



Energy Focus

SnO₂ nanowire lithiation in a TEM viewed in real time

A year ago at Sandia National Laboratories, a nanowire wriggled and twisted like a snake hatching from an egg. Researchers watched in real time as a SnO₂ nanowire electrode charged with lithium inside a tiny electrochemical device. In the December 10, 2010 issue of *Science* (DOI: 10.1126/science; p. 1515), J.Y. Huang, L. Zhong, C.M. Wang, and colleagues across five institutions have reported on the design of the device inside a high-resolution transmission electron microscope and have analyzed the phase and morphological changes that occurred in the electrode. Nanowire electrodes recently have shown the potential for longer life and improved performance over other material structures for electrochemical energy storage.

In a cell with ionic liquid electrolyte, the researchers applied a negative potential to a SnO₂ nanowire with respect to a LiCoO₂ counter electrode. This spurred lithium ions to react with the tin oxide nanowire, producing a reaction front that propagated longitudinally through the single crystal. In the front's wake, an amorphous-reacted phase actively started to bend and coil while lengthening and swelling. After fully charging, the nanowire was composed of amorphous Li₂O and nanoparticles of Li_xSn and Sn, as determined by electron diffraction and electron energy-loss spectroscopy, and had a total volume change of over 200%.

SnO₂ has promising electrochemical storage capacity, but in bulk, the material is brittle. The researchers reported, however, that the tested nanowires showed high plasticity during phase transformation and no signs of fracture after lithiation. During charging, they witnessed

a high density of dislocations continuously nucleate at the amorphous-crystalline interface and subsequently consumed by the advancing reaction front (see figure). The researchers said that the very high stresses resulting from the differ-

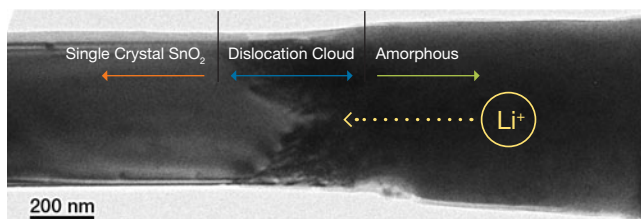
ence in wire diameter at opposite sides of the interface nucleated the dislocations in the crystalline phase. An electrochemically-driven solid-state amorphization of the nanowire took place, possibly caused by the dislocations driving the crystal far away from equilibrium but at a temperature too low for it to become liquid. Plasticity on both the crystalline and amorphous sides of the wire prevented fracture during the phase transformation.

The investigators also studied why the nanowire morphology showed a greater increase in length compared to diameter during charging. Using density functional theory calculations of three-dimensional bulk material, the researchers said that lithium insertion in the material contributed to volume expansion, but the elastic boundary conditions of the nanowire and the low Li ion flux from the ionic liquid at the nanowire surface resulted in preferential wire elongation.

Further experiments investigated the discharge of the nanowires, and the researchers said, "The methodology described [in this report] should stimulate real-time studies of microscopic processes in batteries and lead to a more complete understanding of the mechanisms governing battery performance and reliability[.]"

A video of the nanowire charging can be accessed at <http://www.efrc.umd.edu/highlights/list.php?id=18>.

Ashley Predith



A dislocation cloud forms at the reaction front where the single crystal SnO₂ nanowire charges with lithium ions. The reaction front propagates to the left, leaving behind a plastically-deformed, amorphous phase of Li₂O with nanoparticles of Li_xSn and Sn. Reproduced with permission from *Science* **330** (2010) DOI: 10.1126/science; p. 1515. © 2010 AAAS.

Nano Focus

Individual quantum dots immobilized and positioned at the nanoscale

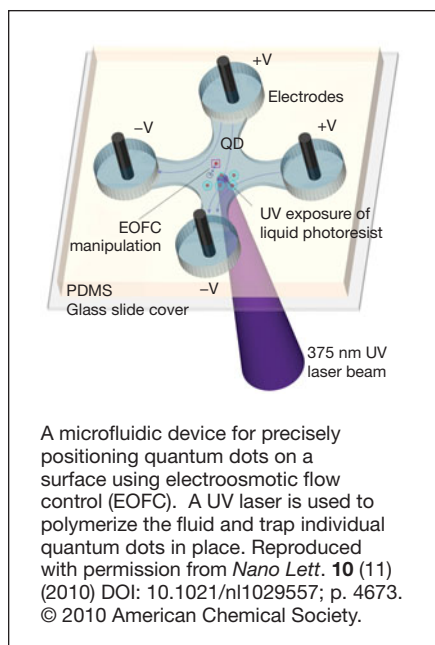
Techniques for precisely arranging nanoscopic objects are essential to fully realizing their potential in emerging technologies. Controlled placement of quantum dots (QDs) on a surface could be key to engineering photonic or plasmonic structures on the nanoscale. C. Ropp and a multidisciplinary team from the University of Maryland have recently devel-

oped a microfluidic technique for moving quantum dots with nanometer precision before individually immobilizing them within a polymer shell.

