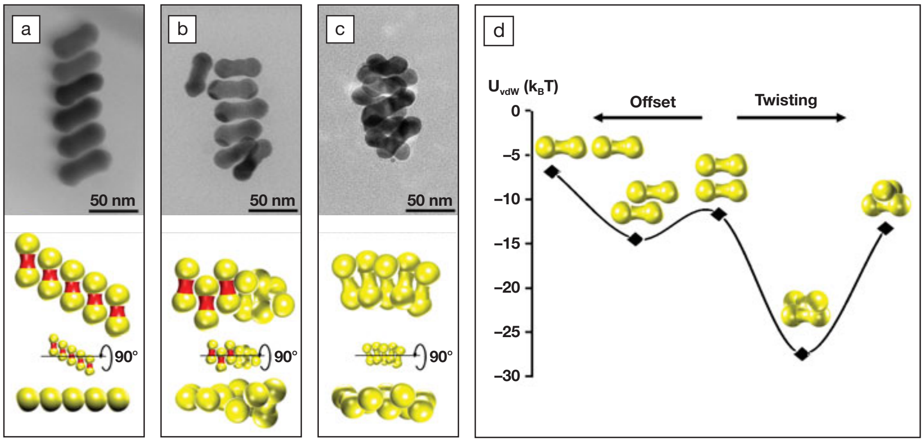
Nano Focus

“Chemical patchiness” guides pH-dependent assembly of nonspherical nanostructures



Different nano-dumbbell assemblies arise from electrostatic patchiness. Transmission electron microscope (TEM) images and schemes show patchy nano-dumbbells assembled into (a) zippers, (b) intermediate zipper/cross-stacks, and (c) cross-stacks; schematics shown are topographic reconstructions based on TEM analysis (red regions denote the loci of highest negative charge); (d) van der Waals energies of different particle arrangements are shown. Reproduced with permission from *Nature Nanotech*. **8** (2013), DOI: 10.1038/NNANO.2013.158. © 2013 Macmillan Publishers Ltd.

Assembling the same type of nanoscale building blocks into different hierarchical structures can be difficult, requiring different surfactants or external forces during the self-assembly process. Researchers D.A. Walker, E.K. Leitsch, R.J. Nap, I. Szleifer, and B.A. Grzybowski from Northwestern University now demonstrate that it does not have to be this way; assembly can be as simple as adjusting the pH of an aqueous solution.

In a recent study, published as the cover article of *Nature Nanotechnology*’s September issue (DOI: 10.1038/NNANO.2013.158), this pH adjustment strategy was used to assemble gold/silver nano-dumbbells into zippers or cross-stacked structures. The secret to this pH-dependent self-assembly lies in the non-uniform curvature and charging across the dumbbell-shaped particle. By surface functionalizing complexly shaped nanoparticles with 1-mercaptoundecanoic acid, the research group engineered “chemical patchiness”, that is, a non-uniform distribution of charge density, across the surface. The nano-dumbbell exhibits a lower curvature throughout the central region, which leads to a higher surface density of the surfactant molecules’ acidic head groups along the “handle” of the dumbbells. This region therefore exhibits a higher volumetric charge density than the ends of the nano-dumbbell.

If the nano-dumbbells are dissolved in a solution with a $\text{pH} > 9$, electrostatic repulsion from this higher charge density around their “handles” overrides van der Waals attractions between the particles, and a zipper-type assembly occurs. In contrast, a gradual reduction in pH results in a cross-stack arrangement as the central regions of the dumbbells are now less charged and can approach each other more closely.

Finite element calculations show that cross-stacking is the energetically most favorable form of assembly, but as the research team found out, it can only be achieved by pre-assembling the particles into the zipper arrangement and then slowly lowering the pH of the surrounding medium. If the pH is lowered too abruptly without utilizing the chemical patchiness of the nano-dumbbells to pre-organize them into the zipper-type assembly, disordered agglomerates form.

This work not only enhances the understanding of the general principles underlying the self-assembly of nanoparticles, but also potentially has broader impact. “Geometry can control chemical properties of molecules tethered onto nano-objects,” said Grzybowski. “In this way, otherwise identical molecules can effectively become chemically distinct and assume different roles depending on their nano-environment. Our ongoing research indicates that this geometric control can be used to make new forms of catalysts, in which familiar molecules start displaying quite unfamiliar properties. The control of surface chemistry by the underlying geometry offers some amazing opportunities for supramolecular chemistry in general.”

Birgit Schwenzer

* * *

Energy Focus

Cu-doping enables high-efficiency flexible-substrate CdTe solar cells

Solar cells based on cadmium telluride (CdTe) currently occupy a market position second only to silicon-based devices, and have recently achieved significant efficiency improvements. However, their manufacturing costs must continue to decrease if they are to remain competitive. One approach to cost reduction involves inverting the conventional device orientation to enable the use of opaque metal-foil substrates. However, such designs have previously offered low efficiencies. Now, L. Kranz and colleagues at the Swiss Federal Laboratories for Materials Science and Technology have demonstrated an inverted-cell fabrication technique that results in flexible-substrate cells with efficiencies well over 10%, an important threshold for industrial production. They reported their results in the August 13 issue of the online journal *Nature Communications* (DOI: 10.1038/ncomms3306).

