CHEMISTRY

Crystals Branch Out Into Exotic Shapes

When it comes to designing individual molecules, chemists are remarkably adept at crafting complex shapes, such as the twists and turns of drug molecules that dock into precise cavities of proteins. But when researchers try to extend that complexity into larger solid materials such as crystals, frustration carries the day. Crystals tend to grow on all sides at once. As a result, they typically adopt simple shapes, such as sheets, spheres, and cubes—the delightful branches of a snowflake notwithstanding. Researchers recently managed to steer crystal growth to make thin rods by controlling the speed at which various faces of crystals grow. Now, a team from the University of California, Berkeley, has elevated this control to an art form, enabling them to make nanosized versions of a variety of shapes including rods, arrows, teardrops, and even four-armed tetrapods shaped like a child's jack.

"It's really beautiful science," says Jim Heath, a chemist at the University of California, Los Angeles, and a specialist in making nanoscale electronic circuitry. "Learning how to control size and shape is a tremendous challenge at this length scale." While these shaped crystallites remain a curiosity for now, their unique shapes could be a boon for researchers trying to shrink computer circuitry and magnetic data storage to nanoscale dimensions.

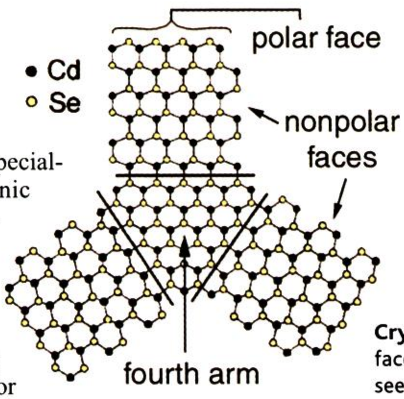
With such applications in mind, the Berkeley researchers—graduate students Liberato Manna and Erik Scher, working with lab director Paul Alivisatos—started by looking for a better way to grow inorganic rods. In recent years, numerous groups have shown that they can grow miniature forests of tiny inorganic trees on a surface from a vapor of precursor compounds. As the inorganics begin to link up, they form a crystallite in which the top surface grows faster than the slightly different crystalline arrangement of atoms on the sides, causing the crystallite to elongate into a rod.

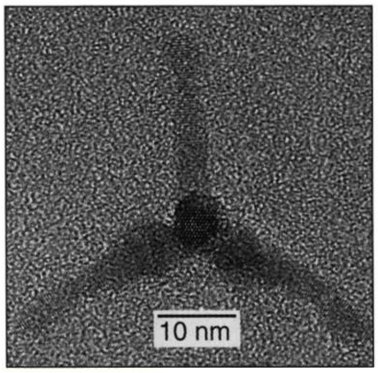
One problem, Alivisatos says, is that because the inorganic trees start growing at different times, researchers typically wind up with a wide range of sizes, from stubby young saplings to towering old growths. That variation can alter the trees' electronic and optical properties. And because the trees are anchored in place, they cannot be moved around. Researchers looking to chop down a few metallic trees and use them to wire up nanodevices are out of luck.

To grow rods without having them planted on a surface, Alivisatos's team turned to two-part molecules called surfactants. The two portions of surfactants prefer hanging out in chemically different surroundings. Common soaps, for example, are surfactants that contain a "polar" chemical group that favors residing in water and a "nonpolar" group that prefers oils.

For their crystal-growing experiments, the Berkeley researchers used two surfactants with similar polar-nonpolar pairs. The first chemical, abbreviated TOPO, contains a slightly polar phosphine oxide group connected to a trio of oil-friendly alkyl chains. The second, called HPA for short, has a more polar phosphine acid group connected to a single alkyl chain.

Earlier this year, Alivisatos's team showed that by varying the amounts of TOPO and HPA and playing with the temperature of the solution and other growth conditions, they could create nanoscale rods from the semiconductor cadmium selenide. Although the exact mechanism is unknown, Alivisatos believes that the rods grow because as CdSe nuclei form in solution, they harbor different crystalline arrangements of atoms on different sides. One face contains alternating cadmium and selenium atoms and is relatively nonpolar, while other faces contain either all selenium or all cadmium atoms, which are more polar. Alivisatos suspects that the TOPO binds to the relatively nonpolar crystalline faces on the sides of a budding nucleus, while the HPA favors either the top or the bottom face, leaving the other face relatively exposed to add new atoms from the solution. As a result, the crystal grows in one direction.





Crystal jack. Arms sprout from four polar faces of a cadmium selenide nucleus (one seen face-on).

Now in the 1 December online version of the *Journal of the American Chemical Society*, Alivisatos's group reports extending their approach considerably. By adding more HPA to the mix, the researchers speed the growth rate of the fast-growing face. The result is an arrowhead shape that forms as new layers of atoms add themselves to the face before the previous layer is filled in. To make CdSe teardrops, the researchers start by growing short rods and then add a bolus of the cadmium and selenium precursor compounds to the mix. The extra inorganics cause the rods to widen at the tops, approaching spheres. Then, as all the inorganics are used up in the reaction, the crystals peter out at the top.

Perhaps the most intriguing crystals are the nanoscale jacks, which resemble branched organic molecules called dendrimers that are being explored for uses ranging from drug delivery to solar cells. Like standard organic polymers, dendrimers are made up of repeating units called monomers. But unlike normal polymers, in which monomers link together in long, spaghetti-like chains, the monomers in dendrimers each have at least three arms that can link to separate neighbors. As new monomers are added, the branches multiply outward, causing dendrimers to grow into little plastic spheres.

To date, inorganic chemists haven't had a similar molecular toy to play with. But by starting with low-temperature growth conditions, Alivisatos's team was able to create CdSe crystallites that harbored four separate fast-growth faces. When they then switched to the rapid growth conditions, rods sprang from all four faces. By then dropping the temperature again, the Berkeley team created new branch points at the end of each rod and then grew new rods on them. Alivisatos says that the inorganic versions of dendrimers are not nearly as complex or as large as the organic variety. "But we observed that it is possible to do this," he says. And it may be possible to add other interesting ingredients as well, growing inorganic dendrimers from several different components.

Even without all the extra branches, simple four-armed jacks could prove useful. Alivisatos notes that when dropped on surfaces, the jacks always rest on a tripod of three legs, leaving one rod pointing straight up. That could come in handy for wiring up neighboring electrical devices in future nanoelectronics and could help solar cells efficiently channel current from one electrode to another.

—ROBERT F. SERVICE

CREDITS: FROM *JOURNAL OF AMERICAN CHEMICAL SOCIETY* ONLINE PAPER