

Nanotube Heals Itself

Pound for pound, carbon nanotubes are stronger and lighter than steel, but unlike other materials, the minuscule cylinders of carbon remain remarkably robust even when chunks of their bodies are destroyed with heat or radiation. Scientists at Rice University offer an explanation: tiny blemishes crawl over the skin of the damaged tubes, sewing up larger holes as they go.

"The shape and direction of this imper-

fection does not change, and it never gets any larger," said lead researcher Boris Yakobson, professor of mechanical engineering and materials science and of chemistry. "We were amazed by it, but upon further study we found a good explanation. The atomic irregularity acts as a kind of safety valve, allowing the nanotube to release excess energy, in much the way that a valve allows steam to escape from a kettle."

The research appears in the February 16 issue of *Physical Review Letters* (075503; DOI: 10.1103/PhysRevLett.98.075503).

The carbon atoms in nanotubes are joined together in six-sided hexagons. Yakobson's "smart repair machine" is a deformity, a blemish in this pattern. The blemish consists of a five-sided pentagon joined to a seven-sided heptagon and contains a total of 10 atoms. Yakobson, who specializes in using computers to

Model Simulates Atomic Processes in Nanomaterials to Explain Ductility and Strength

Researchers from the Massachusetts Institute of Technology, Georgia Institute of Technology, and the Ohio State University have developed a computer modeling approach to study how materials behave under stress at the atomic level, offering insights that could help engineers design materials with an ideal balance between strength and resistance to failure.

When designing materials, there is often a trade-off between strength and ductility—properties that are critically important to the performance of materials.

Recent advances in nanotechnology have allowed researchers to manipulate a material's nanostructure to make it both strong and ductile. Now, a research team led by Subra Suresh, the Ford Professor of Engineering in the Department of Materials Science and Engineering at MIT, has determined why some nano-designed metals behave with that desirable compromise between strength and ductility. The researchers developed a simulation method derived from experimental data that allows them to visualize the deformation of materials on a timescale of minutes. Previous methods allowed for only a nanosecond-scale glimpse at the atomic-level processes.

"It's a method to look at mechanical properties at the atomic scale of real experiments without being bogged down by limitations of nanosecond timescales of the simulation methods such as molecular dynamics," said Suresh, the senior author of an article on the work that appears as the cover story in the February 27 issue of the *Proceedings of the National Academy of Sciences* (p. 3031; DOI: 10.1073/pnas.0611097104).

Using the new method, the researchers found that the ductility and strength of materials are influenced by the twin boundary. Twin boundaries can be introduced in various densities, in a controlled manner, inside a nanocrystalline metal.

For many years, engineers have been able to work with the structure of metals to make them stronger. About two

decades ago, materials engineers discovered that when they made those grains in the metals smaller, typically tens of nanometers in average size, metals become stronger. Known as nanocrystalline metals, they are several times stronger than conventional microcrystalline metals. However, as nanocrystalline metals become stronger, they also become more brittle (less ductile). For example, copper with a grain size of 10 μm may have a ductility of about 50% (depending on exact composition), but at a 10 nm grain size, the ductility is below 5%, according to Suresh.

"In most applications, you need optimum combinations of strength and ductility," Suresh said.

A few years ago, researchers at the Shenyang National Laboratory for Materials Science in China synthesized a novel form of nanostructured metal, nano-twinning copper. The material was created by introducing controlled concentrations of twin boundaries within very small grains of the metal using pulsed electrodeposition.

The Shenyang group, working in collaboration with Suresh's group at MIT, demonstrated in the last two years that

nano-twinning copper has many of the same desirable characteristics as nano-grained copper, and in addition resulted in a good combination of strength and ductility. By controlling the thickness and spacing of twin boundaries inside small grains to nanometer-level precision, they were able to produce copper with different tunable combinations of strength and ductility.

Internal interfaces such as grain boundaries and twin boundaries play a critical role in the strength and ductility of metals.

When there are smaller grains in the metal structure, and hence more grain boundaries for a given volume, there is more interaction between the boundaries and dislocations, or string-like defects in the material that move inside and between grains during mechanical deformation. The larger proportion of these boundaries contributes to the brittleness of the metal.

Adding nanoscale twin boundaries, which effectively subdivide the grains, has a similar strengthening effect, but the twin boundaries do not promote the same level of brittleness as grain boundaries do.

"You can trick the material and optimize both strength and ductility by modifying the interactions between dislocations and these nanoscale twin boundaries inside the grain," said Suresh.

The research team reveals that the ductility of nano-twinning copper can be attributed to changes in the atomic structure of the twin boundaries as the material is deformed (see Figure 1).

