

Nano findings from Berkeley: Nanoparticles stiff from constant strain

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Take something no wider than a human hair and shrink it a thousand fold to a few nanometers across, and its electronic and other properties change radically. But whether the crystal structure of these nanoparticles remains basically the same is a matter scientists continue to debate.

Now, a new report by scientists at the University of California, Berkeley, and Lawrence Berkeley National Laboratory (LBNL) shows that's far from the case.

Zinc sulfide nanoparticles a mere 10 atoms across have a disordered crystal structure that puts them under constant strain, increasing the stiffness of the particles and probably affecting other properties, such as strength and elasticity, according to the team's report.

"In this material, disorder and a kind of strain is pervasive throughout the whole particle," said Benjamin Gilbert, a postdoctoral fellow at UC Berkeley. "That is an important observation, because it emphasizes that the assumption of bulk structure is not good enough. We would expect to find this kind of behavior in a wide range of semiconducting materials."

The disordered structure could have an effect on properties other than stiffness, Gilbert said. He and colleagues in the laboratory of Jillian F. Banfield, UC Berkeley professor of earth and planetary science, also are looking at potential changes in optical and electronic properties.

Aside from helping researchers understand these submicroscopic



nanoparticles, the new findings could help scientists better predict the properties of new nanoparticles and custom design them with specified properties.

The report by Gilbert, Banfield and their colleagues was published July 1 on Science magazine's online Web site, Science Express.

Nanoparticles are one of many nanometer-size materials that are the focus of university and industry research today, with potential applications as sensors, solar power generators, electronic circuit elements, lasers and numerous other nanodevices. Nanoparticles also are akin to nanometer-size minerals produced naturally by some bacteria, which are of interest as possible telltale signs of life on other planets.

Last year, Gilbert, Banfield, research scientist Hengzhong Zhang and their colleagues reported that the crystal structure of nanoparticles made of the semiconducting material zinc sulfide (or zinc sulphide, ZnS) changes when it gets wet, which means surface interactions have a large effect throughout the nanoparticle.

The scientists' latest findings reinforce that message.

"The presence of the surface is a dominant structural perturbation that makes its effects felt throughout the nanoparticle and in the material's properties," Gilbert said.

The researchers studied particles of ZnS containing only 700 atoms and a mere three to four nanometers across, which means the center is only about five atoms away from the surface.

In similar semiconducting nanoparticles, such as those made of cadmium selenide, slight differences in size lead to absorption and emission of different wavelengths of light, making them useful as fluorescent



tracers. The dominant cause of such properties is quantum mechanical confinement of the electrons in a small package. But the disordered crystal structure now found in nanoparticles could affect light absorption and emission also.

"The point is that a nanomaterial's properties are a direct consequence of the structural changes and hence not simply related to the bulk materials' properties," Gilbert said. "If you make a nanoparticle, say a small piece of zinc sulfide, the idea that in the middle it's basically bulk-like with maybe a bit of relaxation on the surface doesn't work."

These results come after Banfield's team, in collaboration with Glenn A. Waychunas at LBNL, developed a new way of analyzing X-ray diffraction images of nanoparticles so as to separate the effects of size from those of disordered structure, which are similar and have been difficult to distinguish. The X-ray experiments were conducted with the Advanced Photon Source at Argonne National Laboratory and with an X-ray beamline at the Stanford Synchrotron Radiation Laboratory.

Gilbert noted that X-ray diffraction of single nanoparticles is not yet possible, but their technique using collections of similar nanoparticles provides a quantitative description of disorder and strain within nanoparticles.

The Science paper is coauthored by Gilbert, Banfield, Zhang, Waychunas and Feng Huang, a postdoctoral researcher in the UC Berkeley Department of Earth and Planetary Sciences. The work is funded by the United States Department of Energy, the National Science Foundation and LBNL.

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