Researchers extend galvanic replacement reactions to metal oxide nanocrystals

24 May 2013, by Bob Yirka

Image showing ?-Fe2 O3 nanocages. Credit: Taeghwan Hyeon]

(Phys.org) —A large team of researchers, most of which are based in Korea, has succeeded in extending the process of galvanic replacement reactions to ionic compounds. In their paper published in the journal *Science*, the team describes how they used preformed nanocrystals to serve as a template to produce hollow box-shaped nanocrystals.

In the early days of nanomaterial research, chemists built environments for the creation of new nanocrystal-based materials using the proper mix of solvents, surfactants and molecular precursors. They then experimented with ways to cause the atoms in the mix to self assemble into the desired shape. More recently, researchers have found that a better way is to use preformed nanocrystals to serve as a template for the creation of new materials. Adding chemicals causes them to be changed in desired ways resulting in nanoparticles with unique properties. With metal nanocrystals, atomic exchange reactions can be brought about by taking advantage of the reduced potential differences between a metal in a template and metal ions in a solution—a method known as galvanic replacement. At its base, it's a process of atomic diffusion—atoms are caused to move away from a structure, creating vacancies. Until now, however, this method has been limited to metals. In this new effort, the galvanic replacement process is extended to ionic compounds.

To cause the galvanic replacement process to work with ionic compounds, the researchers used redox-couple reactions between multivalent metallic ions. More specifically, when they caused manganese oxide nanocrystals to react with iron percholate, a new type of nanocrystal was created in the form of hollow shaped boxes which eventually evolved into hollow crystals that resembled cages. Because of their shape, the researchers dubbed them "nanocages." The process works because higher-oxidation state ions in manganese are naturally replaced by lower-oxidation state ions in the solution.

The team's results demonstrate that ionic compounds can be easily and cheaply used as templates to create new and useful nanocrystal-based materials. Further research, they suggest, is likely to lead to nanomaterials creations that are limited only by the imagination.

For now, the researchers suggest the new type of nanocrystals might be useful in a wide variety of applications ranging from energy production, to biotechnology and electronics, and perhaps even as an anode material for lithium ion batteries.

More information: Galvanic Replacement Reactions in Metal Oxide Nanocrystals, *Science* 24 May 2013: Vol. 340 no. 6135 pp. 964-968 DOI: 10.1126/science.1234751

Abstract
Galvanic replacement reactions provide a simple and versatile route for producing hollow nanostructures with controllable pore structures and compositions. However, these reactions have previously been limited to the chemical transformation of metallic nanostructures. We demonstrated galvanic replacement reactions in metal oxide nanocrystals as well. When manganese oxide (Mn3O4) nanocrystals were reacted with iron(II) perchlorate, hollow box-shaped nanocrystals of Mn3O4/?-Fe2O3 ("nanoboxes") were produced. These nanoboxes ultimately transformed into hollow cagelike nanocrystals of ?-Fe2O3 ("nanocages"). Because of their nonequilibrium compositions and hollow structures, these nanoboxes and nanocages exhibited good performance as anode materials for lithium ion batteries. The generality of this approach was demonstrated with other metal pairs, including Co3O4/SnO2 and Mn3O4/SnO2.