

## Eutectic Melts Improve Stability of Electrolytes Used in Dye-Sensitized Solar Cells

Dye-sensitized solar cells (DSCs) are rapidly emerging as a low-cost alternative to traditional silicon photovoltaics. Based on a photoelectrochemical process that is analogous to photosynthesis, DSCs have intrinsically lower fabrication costs and potentially very high efficiencies. However, one key barrier to their wider commercial adoption and large-scale use is the fact that they incorporate volatile, plastic-permeating solvents. Now a group led by the original inventor of the DSC, M. Grätzel of the Swiss Federal Institute of Technology in Lausanne, and P. Wang of the Chinese Academy of Sciences in Changchun have introduced the use of a eutectic melt to produce solvent-free DSCs with efficiencies that approach the highest reported to date. They reported their findings in the August issue of *Nature Materials* (DOI: 10.1038/nmat2224; p. 626).

The use of solvents in electrolytes has been understood as an obstacle to large-scale adoption of DSCs for some time, and a number of researchers have pursued alternatives such as solvent-free room-temperature ionic liquids. To date, the highest-efficiency solvent-free DSCs have been based on 1-propyl-3-methylimidazolium iodide (PMII), which has a lower viscosity than other iodide melts, enabling high fill factors and no mass-transport limitations on photocurrent. The Lausanne/Changchun group observed that three other salts that are solid at room temperature, 1-ethyl-3-methylimidazolium iodide (EMII); 1,3-dimethylimidazolium iodide (DMII); and 1-allyl-3-methylimidazolium iodide (AMII), are more conductive than PMII above their melting points. This inspired the researchers to mix EMII, DMII, and AMII at a molar ratio of 1:1:1, resulting in a eutectic-based melt with melting point below 0°C and a conductivity of 1.68 mS cm<sup>-1</sup>, almost three times higher than that of PMII.

The group then fabricated a DSC device using this eutectic-based melt (with routine additives guanidinium thiocyanate and N-butylbenzimidazole), as well as

one based on a melt of EMII, DMII, and 1-ethyl-3-methylimidazolium tetracyanoborate (EMITCB). The first device yielded an overall power conversion efficiency in full sunlight of 7.1%, significantly better than corresponding devices based on a PMII electrolyte. The second device displayed overall efficiency of 8.2%, the highest reported to date for a DSC with a solvent-free electrolyte, and retained 93% of this conversion efficiency after 1000 hours of light soaking with full solar intensity at 60°C, confirming that it is highly stable.

These results, and particularly the introduction of the use of eutectic melts to produce electrolytes, offer important clues for further improving the stability and efficiency of DSCs. They may also one day be seen as a critical step on the path to large-scale deployment of low-cost photovoltaics.

COLIN MCCORMICK

## First Principles and Finite Element Calculations Combined to Model Charged Dopants in Nanowires

Semiconducting nanowires (NWs) typically require doping to make them useful in nanoelectronic devices. First principles modeling efforts of carrier transport in NWs (and in carbon nanotubes), however, have heretofore only considered neutral defects because of the computational difficulties related with periodic boundary conditions (PBCs). The long electrostatic screening lengths of charged dopant impurities require huge periodic cells and, therefore, prohibitively expensive calculations. Small periodic cells that incompletely screen out charges lead to divergent Coulomb energies and to physically incorrect interaction between periodic images. Recently, however, R. Rurali from the Universitat Autònoma de Barcelona; T. Markussen of the Technical University of Denmark, A.-P. Jauho of Helsinki University of Technology, Finland, and their colleagues have developed an approach that uses finite element (FE) calculations to correct the potential obtained with density functional theory (DFT) at points far from the charged dopant. The corrected potential is then used to investigate the effect of charged dopant impurities on electron transport.

As reported in the September issue of *Nano Letters* (DOI: 10.1021/nl801409m; p. 2825), Rurali and co-researchers modeled Si NWs with a diameter of ~2 nm, oriented along the <100> axis, which approximate the thinnest wires grown to date. DFT, as implemented in a previously published software code, was used to calculate the atomic and electronic structures of the NWs. Subsequently, techniques

based on recursive Green's functions were used to calculate electron transport, that is, the NW conductance. The researchers simulated *n*-type and *p*-type doping with B<sup>-</sup> and P<sup>+</sup> substitutional dopants at the innermost regions of the NWs. Because the electrostatic potential, *V*, converges slowly for single-dopant simulations, the researchers calculated the change in the potential, Δ*V*, between NWs with and without the substitutional dopant. For supercells composed of five- and nine-unit cells, the researchers found that the DFT potential around the dopant is well converged and does not change significantly with increasing cell size, and that a few nanometers from the dopant, Δ*V* from DFT calculations is reproduced remarkably well by inexpensive FE calculations (although poorly in the vicinity of the dopant).

The researchers found that while the P<sup>+</sup> dopant qualitatively reproduces the majority-carrier transmission profile of a neutral dopant, the B<sup>-</sup> dopant can reduce the transmission by up to 50%. For the minority carriers, both dopants constitute an effective barrier in the potential landscape, increasing minority-carrier scattering by a factor of 1000. The researchers said that these findings "have far-reaching consequences for nanodevices that rely on minority carrier transport, such as nanowire solar cells. On the other hand, a scattering rate three orders of magnitude larger for minority than for majority carriers can be exploited for reducing the off-current in Schottky barriers, thereby improving the performance of metal-semiconductor junctions."

