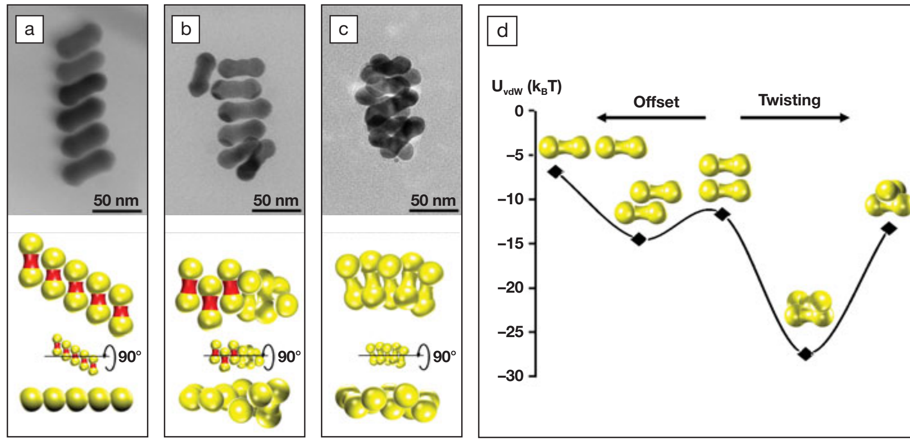
Nano Focus

"Chemical patchiness" guides pH-dependent assembly of nonspherical nanostructures

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 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.



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.

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

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