NEW MATERIALS

IT'S A NANO WORLD

Manipulating molecules can create tomorrow's miracle materials

BY OTIS PORT

Materials technology is the real wealth of nations. It has been the hallmark of civilizations stretching back 8,000 years to the Bronze Age. Today's Information Age is no different. Without silicon that is 99.99999% pure, there wouldn't be computer chips, cell phones, or fiber-optic networks. In recent decades, inorganic chemists have concocted an impressive array of metals, alloys, and ceramics—sending skyscrapers ever higher, making cars lighter and more fuel-efficient, and launching air travel for the masses.

Organic chemistry, meanwhile, contributes its own share of modern conveniences. It produces the plastic packages that keep foods fresh, the housings that protect TVs and appliances, and synthetic fleeces that ward off the cold. Organic chemists created the fertilizers that help feed the world—and the ever-growing medley of wonder drugs that keep people healthy.

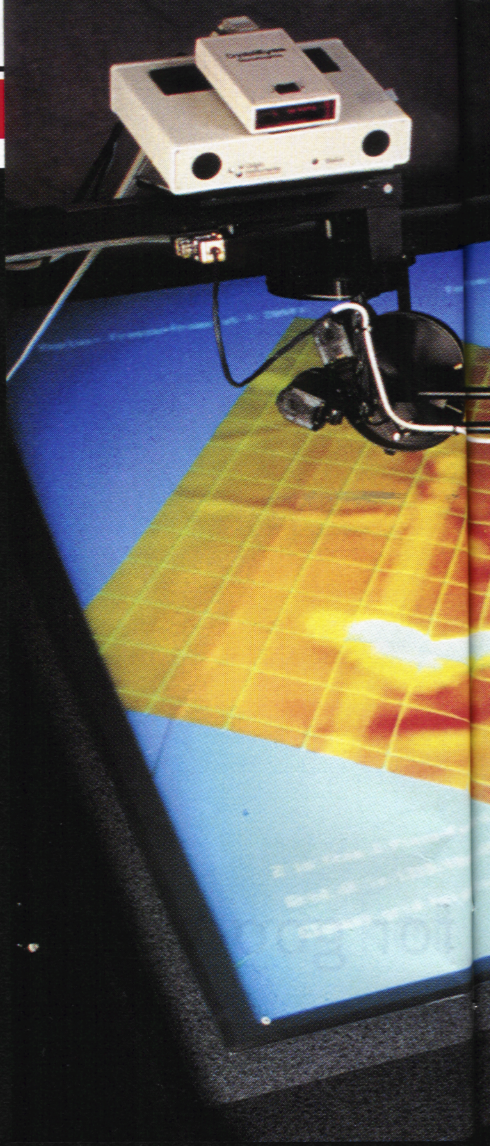
BOUTIQUE. Now, materials scientists are determined to transform the world yet again. Not content with the raw materials that can be extracted from the earth, researchers are mining their imaginations for totally new structures. They're doing it by tearing down the walls between organic and inorganic chemistry, something that not long ago would have been dismissed as pseudoscience. Tomorrow's inorganic-organic combos will be tailored from the bottom up—patched together from individual atoms or molecules—to provide the precise properties needed for each specific application. Arden L. Bement Jr., an engineer at Purdue University, calls it the dawn of "the boutique materials age." And it promises to turn Mother Nature green with envy.

The possibilities are almost endless: Polymer-based paints and coatings that contain tiny ceramic particles to defy scratching and corrosion. Improved catalysts that spawn new pharmaceuticals and plastics. Iron-polymer batteries that generate twice as much power. We could also see resilient metal-composite car-body panels that pop back into shape after minor fender-benders. Tough yet lightweight composites that boost jet-engine performance—including turbofans that self-repair tiny stress cracks. And there'll be all manner of materials with internal smarts that emulate biological systems, enabling them to adapt to changing conditions, compensate for wear, and warn of impending trouble.

Biological metaphors are a frequent theme among nano researchers, partly because they work with things measured in nanometers. This is the scale at which molecules mingle to create DNA and proteins, the building blocks of life. A nanometer is a billionth of a meter. Individual atoms are a few nanometers in diameter.

Indeed, a chief goal of organic-inorganic weddings is to breathe a spark of life into tomorrow's materials progeny. That's not just a dream. With nano engineering, "almost anything you can think of will be possible," declares W. Lance Haworth, executive officer for materials research at the National Science Foundation (NSF). The idea, says John H. Weaver, head of materials science at the University of Illinois, is to harness the molecular mechanisms that Nature has evolved for the production of new materials.

The appeal of bio-inspired materials is



JUST LIKE CHILD'S PLAY

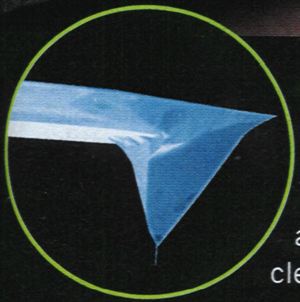
With the nanoManipulator system at the University of North Carolina, experiments in nano land are almost child's play. Holding a pencil-like device, researchers can nudge molecules, like the carbon nanotubes projected onto the table, into different arrangements. A computer tracks every motion, reduces it a millionfold, and steers the tip of an atomic-force microscope, or AFM.

easy to understand: The human body is a marvelously efficient factory. Most cells in the body contain the entire genetic code—4 billion "base pairs" of data that contain the recipes for making every one of the body's 10 trillion cells. But each cell actually needs just a tiny chunk of the genetic code to reproduce itself, and it manages to track down only that data. Since all 10 trillion cells replace themselves every few years, the body cranks out new DNA at the amazing rate of 10,000 miles an hour, day in and day out. But before nanotechnology can give birth to "living" materials, many fundamental issues must be resolved. Biological systems, Haworth notes, "know when to switch various functions on and off. How do you mimic those processes in synthetic materials? How do you get organic and inorganic materials to grow cooperatively together?"

