Bubbly synthesis yields iron nanocolloids

Using high-intensity ultrasound, chemistry professor Kenneth S. Suslick has been creating potentially useful materials that are made of nanometer-sized particles. In the latest advance on this research theme, he and his coworkers at the University of Illinois, Urbana-Champaign, have found a way to sonochemically prepare stable ferromagnetic colloids of iron, which have potential applications as magnetic fluids.

Suslick and coworkers previously have shown that organometallic compounds in solution can be decomposed ultrasonically to yield individual metal atoms. When the solution is irradiated with ultrasound, bubbles form in the liquid, expand, and then collapse implosively. This process generates hot spots where the temperature shoots up to about 5,000 K within a microsecond before cooling off even faster. This local heating is accompanied by local pressures on the order of 1 kilobar. Any organometallic molecules that happen to be inside the cavitating bubble are decomposed in an instant.

When the metal-containing compound is decomposed in an alkane, the resulting atoms agglomerate to give highly porous nanostructured materials such as amorphous metals, alloys, or carbides. Iron pentacarbonyl, $Fe(CO)_5$, for example, gives corallike formations of amorphous iron. Molybdenum hexacarbonyl, on the other hand, yields molybdenum carbide (Mo_2C) powder, an excellent dehydrogenation catalyst [*J. Am. Chem. Soc.,* **118,** 5492 (1996)].

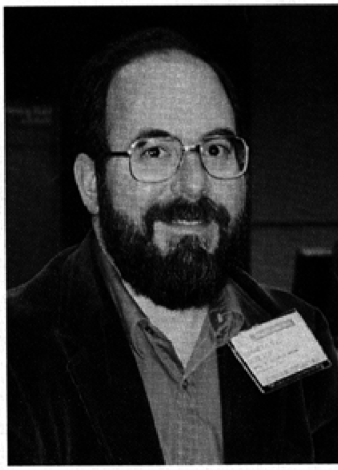

Photo by Ron Dagani

Suslick: sonochemical method simple, quick

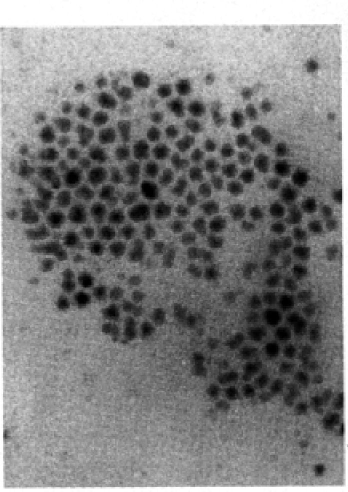

Photo by Kenneth Suslick and Taeghwan Hyeon

Transmission electron micrograph of sonochemically prepared iron colloid particles (with average particle size of 8 nm) stabilized by oleic acid.

Suslick's group now has found that the metal nanoclusters produced in such a decomposition reaction can be stabilized so that, rather than clumping together to form a powder, they yield a stable, isolable colloid.

In a paper published a few weeks ago [*J. Am. Chem. Soc.,* **118,** 11960 (1996)], Suslick and coworkers Mingming Fang and Taeghwan Hyeon describe how they sonochemically decompose iron pentacarbonyl to create a nanosized iron colloid. When the reaction is carried out in octanol in the presence of the colloid stabilizer polyvinylpyrrolidone (PVP), the resulting black colloidal solution contains iron particles 3 to 8 nm in size. Alternatively, when the reaction is carried out in hexadecane with a different stabilizer—oleic acid [(*Z*)-9-octadecenoic acid]—the colloidal particles are slightly larger, with a much more uniform size distribution centered on 8 nm.

"Colloids of ferromagnetic materials are of special interest due to their many important technological applications as ferrofluids," Suslick notes. Such magnetic fluids find uses in stereo speakers, magnetic inks for bank checks, magnetic refrigeration units, and magnetofluid seals, lubricants, and bearings. Ferrofluids also have been applied widely in medicine, for example to deliver drugs, restrict blood flow to selected parts of the body, or act as opaque materials for diagnostic imaging using X-rays or nuclear magnetic resonance.

Unfortunately, Suslick says, commercial magnetic fluids have been difficult to make. Generally, they are produced by exhaustive grinding of magnetite (Fe_3O_4) in ball or vibratory mills for several weeks in the presence of surfactants, which produces a very broad range of particle sizes. "By comparison," he points out, "this new sonochemical synthesis of ferrofluids is simple and quick."

Suslick also notes that chemists have had difficulty in generating nanometer-sized colloids of iron or other group 8 transition metals. "There aren't many ways of doing it compared with the preparation of noble-metal colloids," he says.

Because of their small particle size, the metal colloids produced in Suslick's lab have an interesting property called superparamagnetism. This means that the magnetic moments consist of clusters of atomic spins, in which all the spins are aligned in the same direction. The magnetic moments of the individual clusters, though, can point in random directions until a magnetic field is applied, at which point the moments line up. "Each cluster behaves like a separate magnet," Suslick explains, and the magnetic moments of these clusters are more than 100 times greater than those in conventional paramagnetic materials.

The advantage of a superparamagnet is that, unlike an ordinary ferromagnet, it immediately loses its magnetization when the magnetic field is turned off. This property is useful in a number of applications, including magnetic recording heads for tape recorders and radar-absorbing materials for "stealth" aircraft.

For a magnetic fluid to be practical, it should have a high saturation magnetization. On this measure, one of Suslick's nanocolloids is comparable to, though somewhat lower than, a commercial magnetite-based magnetic fluid. The difference is not significant, he says. In any case, he adds, "We're not really at the point of technological application of these materials yet." Nevertheless, he and his collaborators are exploring the potential of these nanocolloids as contrast agents for magnetic resonance imaging.

The overriding theme in this and some earlier work in Suslick's lab is that metal clusters formed during cavitation can serve as nanoscale building blocks to make nanostructured materials with diverse structures and properties. The chemical effects of ultrasound, he believes, are likely to find important industrial applications in the years to come.

Ron Dagani