixing. Kent Abney of Isotope and Nuclear Chemistry (C-INC), along with Anthony Lupinetti, a postdoc with a dual C-Division and Nuclear Materials Technology (NMT) Division appointment, and Ed Garcia also from NMT, have developed a reactive process that occurs at more easily attainable temperatures, between 400°C and 800°C , and does not involve repeating the process. While the researchers used uranium, the implication is that the process will work similarly for plutonium.

Lupinetti said, "By combining actinide metal halides, like uranium tetra- and trichlorides with molecular boron precursors like magnesium diboride or calcium hexaboride, we've been able to do reactions at temperatures in the $500\text{--}800^\circ\text{C}$ range."

As the researchers reported at the 221st American Chemical Society National

Meeting in San Diego in April, they studied the reactions taking place in a small sealed quartz tube. The tube, under vacuum to remove all gasses and water vapor, was heated in a small electric furnace over a period of 1–5 days with a three-day cool down. The resultant compounds were later analyzed through x-ray powder diffraction.

The researchers found that the end result of a uranium tetra-chloride reaction with magnesium diboride yields uranium boride mixed with a magnesium chloride. The latter is easily washed away, leaving behind the uranium-boride, a compound that is stable and insoluble. In addition, actinides mixed with boron, which readily absorbs neutrons, are not easily converted to their pure form, making them harder to use in weapons.

Spectroscopic Technique Reveals Motion of Single Molecules Within a Medium

Using single-molecule spectroscopy, researchers at the University of Texas—Austin have discovered a method for observing the movement of individual molecules as well as insights into molecular motion in supercooled liquids. As reported in the April 13 issue of *Science*, graduate student Laura A. Deschenes and assistant professor David A. Vanden Bout, of the Department of Chemistry and Biochemistry, made refinements in previously used laser technology to isolate and illuminate a molecule called rhodamine 6G. Rhodamine 6G is a strongly fluorescent molecule used as the lasing medium in a yellow/orange/red dye laser. Because the method allowed molecules to be observed individually, the researchers were able to avoid the jumbling effect that masks what is really happening.

"If you look at all the molecules at the same time, you can't tell the difference in their movements. You get a jumble of times," Vanden Bout said. "What we discovered is that the rotations of individual molecules are all very different from each other. Some of the molecules are moving really fast, and some are really slow. In our supercooled liquid, there are regions within the liquid that are different from one another."

With single-molecule spectroscopy, the researchers were able to measure the dynamics of any region where a probe molecule is found. They found that the domains move at different rates from one another, and within each domain, the motion appeared as the motion of normal liquid.

Vanden Bout said they also discovered that "the domains are not static. We can watch them interchange with one another. When a fast-moving molecule switches environments, it becomes slow." □