

MEETING MATERIALS RESEARCH SOCIETY

Finding Speed on the Smallest Scales

BOSTON—The speedy and the slight were on display at the semiannual Materials Research Society meeting held here from 30 November to 4 December. Among the highlights were tiny catalysts trapped in porous polymer spheres, a high-speed combinatorial study of corrosion, and a chemically triggered nanotransistor.

Starburst Cages for Catalysts

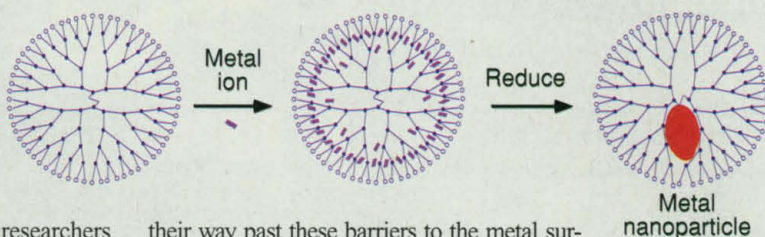
Like master chefs, catalyst makers are always refining their recipes. One of the surest ways they've found to get winning results from a metal catalyst is to divide it into smaller and smaller particles, which increases the overall surface area on which chemical transformations can occur. Yet this isn't as simple as it sounds. Like unsifted flour, tiny catalyst particles can clump together, reducing the surface area. At the meeting, a team of researchers led by chemist Richard Crooks of Texas A&M University in College Station described a new ingredient that can get the lumps out of this recipe: small porous polymer spheres called dendrimers that can encapsulate metal particles and keep them from sticking together while allowing reactants and products to diffuse in and out.

Already, Crooks and his team have grown dendrimer-encapsulated nanoparticles of several metals, including copper, silver, platinum, ruthenium, palladium, nickel, and even composites of platinum and ruthenium. The new work is "a nice approach," says Richard Finke, a nanoparticle expert at Colorado State University in Fort Collins. Besides protecting the metal particles, he notes, the dendrimers can also serve as molds for growing them in a precise size. If the work pans out, it could lead to better catalysts for the fuel cells that burn methanol or hydrogen gas. But Finke cautions, "It's still early on." Among other things, researchers have to prove that the polymer shields are stable and don't reduce the catalytic efficiency of the particles.

That's been a problem for earlier strategies that envelop

catalysts in detergent-like molecules called surfactants or in layers of conventional linear polymers: Reactants can't easily make

Round robin. Catalytic metal nanoparticle is formed inside protective polymer sphere.



their way past these barriers to the metal surface. But Crooks and his colleagues suspected that dendrimers might work better. These molecules branch repeatedly, forming a spherical starburst of branches that can trap nanoparticles while allowing reactants and products to diffuse freely. Moreover, because the branching is easy to control, all the dendrimers in a batch are virtually identical, allowing them to act as templates for nanoparticles with a consistent size and makeup.

To create encapsulated copper particles, Crooks's team combined dendrimers made

from polyamidoamine, which contain numerous amine groups that bind positively charged metal ions, with a solution of copper sulfate. When the researchers added sodium borohydride, a strong reducing agent, the copper ions precipitated out into metallic copper particles, which grew within the dendrimer. Depending on the size of the dendrimer, the particles contained from just four to 64 atoms—small enough to be an efficient catalyst.

"That's it," says Crooks. "It's really easy. It only takes about 1 minute to do this." By simply changing the initial metal salt, the researchers were able to create other encapsulated metal particles.

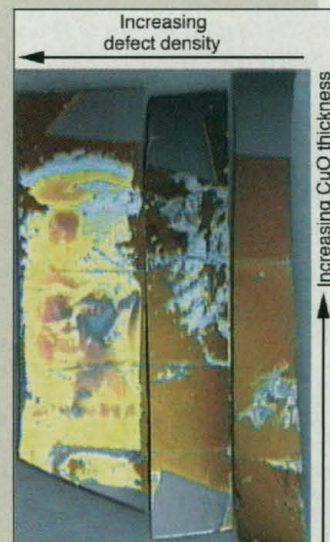
Already Crooks and his colleagues Mingqi Zhao and Li Sun have shown that their new dendrimer-bound catalysts are effective at adding hydrogens to small hydrocarbons such as alkenes, a chemical transformation that's done by the trainload in industry as a step toward making everything from drugs and dyes to rubber products. What's more, dendrimer-based catalysts might be better than existing versions at selecting the right feedstocks from a mixture, says Crooks. The team found that whereas linear alkenes—simple, spaghetti-like molecules—easily diffuse into the dendrimers, more complex branched versions have a harder time wrig-

Combinatorial Test of Corrosion

On this copper plate, J. Charles Barbour and his colleagues at Sandia National Laboratories in Albuquerque, New Mexico, are turning combinatorial chemistry on its head. The technique is typically used to create all possible combinations of a handful of chemical building blocks, thereby synthesizing in one fell swoop thousands of compounds to test, say, as possible drugs. But at the meeting, Barbour and his colleagues showed how the same approach can also be used to study a destructive chemical reaction: corrosion.

The researchers created a grid of differing conditions in the thin copper film. First they increased the thickness of a protective copper oxide coating in half-centimeter horizontal strips from bottom to top; then they boosted the number of defects, created by bombarding the metal with copper ions, in vertical strips from right to left. The researchers exposed the foil to air spiked with hydrogen sulfide to see where the sulfur reacted with the copper to create copper sulfide (yellow), a hallmark of corrosion. A lower number of defects turned out to be far more important in limiting corrosion than a thick copper oxide overcoat. Such studies, says Barbour, could help researchers prevent the corrosion of copper in advanced electronics circuitry and aluminum in aircraft.

