Quantum-dot aerogels

Highly porous networks of CdSe nanoparticles retain their quantum properties and can be chemically tailored.

From collecting stardust while zipping past a comet to storing vast amounts of electric charge as “supercapacitors”, aerogels have shown their versatility and importance. And their potential still seems far from exhausted. For instance, Stephanie Brock and colleagues at Wayne State University are developing a new class of aerogels that could lead to applications in photovoltaics and nanotechnology (J. Am. Chem. Soc. 2006, 128, 7964–7971).

Unlike their traditional silica and carbon counterparts, the aerogels created by Brock and colleagues are made from metal chalcogenides, such as metal selenides and metal sulfides. The band gap of these salts falls between those of insulating metal oxides and electrical conductors; this opens the door to a myriad of new applications, says Brock. “These materials can be tuned to absorb throughout the solar spectrum, so now we can think about photocatalysis and photovoltaic applications,” she explains. Because the aerogels have a large, interconnected pore volume, diffusion within them is similar to that in air. This allows you “to get molecules in and out rapidly,” she adds. It makes large-surface-area, self-supported sensors and catalytic applications feasible.

Brock and colleagues produced the aerogels by polymerization of the individual building blocks at the wet-gel stage followed by supercritical drying with CO2. The process allowed the preservation of the wet-gel morphology as the liquid was removed. The traditional way of making aerogels is to let the building blocks form and react randomly. Instead, the group either trapped CdSe quantum dots (QDs) inside tiny water pockets formed by inverse micelles or created the nanoparticles by a high-temperature precipitation method.

The researchers then added thiolate ligands that bound to the surfaces of the QDs and formed complexes around the nanoparticles. Through targeted oxidation of the thiolate capping groups, by either a chemical oxidizing agent or photooxidation, the researchers opened up a limited number of reactive sites for controlled nanoparticle aggregation. “One of the important features of Brock’s [work] is the ability to crystallize the nanoscale framework of the aerogel and still retain high surface area,” says Bruce Dunn of the University of California, Los Angeles.

The aerogels are important in nanotechnology. However, finding ways to assemble nanocrystals into functional 3D devices without collapsing them into bulk material—thereby spoiling their unique nanoparticulate properties—is one of the current challenges in the field. When the researchers studied the aerogels made from CdSe QDs, their optical-band-gap measurements and photoluminescence data showed that the individual building blocks retained their quantum characteristics despite being part of a macroscopic structure. “Our most important overall finding is really how general this phenomenon is,” says Brock. “It’s nothing magic about CdSe. With our method, the quantum confinement effects were retained for a wide variety of metal chalcogenides.”

“It’s very pretty to make a quantum dot, but I am not sure how ultimately useful it is,” says Debra Rolison of the U.S. Naval Research Laboratory. “We need to find out how to get communication between the individual particles, and Brock’s group used a very elegant approach to do that.”

Powder X-ray diffraction of the CdSe networks showed that the aerogels maintained the crystal structure of the primary nanoparticles. By varying the characteristics of the nanoparticle building blocks and by surface-ligand exchange at the wet-gel stage, the researchers could adjust the structural, optical, electronic, and surface properties of the aerogels. “The ability to change the nature of what’s on the surface gives you many possibilities of doing further chemical tailoring inside the architecture, because in an aerogel you can talk to the entire surface,” says Rolison.

Currently, Brock and colleagues are working on developing photovoltaic applications, investigating the nature of the interface between the individual particles, and building a CdSe aerogel sensor. Researchers have done sensor work with individual nanoparticles before, “but the problem with those systems is that the QDs have to be embedded in a matrix, and that leads to activation issues,” Brock points out. “Our preliminary work on quantum-dot aerogel sensors indicates clear and very rapid changes in the luminescence response when a molecule is bound to the sensor.”

—Nicole Branan