Metals with more twin boundaries also maintain their electrical conductivity better than metals with more grain boundaries, making them potentially more useful for applications such as computer chip components. Nanocrystalline metals that are both strong and ductile could also be useful for many wear-resistant thin-film coating applications and microelectromechanical systems devices, Suresh said.

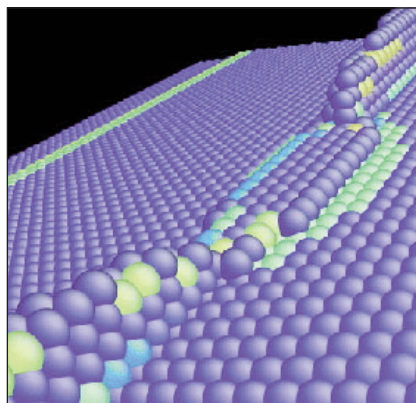


Figure 1. Atomic simulation shows the absorption of a line defect by an existing twin boundary in nano-twinning copper. Image courtesy/Subra Suresh.

decipher the atomic peculiarities of materials, discovered several years ago that mechanically stressed nanotubes—like those being pulled very hard from both ends—are predisposed to develop these 5/7-defects due to the complex interplay of thermodynamic forces at work in the nanotube.

In the latest study, Yakobson, research associate F. Ding, and students K. Jiao and M. Wu used atomistic simulations to examine the effects of other types of stress, including exposure to heat and

radiation. The simulations confirmed the predisposition of nanotubes to develop the 5/7 blemishes, and they revealed the blemishes' unexpected healing abilities.

"The 5/7-blemishes move across the surface of the nanotube like a steamship, giving off puffs of carbon gas," said Ding. "In their wake, the skin of the tube appears pristine, in its characteristic hexagonal arrangement."

Yakobson said the blemishes consume all larger defects, and proceed indefinitely, rearranging atoms and healing the

skin of the damaged nanotubes. This explains how nanotubes retain their strength, even when severely damaged. But the healing comes with a price.

"In their role as a safety valve, the 5/7-steamers give off energy and mass, which is released as pairs of gaseous carbon atoms," Yakobson said. "Since they never change shape or stop moving, they ever so slowly eat away the surface of the nanotube, one pair of atoms at a time."

Yakobson said the 5/7-blemishes turn when they reach the end of the nanotube

Supramolecular Switches Display Stable Molecular Memory

Data storage, molecular electronics, and chemical signaling all rely on molecular switches that respond to guest molecules. Stability of the ON state and/or OFF state, however, is a limitation of typical supramolecular switches developed to date. Although switch instability may be an advantage in sensing applications, disadvantages include limitations in memory in this and other applications. Switch instability typically results from the fragility of the guest–host complex that defines the ON state; mild conditions and the constant presence of the guest are required to maintain the ON state. Recently, however, J.M. Lavin and K.D. Shimizu at the University of South Carolina in Columbia demonstrated a supramolecular switch that can be turned on or off with high fidelity by heating with a guest molecule. On cooling, the state of the switch is stable even

in the absence of the guest and can be read with great accuracy.

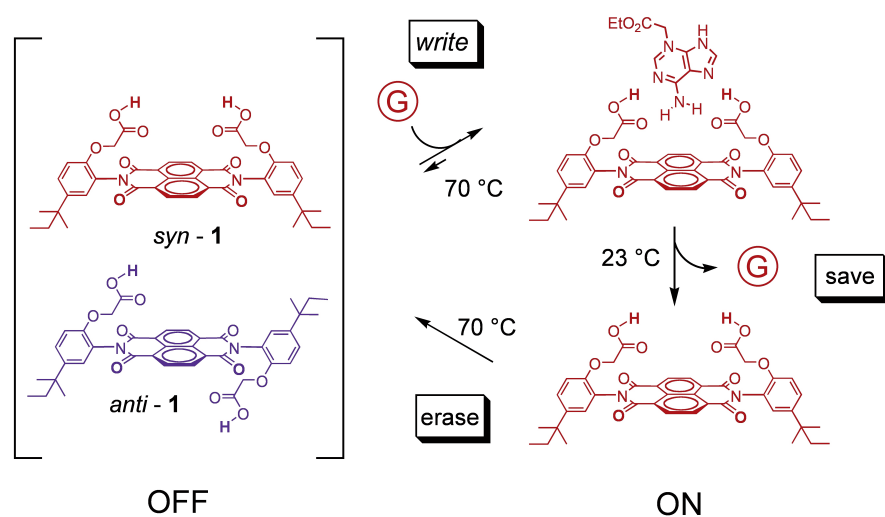
As reported recently in *Chemical Communications* (Issue 3, 2007, p. 228; DOI: 10.1039/b614853k), the supramolecular switch is an atropisomeric diacid whose ON and OFF states correspond to *syn* and *anti* diastereomers (see Scheme 1). The terminal aryl rings of the diacid are out of plane with the central diimide moiety because the rotation about two C_{aryl}-N_{amide} bonds are sterically hindered. The researchers previously published the synthesis and binding characteristics of the diacid, and confirmed with x-ray crystallography the *syn* and *anti* configurations. Addition of adenine—a hydrogen-bonding guest—to the diacid and heating to 70°C in an organic solvent turned the switch on, that is, converted the configuration from *anti* to *syn*. After cooling the solution to

