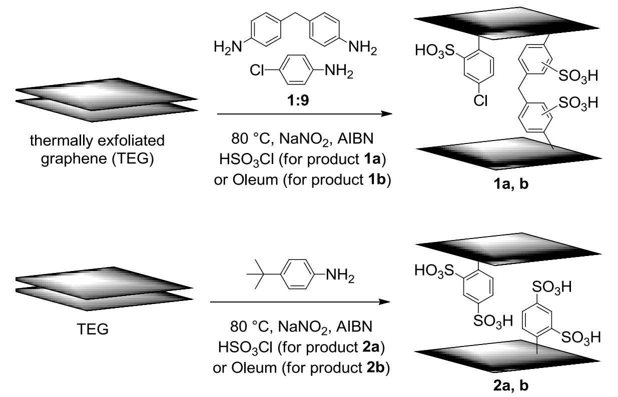
cm1025188; p. 923), the researchers used a modified procedure to make the TEG, in which most of the oxygen was removed by reduction at elevated temperature. Dispersion and functionalization of the graphene sheets were achieved by reaction with either a diazonium compound or *t*-butylaniline in the super acids chlorosulfonic acid or oleum (see Scheme). Cross-links between the graphene sheets were obtained with the diazonium reaction in oleum (see Scheme).

The researchers monitored the degree of functionalization with x-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis. Scanning electron micrographs of the functionalized TEG show that the aryl groups serve as spacers, and open up nanometer-sized interstitial gaps between the graphene planes where H_2 can adsorb, in contrast to the original TEG sheets, which appear as disordered, fluffy conglomerates.

Another factor leading to increased H_2 adsorption is the charge transfer generated by the sulfonic acid groups. The H_2 uptake and surface areas were measured for TEG and functionalized TEG with a custom-built, high-precision system at NREL. The H_2 uptake (measured as a weight-percent per 500 m^2/g at 77 K and 2 bar) for the functionalized TEG samples were higher than the H_2 uptake for TEG by 60%, 40%, 40%, and 10% for 1a, 1b, 2a, and 2b, respectively (see Scheme). The researchers said that they expect the H_2 uptake by the functionalized TEGs to be substantially higher at higher pressures, and that the “hydrogen uptake enhancement of TEG by organic cross-linking demonstrates a possible route to further increase the hydrogen storage capacity of graphene materials.”

Steven Trohalaki



Functionalization and cross-linking of thermally exfoliated graphene (TEG) sheets were performed in chlorosulfonic acid and in oleum. The degree of functionalization in chlorosulfonic acid is higher than in oleum. Reproduced with permission from *Chem. Mater.* **23** (4)(2011) DOI: 10.1021/cm1025188; p. 923. © 2011 American Chemical Society.

Energy Focus

Study on energy transfer in CdSe/CdS nanocrystals uncovers role of particle morphology

Semiconductor heterostructures that have large absorption cross sections, high stability, and quantum yields as well as size-tunable electronic structures are good candidates for light-harvesting and energy conversion applications. Nanoscale CdSe/CdS heterostructures have been reported to exhibit either Type I behavior, in which a photogenerated electron–hole pair remains in one of the materials, or Type II behavior in which the electron and hole separate between the materials. This distinction in carrier migration behavior determines for which applications a structure may be used, light emission (Type I) versus photovoltaics (Type II) for example. A detailed understanding of the origin of the electronic structure of such heterojunctions is not only crucial for engineering particles for the desired application, but can also lead to the ability to fine-tune the material for optimal performance. N.J. Borys and M.J. Walter from the University of Utah, J. Huang and D.V. Talapin from the University of Chicago, and J.M. Lupton from the University of Utah and the Universität Regensburg, Germany, report on the morphological effects of CdSe/CdS nanocrystals on interfacial energy transfer properties as published in the December 3, 2010 issue of *Science* (DOI: 10.1126/science.1198070; p. 1371).

The researchers used single-particle light-harvesting action spectroscopy on a range of CdSe/CdS heterostructures to probe the electronic structure of the heterojunctions. Specifically they measured photoluminescence excitation (PLE) of absorbing CdS through emission from CdSe. The single-particle approach enables the detection of properties that might be obscured in ensemble measurements. Typically nanoscale CdS exhibits a peak in its PLE spectrum due to the quantum-confined exiton state. Intriguingly, results from single-particle spectroscopy showed this peak only occurred in some fraction of the spectra collected from tetrapods, a CdSe core connecting four arms of CdS.

By studying other particle morphologies, including rods and spheres, the researchers were able to isolate structural features that seemed to control the presence or absence of the peak. A crucial part of this study was developing a method to correlate the single particle PLE with scanning electronic microscope images of the same particle to unambiguously show the connection to particle shape. Notably, spheres and rods with a bulbous coating around the CdSe particles did not show a peak. The researchers said that nonuniform diameter in the arms of the tetrapods or overgrowth of the CdS shell around the central core broadens quantum confinement effects and is responsible for the distinct spectra observed in the tetrapod population.