—R.F.S.



gling their way inside.

What's not yet known is whether the new dendrimer-bound catalysts are actually more efficient than their brethren. But Crooks says his team is looking into that now. If so, dendrimers could be in for a big future as tiny reaction chambers.

Single Electrons With a Chemical Sense

Single-electron transistors, which coax electrons to flow one at a time through nanometer-sized specks of material, could take electronic devices to extremes of tininess. Now, new work suggests that these devices could also find their way into ultrasmall, ultrasensitive chemical sensors.

At the meeting, a team led by chemist Dan Feldheim from North Carolina State University in Raleigh reported a new scheme in which the electrical current flowing through what amounts to a single-electron transistor (SET) varies depending on the chemical makeup in a solution surrounding the device, a phenomenon analogous to a nerve cell firing in response to specific neurotransmitters. By harnessing this ability to convert a tiny chemical signal into an electronic response, the new scheme could lead to a bevy of simple and sensitive chemical sensors, useful for detecting everything from chemical toxins to trace components in cells. "It's a very clever approach" to making chemical sensors, says Northwestern University chemist Chad Mirkin.

To make their sensors, the NC State team started with two electrodes, one a simple gold pad and the other the electrically conductive tip of a scanning tunneling microscope (STM). An STM maps the contours of conductive surfaces by nudging its tip up close and allowing electrons to leap across to the surface, in a flow that's proportional to the separation. Other researchers have shown that placing a metal or semiconductor nanocrystal between two electrodes can turn this setup into an SET.

Because electrons repel one another, only a limited number can reside on the tiny nanocrystal. As a result, additional electrons can hop from one electrode, the STM in this case, to the nanocrystal only as other electrons leave by jumping to the other electrode. As in a conventional transistor, a third "gate" electrode controls the tempo of the electron movements. Placed near the nanocrystal, the gate raises the electrical conductivity of the tiny island when it is charged, getting the electrons to hopscotch faster.

Feldheim and his colleagues wanted to see, he says, "if we could get that same [gating] effect chemically." Their idea was to coat gold nanocrystals with organic compounds that can alter their charge and thereby act like

a gate electrode. In this case, the researchers coated gold nanocrystals with small ring-shaped molecules of an organic substance called galvinoxil. After attaching the coated nanocrystals to a gold electrode with the help of Velcro-like molecules called hexanethiols, they then dunked the assemblage in a water-based solution, maneuvered an STM tip close to the surface, and raised the solution's pH by adding a buffer. As the solution grew more basic, it pulled protons away from the galvinoxils, leaving the molecules negatively charged. This added charge makes it more difficult for an electron to hop onto the island and find its way to the gold electrode, creating a drop in the electrical current. The result,

in short, was a SET-based pH sensor.

The NC State team's approach is still tied to a tabletop-sized STM, which restricts its possible applications. But the researchers are at work on a scheme to make arrays of tiny electrodes in pairs separated by just 5 nanometers or so, with a single nanocrystal perched between the paired electrodes. Because it's relatively easy to coat nanocrystals with a variety of compounds that are themselves sensitive to the presence of other chemicals, a single array could signal the presence of a range of molecules. Cells, which manage this type of sensitive chemical detection day in and day out, may be in for a little competition.

—ROBERT F. SERVICE

MEETING AMERICAN SOCIETY FOR CELL BIOLOGY

New Findings Point to an Abundance of Cellular Riches

SAN FRANCISCO—An air of optimism pervaded the annual meeting of the American Society for Cell Biology, held here last month. The \$2 billion boost the National Institutes of Health budget got this year explained some of the good cheer. But the 8000 participants also found much excitement in the science, which ranged from new roles for the giant protein titin to the subtle tricks of the salmonella pathogen.

Bacteria Pull Cell Skeletons Out of the Closet

The ability of disease-causing bacteria to manipulate the cells they infect can make cell biologists drool with envy. Take the food-poisoning bacterium *Salmonella typhimurium*: When this pathogen encounters target cells, it stimulates a dramatic ruffling in the cellular membrane at the point of contact. The ruffled membrane then grabs the bacteria and pulls them inside. Biologists are now learning just how *S. typhimurium* tricks cells into aiding it.

At the meeting, Daoguo Zhou, a postdoc in microbiologist Jorge Galán's lab at Yale University School of Medicine, reported that a bacterial protein called SipA appears to play a key role in this uptake. Injected into cells by the bacteria, it apparently binds to one of the main components of the cell's internal skeleton, a protein called actin. By modifying the properties of actin, SipA helps stabilize the fibers supporting the ruffles.

In addition to providing insight into how *S. typhimurium* coopts host cell molecules and causes disease, the result may lead to a

better understanding of normal mammalian cell behavior. Actin rearrangements similar to those triggered by SipA also occur during the

cell migrations needed for embryonic development and in cells responding to growth factors or becoming cancerous. The pathway that results in membrane ruffling "touches on almost every aspect of cell life," says Dafna Bar-Sagi, a cell biologist at the State University of New York, Stony Brook. Studies of bacterial mutants unable to stimulate events critical to ruffling could help scientists dissect the separate steps of the pathway and thus those of normal events.



Getting focused. SipA helps host cells form the bacteria-grabbing ruffles.

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The current finding is an outgrowth of a discovery made several years ago when researchers learned that many bacterial patho-