Conventional CdTe solar cells are grown on glass substrates, with sunlight entering the device through the substrate (the “superstrate” configuration). Reversing this configuration would enable the use of opaque substrates such as flexible metal foils, and enable roll-to-roll manufacturing techniques. However, previous attempts at this approach have foundered on the inability to dope CdTe with Cu, as is required to achieve high hole density. The efficiencies of inverted devices have therefore remained stuck at around 8%.

To overcome this problem, the researchers investigated a high-vacuum evaporation and annealing technique. Starting with three different types of substrates (glass, 50-μm-thick Mo foil, and 30-μm-thick steel foil with a 60/230-nm-thick Ti/TiN impurity diffusion barrier), they first deposited a 600-nm-thick Mo electrical back contact by dc sputtering and layers of MoO_3 (150 nm) and Te (50 nm) by vacuum evaporation. Next, they used high-vacuum evaporation to deposit 4–6 μm of CdTe, followed by a standard recrystallization step. They then deposited a carefully controlled layer of Cu through high-vacuum evaporation followed by annealing at 400°C to promote diffusion into the CdTe. The cells were completed with a CdS layer and an i-ZnO/ZnO:Al bilayer front contact. Using secondary ion mass spectroscopy, the researchers found that the CdTe layer was successfully doped with Cu. For the optimal Cu concentration (equivalent to a submonolayer of approximately 1 Å thickness), the glass-substrate cells displayed efficiencies of up to 13.6%, while the Mo-foil-substrate and steel-foil-substrate cells achieved 11.5% and 10.9%, respectively.

These results suggest that roll-to-roll manufacturing of CdTe solar cells with efficiencies approaching those of conventional CdTe cell configurations may be possible, offering significant manufacturing cost reductions and potentially positioning CdTe as an even more notable competitor to silicon-based solar cells.

Colin McCormick

Nano Focus

Stretchable gold conductor grows its own wires

Networks of spherical nanoparticles embedded in elastic materials may make the best stretchy conductors yet, engineering researchers at the University of Michigan and Korea Basic Science Institute have discovered.

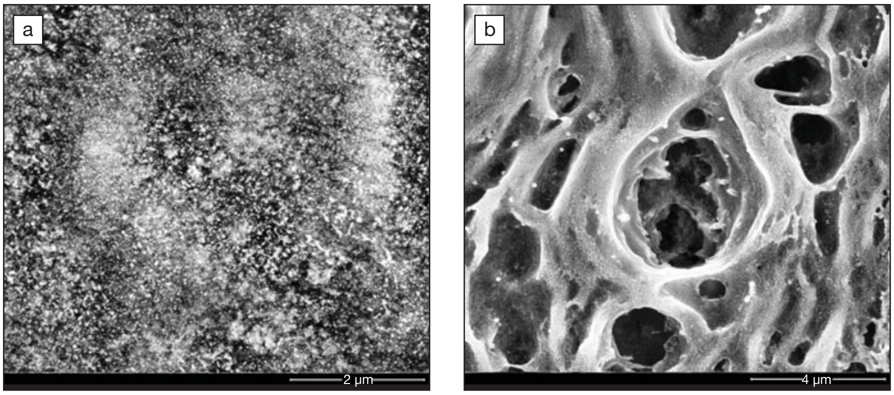
Flexible electronics have a wide variety of possibilities, from bendable displays and batteries to medical implants that move with the body.

“Essentially the new nanoparticle materials behave as elastic metals,” said lead researcher Nicholas Kotov, the Joseph B. and Florence V. Cejka Professor of Engineering.

Finding good conductors that still work when pulled to twice their length is a tall order—researchers have tried wires in zigzag or spring-like patterns, liquid metals, and nanowire networks. The team was surprised that spherical gold nanoparticles embedded in polyurethane could outcompete the best of these in their stretchability and concentration of electrons.

“We found that nanoparticles aligned into chain form when stretching. That can make excellent conducting pathways,” said U-Mich. graduate student Yoonseob Kim, first author of the study published in the July 17 online edition of *Nature* (DOI: 10.1038/nature12401).

To find out what happened as the material was stretched, the team took state-of-the-art electron microscope images of the materials at various tensions. The nanoparticles started out dispersed, but under strain they could filter through the minuscule gaps in the polyurethane, connecting in chains as they would in a solution.



(a) An electron microscope image of the gold nanoparticles in a relaxed sample of the layer-by-layer material. The nanoparticles are dispersed. (b) A similar sample stretched to a little over twice its original length, at the same magnification. The nanoparticles form a distinct network. Reproduced with permission from *Nature* **500** (2013), DOI: 10.1038/nature12401. © 2013 Macmillan Publishers Ltd.

“As we stretch, they rearrange themselves to maintain the conductivity, and this is the reason why we got the amazing combination of stretchability and electrical conductivity,” Kotov said.

The team made two versions of their material—by building it in alternating layers or filtering a liquid containing polyurethane and nanoparticle clumps to leave behind a mixed layer. Overall, the layer-by-layer material design is more conductive while the filtered method leads to extremely supple materials. Without stretching, the layer-by-layer material with five gold layers has a conductance of 11,000 Siemens per centimeter (S/cm), on par with mercury, while five layers of the filtered material came in at 1800 S/cm, which is more akin to good plastic conductors.

The blood-vessel-like web of nanoparticles emerged in both materials upon stretching and disappeared when the materials relaxed. Even when close to its breaking point, at a little more than twice its original length, the layer-by-layer material still conducted at 2400 S/cm. Pulled to an unprecedented 5.8 times its original length, the filtered material had an electrical conductance of 35 S/cm—enough for some devices.