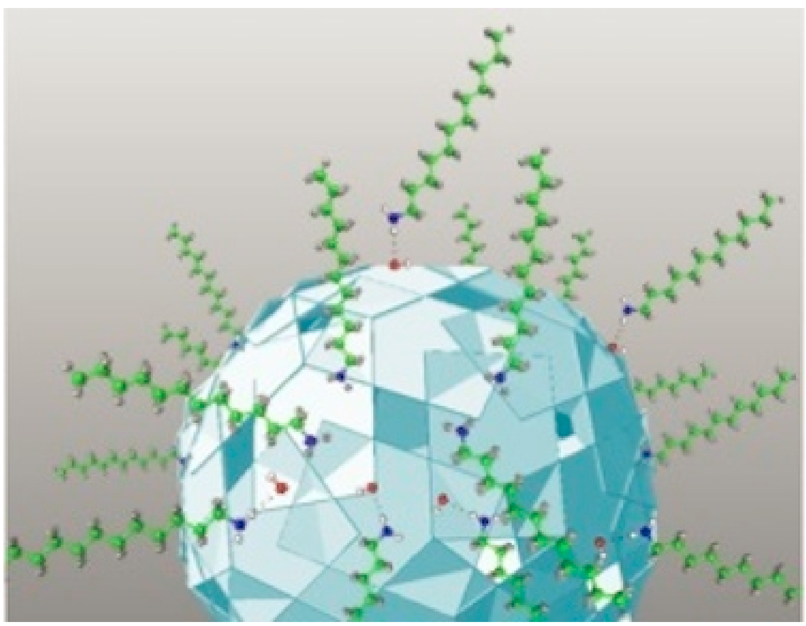
nanotechweb.org

Aug 29, 2014

Ligands can make for patchy nanocrystal surface

“Capping” ligands are routinely added to the surfaces of nanocrystals to change the properties of these crystals and make them easier to process in solution. To their surprise, and contrary to what was expected, researchers from the University of Washington in Seattle and Yale University have now found that the ligands only sparsely cover the surfaces of the nanocrystals, leaving wide patches of the surface exposed. The result will be important when developing real-world applications for these nanostructures, especially in the areas of catalysis or solar photochemistry.



(http://images.iop.org/objects/ntw/news/13/8/30/pic1.jpg)

Sparse surface coverage by ligands (http://images.iop.org/objects/ntw/news/13/8/30/pic1.jpg)

Colloidal semiconductor nanocrystals are up-and-coming technologically important materials that might be ideal in various electronics, optoelectronics and thermoelectric applications. They can be easily processed in solution if their surfaces are modified with capping ligands. These ligands can also change the chemical and physical properties of the nanocrystals and determine how they will react with other molecules in solution during or after processing.

“Most of the time, these small ligands simply stick to the surface of the nanocrystals and help make them soluble in the solution they are being processed in,” explains team member Carolyn Valdez. “The molecules can also enhance the nanoparticles’ fluorescence or change their reactivity in other ways. Recently, researchers have started to investigate how the ligands actually do their job on the crystal surface, and it turns out that our findings are quite different to what we first expected."

"Counting" ligands

The Washington-Yale team, led by Daniel Gamelin and James Mayer, used an NMR spectroscopy technique called Diffusion Ordered Spectroscopy (DOSY) to "count" the number of dodecylamine (DDA) ligands on the surface of ZnO nanocrystals and was surprised to find that there were fewer ligands than expected – just 25% of initial estimates. "The behaviour of the ligands also appears to be more 'dynamic' than we first thought, with some ligands being stuck quite tightly to the surface and others only weakly attached," Valdez tells *nanotechweb.org*. "This leaves the surface patchy, which has implications for how the nanoparticles themselves will react with other molecules in solution."

The technique not only allows the researchers to tell how many ligands are attached to the ZnO nanocrystals but also lets them count how many ligands (which are relatively light compared to the nanocrystals themselves) move about freely on their own in solution.

Handling nanocrystals like molecules

ZnO colloidal nanocrystals are important in two main application areas, explains Gamelin: as precursors for oxide thin films (for example in transparent electrodes or conductive films); and as model systems for fundamental investigations into semiconductor-liquid interfaces. "The surface ligands in fact allow us to handle the nanocrystals in solution like molecules.

"Our previous studies showed these colloidal nanocrystals as displaying extremely rich physical and chemical properties that are sometimes more molecule-like and sometimes more semiconductor-like," he adds. "By understanding these ligand shells, we should be able to better employ these fascinating materials in real-world applications."

The team, reporting its work in *ACS Nano* (http://pubs.acs.org/doi/abs/10.1021/nn503603e), says that it is now going to look at how the amount and types of surface ligands affect the reactivity of colloidal nanoparticles. "For example, if a nanoparticle has a fully saturated surface, does that change how stable it is?" asks Valdez. "Does a nanocrystal batch with a particularly patchy surface react very differently with other molecules in solution than a batch that is more saturated?"

About the author

Belle Dumé is contributing editor at *nanotechweb.org*

Further reading

Doped semiconductor nanocrystals boost solar concentrators (Apr 2014) (http://nanotechweb.org/cws/article/tech/56806)
Ligand influence on the synthesis of emission-tunable water-soluble CdTe and CdSe QDs (Nov 2008) (http://nanotechweb.org/cws/article/lab/36587)
The art of colloidal quantum dots: micropatterning (May 2014) (http://nanotechweb.org/cws/article/lab/56484)
Mild post-deposition treatments benefit colloidal nanocrystal solar cells (Aug 2012) (http://nanotechweb.org/cws/article/lab/50473)
Synergistic effect of nanocrystal integration and process optimization ramps up polymer solar-cell efficiency (Feb 2012) (http://nanotechweb.org/cws/article/lab/48638)
Thin-film solar: low-cost synthesis of CZTS nanocrystals (Jul 2011) (http://nanotechweb.org/cws/article/lab/46463)