Published in the November 10, 2010 issue of *Nano Letters* (DOI: 10.1021/nl1029557; p. 4673), their work makes use of the electroosmotic control of CdSe/ZnS QDs in microfluidic channels. These particles are suspended in a unique water-based photoresist, which fills two channels formed between molded poly(dimethylsiloxane) and a glass slide. The X-shaped channels connect

two pairs of electrodes which allow two-dimensional control of the electric field in the 100 μm square intersecting region. The flow direction of the fluid in this region, along with the suspended QDs can be precisely controlled using the electroosmotic effect of the applied field (see figure).

The real strength of this technique, however, is a continuous feedback loop between the electrodes controlling the movement and a camera imaging the position of the QD, which emit light when illuminated with a green laser. Using a

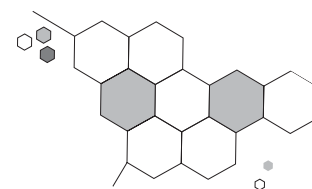


precise, sub-pixel, imaging algorithm, a specific QD can be manipulated into position with more and more slight adjustments to the flow, while other QDs drift in a divergent fashion. When the QD has reached the desired location, the spot is automatically irradiated with a UV laser, which causes cross-linking of the photoresist around the QD and effectively encapsulates it. The nature of the photoresist fluid, comprised of a photoinitiator, a water-soluble acrylic monomer, and a viscosity modifier, is crucial to the process. Using high concentrations of the monomer causes segregation of the QDs near the glass surface, providing an element of control over the third dimension and enhancing the actuation effect.

Immobilizing the QDs allows succes-

sive objects to be moved without disturbing them, and introduces the possibility of surface patterning. The team demonstrates this, as well as the ability to spectrally select for QDs, by organizing a 3×3 array of alternating color QDs, $5 \mu\text{m}$ apart. The technique could easily be extended to positioning any imageable nanoparticle on water-compatible surfaces, and should prove to be a powerful tool to the nanotechnologist.

Tobias Lockwood



Energy Focus

PV composites with enriched semiconducting SWNTs display prolonged charge separation

Current organic photovoltaic (OPV) solar cells utilize bulk heterojunctions (BHJs) comprised of conjugated polymers acting as electron donors, and derivatized fullerenes acting as electron acceptors. With electron mobility dependent on fullerene clustering and hopping transport, solar power conversion efficiencies (PCEs) now approach 8%. The properties of single-walled carbon nanotubes (SWNTs) have led to speculation that superior PCEs would result if they were to replace the fullerene phase in OPV solar cells. However, the maximum PCE achieved by SWNT-composite solar cells is only about 0.5%. This low performance has been hypothesized to be due, in part, to the relatively large fraction of metallic (m-) nanotubes in as-produced samples—about one-third, with the remainder semi-conducting (s-) nanotubes—because m-SWNTs lack a true bandgap and can therefore act as recombination centers for charge-carriers or excitons, lowering charge-separation efficiency. One obstacle to a systematic investi-

gation of this hypothesis has been the controllable incorporation of only m-SWNTs or s-SWNTs into photovoltaic blends with semiconducting polymers. Recently, however, J. Blackburn, J. Holt, and a team of researchers at the National Renewable Energy Laboratory produced blends enriched in either m-SWNTs or s-SWNTs dispersed in a semi-conducting polymer matrix, and presented conclusive experimental evidence that charge separation is significantly enhanced as the concentration of m-SWNTs is reduced.

As reported in the November 10, 2010 issue of *Nano Letters* (DOI: 10.1021/nl102753z; p. 4627), the research team separated m-SWNTs from s-SWNTs with density-gradient ultracentrifugation. Photoabsorption spectroscopy was used to determine the ratios of s- and m-SWNTs in the separated bands. Then, enriched aliquots were combined into large volumes of dispersions with varying ratios of s- and m-SWNTs. Surfactants were removed before the SWNTs were blended with poly(3-hexylthiophene) (P3HT, a prototypical conjugated polymer) to form solutions and films. The researchers used photoluminescence excitation (PLE) spectroscopy to show that P3HT effectively isolates SWNTs primarily as

individual SWNTs in dispersions of 90% s-SWNTs and P3HT.

The researchers then used time-resolved microwave conductivity (TRMC), which is sensitive only to mobile carriers and not to charge-neutral excitons, to study the yield, mobility, and decay dynamics of free carriers generated by illumination of composite films with varying fractions of s-SWNTs. They found that the long-lived population of charge carriers increases substantially for samples highly enriched in s-SWNTs in comparison to samples enriched in m-SWNTs.

The researchers concluded that m-SWNTs blended with P3HT are detrimental to PCEs and that eliminating them can significantly improve photocurrents. To summarize, the researchers said that “effectively, what has often been considered as a two-component hybrid system (conjugated polymers and SWNTs) should be treated at a minimum as a three-component system: conjugated polymer, s-SWNTs, and m-SWNTs. Moreover, since every species of SWNT with distinct chiral (n,m) indices expresses unique electronic properties, future work will likely afford valuable insight into specific electronic traits of even more well-defined blends of polymers with chiral-specific s-SWNTs.”

Steven Trohalaki