By spectrally resolving the emission energies observed in tetrapods, a surprising dependence on the excitation energy was observed, primarily in tetrapods exhibiting an overall PLE signature indicating uniform morphology. The researchers said that this phenomenon is due to misalignment of the CdSe and CdS conduction bands, which should be more pronounced in a system with more narrowly defined energy levels. Because both the CdSe core exciton energy and the CdSe/CdS interfacial exciton energy are observed in the emission spectra, the research team asserts that an interfacial barrier preventing complete transfer of the electron to the lowest energy conduction band exists.

The researchers conclude that uniformity of morphology is directly related to the uniformity of quantum confinement in the particles, and affects electronic delocalization across the heterojunction. Band misalignment is more prevalent in morphologically uniform particles, and there appears to be a barrier to electron transfer between CdS and CdSe in these cases.

The researchers suggest that nanostructures with uniform morphologies are desirable for light-emitting devices while those with some structural variation are more suited for light-harvesting applications because the barrier to electron transfer across the junction is less prevalent.

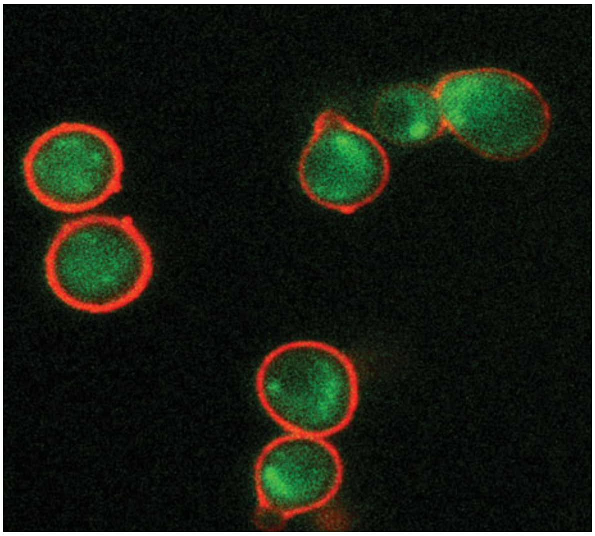
Alia P. Schoen

Bio Focus

Hydrogen-bonded shell enhances cell survivability

Modifying the surface of cells is a useful way of altering their functionality or protecting them from hostile environments. As living cells become increasingly exploited for uses in biomedicine and biosensing, the ability to tailor their external properties is of growing importance. In order to avoid the cytotoxicity of ionic polymer coatings, the groups of V. Tsukruk from the Georgia Institute of Technology and M. Stone from the Air Force Research Laboratory have developed a hydrogen-bonded layer-by-layer coating for genetically engineered yeast cells, which offers high permeability and biocompatibility.

The research, published in the 2011 online edition of *Soft Matter* (DOI: 10.1039/c0sm01070g), looks at yeast cells (*S. cerevisiae*) engineered to express green fluorescent protein (GFP) (see Figure). These cells can be used as biosensors, as the production of the fluorescent protein is triggered by certain inducer molecules. By dispersing them in aqueous solutions, the cells are coated in successive layers of poly(*N*-vinylpyrrolidone) and tannic acid, in which the hydroxyl groups of the acid form a hydrogen bond to the carbonyl groups of the polymer. The properties of the polymer membrane are assessed with respect to the number of bilayers applied and also compared with the commonly used polyelectrolyte cell coating poly(allylamine hydrochloride)/poly(styrene sulfonate) (PAH/PSS).



A confocal microscopy image of green fluorescing yeast cells (~5 μm) that have been coated with polymer shells (labeled for red fluorescence). Reproduced with permission from *Soft Matter* (2011) DOI: 10.1039/c0sm01070g. © 2011 Royal Society of Chemistry.

Using the resazurin assay to test cell viability shows that while three of the hydrogen-bonded bilayers cause only 20% cell death, the same number of traditional polyelectrolyte layers results in over 80%. The topography and permeability of the coatings are studied on hollow polymer shells formed by coating silica particles and then removing the interior. The surface of the tannic-acid/polymer structures appears grainy and porous in atomic force microscopy imaging, and correspondingly they have a much higher (up to five times) diffusion coefficient than PAH/PSS coatings. Most significantly, the new coating has very little adverse effect on the sensing functionality of the cells, in which fluorescence from GFP is increased dramatically by the introduction of galactose, whereas PAH/PSS layers cause almost complete suppression of it.

Using nontoxic and biocompatible molecules such as these is an unintrusive route to cell encapsulation, as is evidenced by the yeast's continued ability to bud new cells and reproduce. Not only do the porous hydrogen-bonded layers interfere very little with cell nutrition and sensing, they could also provide a way of adjusting membrane permeability with pH. The potential for environment responsive functionality will make these layer-by-layer membranes fertile ground for future cell modification research.

Tobias Lockwood

Correction

In the article by Browning et al. **35** (12)(2010) p. 1009, Figure 2 was devised and prepared by T. LaGrange at Lawrence Livermore National Laboratory as an extension of the previously published results cited in T. LaGrange, D.S. Grummon, B.W. Reed, N.D. Browning, W.E. King, G.H. Campbell, *App. Phys. Lett.* **94** (2009) 184101.