STEVEN TROHALAKI

## Revisiting Copper (I) Sulfide for Use in Photovoltaics

The challenge of the solar energy future is to replace single-crystalline silicon with a low-cost, high-performing alternative. The first generation of alternatives approached the dilemma by using thin films of different semiconductor materials, such as cadmium sulfide (CdS) and copper (I) sulfide (Cu<sub>2</sub>S). However, after much investigation into the use of Cu<sub>2</sub>S/CdS films, interest in this system declined because of poor long-term performance and low stability. As nanocrystals emerge as a method for constructing solar cells, the use of Cu<sub>2</sub>S/CdS is once again a potential photovoltaic material. At the current time there is little published work on the fabrication and photoelectrochemical properties of Cu<sub>2</sub>S nanocrystals. Y. Wu, C. Wadia, W. Ma, B. Sadler, and A.P. Alivisatos from the University of California–Berkeley provide insight into a method of manufacturing Cu<sub>2</sub>S-nano-



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Elizabeth L. Fleischer, Editor  
bulletin@mrs.org

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crystal-based solar cells with increased performance on a range of substrates.

As reported in the August issue of *Nano Letters* (DOI: 10.1021/nl801817d; p. 2551), the research team developed a method of synthesizing Cu<sub>2</sub>S nanocrystals and assembled solar cells with the material. To prepare the nanocrystals, a suspension of copper (II) acetylacetonate and oleic acid is injected into a solvent containing ammonium diethyldithiocarbamate, dodecanethiol, and oleic acid in an Argon atmosphere, while being heated to 180°C. After cooling and cleaning, the crystal structure is confirmed by x-ray diffraction to be of hexagonal chalcocite. Transmission electron microscopy (TEM) shows the crystals to be single-crystal structures, and having a diameter of 5.4 nm ± 0.4 nm. Additionally, two-dimensional Fourier transform (2DFT) of the lattice-resolved image of a single crystal shows the zone axes along the [1 $\bar{2}$ 13] direction. Additional analysis shows absorption in the UV-visible-near infrared across a range of ~1000 nm, and a bandgap of 1.32 eV.

After synthesis and analysis of the Cu<sub>2</sub>S nanocrystals, solar cells were fabricated from the Cu<sub>2</sub>S nanocrystals and CdS nanorods. Solutions of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), the Cu<sub>2</sub>S nanocrystals and the CdS nanorods were spun, in sequence, onto an indium-tin-oxide (ITO) glass substrate, followed by the evaporation of aluminum onto the film. This fabrication process also had the distinct advantage of being processed at temperatures no greater than 150°C, a parameter that will allow for the use of plastic substrates, which was also demonstrated in this work. The newly formed nanocrystal-based solar cell also showed several significant improvements over the thin-film cells. Upon comparing the open circuit voltage ( $V_{oc}$ ), it was determined that the  $V_{oc}$  for the Cu<sub>2</sub>S/CdS nanocrystal cell was 0.6 V, which is better than the 0.54 V for the Cu<sub>2</sub>S/CdS thin film cells, and that power conversion efficiency

can exceed 1.6%. Additionally, after four months, the performance of the solar cell did not degrade like that of thin films. Re-examining the use of Cu<sub>2</sub>S as a nanocrystal shows that there is great potential for this low-cost, environmentally safe material to be used in the next generation of photovoltaics.

TARA WASHINGTON

### Toughness of Human Cortical Bone Measured with Realistically Short Cracks

Bone is harder to break than to split. However, the importance of short-crack (less than 500  $\mu$ m) toughness cannot be overstated. K.J. Koester, J.W. Ager III, and R.O. Ritchie from Lawrence Berkeley National Laboratory have found that the true transverse toughness of human cortical bone is far higher than found in previous studies. Few fracture mechanics measurements have been made in the transverse (breaking) orientation in bone because the cortical shell in human bone is fairly thin, <5 mm. Here, the researchers measured the toughness *in situ* in a scanning electron microscope (SEM) using small samples containing short cracks, and reported that the driving force for crack propagation in the transverse direction was more than five times larger than that for the longitudinal (splitting) direction.

As described in the August issue of *Nature Materials* (DOI: 10.1038/nmat2221; p. 672), the researchers prepared samples from the midsection of frozen cadaveric humeral cortical bone oriented either longitudinal or transverse to the bone long axis. They notched each sample about half way through to form an initial crack. The crack-initiation toughness and the crack-growth resistance (*R*-curve) behavior of cortical bone were assessed *in situ* in an environmental SEM and *ex situ* using both nonlinear-elastic fracture mechanics and crack-deflection/twist mechanics complemented with *ex situ*

fractographic analysis and synchrotron x-ray computed tomography (CXRT).

Bone has the desirable characteristic of increasing toughness with crack extension. As shown in supplemental movies, the mechanisms responsible for this effect develop differently in each orientation. Propagation across the Haversian (osteon) structures, which are the basic structural elements of compact bone, causes the crack to deflect and twist, while parallel propagation results in crack bridging. While all of these mechanisms toughen bone, the mechanisms operating for cracks propagating in the transverse orientation are more potent. That is, the stress intensity required to initiate a crack is similar in the two orientations; however, the deflection and twisting of the crack in the transverse orientation very rapidly increase the toughness of bone to higher levels than have been yet reported.

Using two-dimensional ESEM and three-dimensional CXRT imaging techniques, the mechanistic interactions between the internal weak interfaces in bone and the crack path were visualized. Crack growth parallel to the weak interfaces, that is, in the longitudinal direction, resulted in microcrack initiation ahead of the crack tip and toughening primarily by crack bridging. In the transverse direction the crack encountered perpendicular refractile boundaries, that is, cement sheaths, such that toughening could be associated with crack trajectories that undergo multiple in-plane deflections of ~90 degrees and simultaneous through-thickness twists of 0–90 degrees. This is the reason why transverse fractures in bone have extremely rough fracture surfaces; indeed, the toughness of bone develops much quicker and higher during crack growth in this orientation and is the reason why bone is more difficult to break than to split.

SIRINRATH SIRIVISOOT

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