room temperature and removing the adenine by washing with acid, the researchers measured a diacid *syn:anti* ratio of 93:7, which they designated as the ON state and which was shown to be stable at room temperature regardless of the environment or presence of adenine. Heating this *syn*-enriched sample to 70°C for 12 h in the absence of adenine resulted in diacid *syn:anti* ratio of 52:48, which the researchers designated as the OFF state.

Lavin and Shimizu said the ability of adenine to shift the diacid *syn:anti* ratio at elevated temperature is due to differential binding affinities of the *syn* and *anti* isomers for the adenine guest; the association constants were measured to be 1820 M⁻¹ and <10 M⁻¹ for the *syn* and *anti* isomers, respectively. The stability of the system allowed the researchers to measure isomer ratios using high-pressure liquid chromatography, which would disrupt the typically fragile guest–host complexes of other molecular switches.

The researchers tested the fidelity of their molecular switch by repeatedly heating (to 70°C for 12 h) the diacid in the presence and absence of adenine in solvent. The adenine was removed by extraction after each cycle and the diacid, recovered by evaporating the solvent under reduced pressure, was used in the next cycle. No significant loss in material or in switching efficiency was observed by the researchers after seven ON-OFF cycles. Kinetic studies showed that a system without solvent would maintain the fidelity of the ON and OFF states for longer periods of time. Lavin and Shimizu said that "this new platform offers a synthetically accessible and soluble molecular switch with room temperature stability and potential in interim memory storage."

STEVEN TROHALAKI



Scheme 1. Schematic shows ON-OFF switching of the atropisomeric diacid. The addition of a hydrogen-bonding guest with heating converts the configuration from *anti* to *syn*, that is, turns the switch on, which is stable after cooling and removal of the guest. The switch is turned off by heating.

and return in the opposite direction. The only thing that stops them is another 5/7 blemish. If two of the blemishes run headlong into one other, they cancel each other out and disappear.

Light-Emitting Nanofibers Operate as Subwavelength and Multiple Point Sources

Light-emitting sources with constrained dimensions may play an important role in sensing and lab-on-a-chip applications operating without external optics, enhancing the sensitivity and improving the signal-to-noise ratio of detected fluorescence. J.M. Moran-Mirabal and co-workers from Cornell University produced point illumination sources based on fibers of $[\text{Ru}(\text{bpy})_3]^{2+}$ (PF_6^-)/PEO, with electroluminescent ionic transition metal complexes (iTMCs) embedded in a polymer electrolyte on interdigitated electrodes, as reported in the February 14 issue of *Nano Letters* (p. 458, DOI: 10.1021/nl062778+).

To a solution of 50 mM ruthenium(II) tris(bipyridine) in dry acetonitrile filtered through a 450 nm polycarbonate membrane, the researchers added poly(ethylene oxide) (PEO) as the carrier polymer, whose concentration tuned the viscosity of the electrospinning solution and affected the size of the fibers with diameters ranging from 150 nm to several microns. Fibers were electrospun at 8–10 kV on silicon substrates with a 300–600 nm thermal oxide insulating layer and with micropatterned gold interdigitated electrodes (IDEs) on top, using a microfabricated tip coated with gold and keeping the tip-to-substrate distance between 25 mm and 40 mm.

Fibers deposited on a device having a 5 μm interelectrode spacing emitted light confined to a planar region $540 \times 540 \text{ nm}^2$ with the out-of-plane dimension limited by the thickness of the fiber when applying a dc bias across the IDEs in a dry nitrogen atmosphere. These devices showed additional emission zones as the voltage increased, resulting in multiple light sources within a fiber. This represents an advantage to develop multiple light sources in parallel, with emission sites defined by interelectrode gaps. Fibers deposited on a device with 500 nm interelectrode spacing showed a single homogeneous emission zone confined to planar regions of $240 \times 325 \text{ nm}^2$ or smaller with the emission spectrum centered at 600 nm, which implies that these devices operate as subwavelength point sources, as well as a reduced turn-on voltage. For the electroluminescent fibers deposited on 5 μm IDEs, emission could be detected by a CCD camera when applied voltages were

$\sim 10 \text{ V}$ and by eye in a dark room at 100 V. For the electroluminescent fibers deposited on 500 nm IDEs, emission could be detected at voltages as low as 2.6 V. Relatively long lifetimes were achieved during continuous operation at high voltages, which could be improved, in air, by encapsulation of the light-emitting fibers or substitution of the carrier polymer.

By using other ionic transition metal complexes with emission at different wavelengths in the visible spectrum, nanoscopic light-emitting sources can be produced that excite multiple fluorescent tags, enabling the full integration of excitation and detection mechanisms on lab-on-a-chip devices.

JOAN J. CARVAJAL

Integrated Optical Device Fabricated from $\text{KY}(\text{WO}_4)_2$

In the March 1 issue of *Optics Letters* (p. 488), researchers from the Advanced Photonics Laboratory at the Ecole Polytechnique Fédérale de Lausanne (EPFL, Switzerland), led by M. Pollnau, have reported the fabrication of riblike waveguide structures based on $\text{KY}(\text{WO}_4)_2$ (i.e., KYW) doped with Yb ($\text{KYW}:\text{Yb}$), and codoped with Lu^{3+} and Gd^{3+} . The researchers also demonstrated the fabrication of a Y-junction with a splitting ratio close to 1:1. According to the researchers, “these riblike structures offer great potential for applications toward integrated optics on KYW.”

The researchers said that bulk KYW crystals doped with rare-earth ions are one of the most promising materials for obtaining novel solid-state lasers. In this crystal, the $3+$ rare-earth ions can easily be incorporated, replacing the Y^{3+} ions. This results in an optically active material with high emission and absorption cross-sections for the rare-earth ions. Doping with Yb ions is of particular interest because an extremely small laser quantum defect ($\sim 1.6\%$) can be achieved in $\text{KYb}(\text{WO}_4)_2$. The realization of waveguide structures is also of great interest for the development of integrated optical devices.

Recently, in previous work, planar Yb-doped KYW was demonstrated based on high-quality monoclinic $\text{KYW}:\text{Yb}$ epitaxial layers grown on KYW substrates. In this case, the refractive index contrast (Δn) between the active layer and the substrate was only $\sim 6 \times 10^{-4}$. This Δn is enough to demonstrate waveguide laser action but not for the development of efficient planar integrated structures with high optical confinement.

In the new work reported here, the researchers grew crack-free $\text{KYW}:\text{Yb}$ epitaxial layers codoped with Lu^{3+} and Gd^{3+}

ions. The Lu^{3+} and Gd^{3+} ions were optically inert and their role was to increase the refractive index of the active layer. The refractive index contrasts between KYW and $\text{KLu}(\text{WO}_4)_2$ and $\text{KLu}(\text{WO}_4)_2$ are $\sim 2 \times 10^{-2}$ and $\sim 1 \times 10^{-2}$, respectively. The incorporation of different rare-earth ions in the KYW matrix leads to changes in the lattice parameter. While Gd^{3+} ions lead to compressive strains, the incorporation of Yb^{3+} and Lu^{3+} ions induces tensile strains. Therefore, by adjusting the concentration of the different rare-earth ions, it is possible to achieve an epitaxial layer characterized by a high refractive index and a low lattice-induced strain, and with large flexibility concerning the concentration of the optically active Yb^{3+} ions.

The epitaxial Lu,Gd -codoped $\text{KYW}:\text{Yb}$ layers were grown by liquid phase epitaxy. Using concentrations of 25.3% for the Lu, 13% for the Gd, and 1.7 at % for Yb, the researchers were able to grow crack-free layers with a thickness of up to 8–10 μm and with a $\Delta n = 7.5 \times 10^{-3}$. Subsequently, two-dimensional waveguide structures were fabricated using standard UV photolithography and reactive ion etching. Ribs with widths from 3 μm to 9 μm exhibit single mode behavior. The researchers established that the losses at the fluorescent wavelength of 1020 nm will be below 1 dB/cm for straight waveguides. In order to analyze the potential for building integrated optical devices, the researchers have designed and produced a Y-splitter with a splitting ratio of 1:1 and additional losses of 1.4 dB.

ROSALÍA SERNA

Nanoelectrodes Probe Microscale Environments

Investigating the composition and behavior of microscale environments, including those within living cells, could become easier and more precise with nanoelectrodes being developed at the University of Illinois at Urbana-Champaign (UIUC).

“The individual nanotube-based probes can be used for electrochemical and biochemical sensing,” said M.-F. Yu, a professor of mechanical science and engineering at UIUC, and a researcher at the university’s Beckman Institute. “The position of the nanoelectrodes can be controlled very accurately.”

To fabricate the nanoelectrodes, Yu and graduate students K. Yum, J. Hu, and H.N. Cho begin by attaching a strong, rigid, boron-nitride nanotube to a much larger, conductive probe. The nanotube will form the insulating core of the nanoelectrode.

The researchers then coat the nanotube with a thin film of gold ~ 10 –50 nm thick.