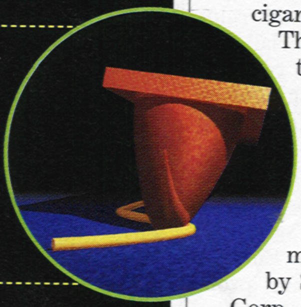
EXOTIC TOOLS. To find the answers, materials wizards are using exotic tools such as scanning-probe microscopes with supersharp tips. These not only trace the outlines of individual atoms but also move them around to explore how nanosize elements fit together. For example, the nanoManipulator at the University of North Carolina makes dabbling in chemistry so easy that biologists and physicists regularly use it to play with atoms and molecules as if they were Tinkertoys. "What we're having the most fun with now," says Sean Washburn, a North Carolina physicist, "are cigar-shaped nanotube molecules."

These are elongated versions of the carbon buckyballs discovered in 1985 by Richard E. Smalley, a professor of physics and chemistry at Rice University. The discovery earned Smalley a Nobel Prize in 1996.

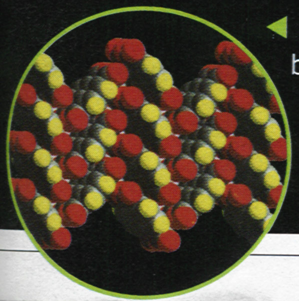
Nanotubes are truly wonder molecules. First created in 1991 by Sumio Iijima, a scientist at NEC Corp., nanotubes are at least 100 times stronger than steel, but only one-sixth as heavy—so nanotube fibers could bolster just about any material. Moreover, nanotubes can conduct heat and electricity far better than copper, so reinforcing strands could do double duty as computer circuits, creating the nervous system for "smart" materials. Or



◀ AFM tips are so pointy they can trace the outlines of individual atoms. The whisker on the tip at left is a carbon nanotube that improves the resolution of images. For physically manipulating molecules, clean-shaven tips are used.

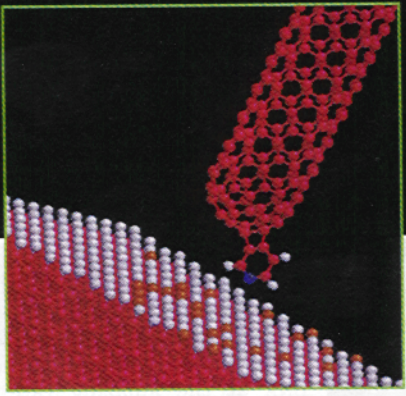


▶ Here, an AFM tip touches and bends a carbon nanotube. Because it would be incredibly tedious to create electronic circuits by nudging millions of nanotubes into place, researchers are working on techniques that will cause nanotubes to self-assemble into desired shapes and patterns.



◀ As an alternative, conductive polymers can be coaxed into specific patterns. The Z-shaped structure here is formed by a conductive polymer with a tongue-twisting name: naphthalene-tetracarboxylic-dianhydride.

(TOP TO BOTTOM) PHOTOGRAPHS COURTESY UNIVERSITY OF NORTH CAROLINA, DEPT. OF COMPUTER



THE ULTIMATE LIBRARY Incredible amounts of information could be saved on a postage stamp if digital bits were stored as individual atoms. In NASA's visionary scheme, a nanotube is used as the read/write head, and zeros and ones are represented with hydrogen and fluorine atoms, respectively. A stamp might hold the entire Library of Congress and then some.

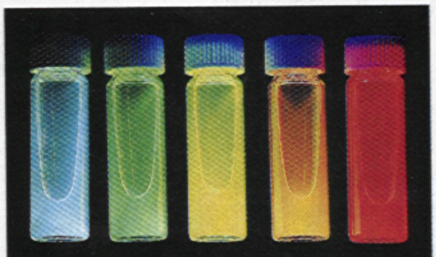
they could serve as heat pipes to keep composite-plastics parts cool enough to be used in engines.

These new molecules extend the performance of organic materials to unprecedented levels. But inorganic substances still offer many advantages. And nanotechnology provides the means to fashion inorganic-organic hybrids. "Now you can develop materials that you couldn't even imagine before, because the mix of properties just wasn't available," says Ralph E. Taylor-Smith, a chemical engineer at Lucent Technologies Inc.'s Bell Laboratories. Inorganic materials tend to be hard but brittle—glass being a prime example. Organic materials, on the other hand, are typically soft and rubbery. Merge the two sets of properties, says Taylor-Smith, and you could get a substance that's very strong and hard, yet with enough "give" to impart good impact resistance. One example: a big flat-panel display for handheld computers that folds up.

SCATTERSHOT. Inorganic-organic hybrids are hardly new, of course. Fiberglass-reinforced plastics have been around for decades. But these are essentially physical mixtures. They often suffer from weak chemical bonds between the reinforcements and the bulk material. Beyond a certain stress level, the two materials can delaminate, which often leads to structural failure. Nano engineering promises to cure that by tailoring the surfaces of components so they have chemical hooks specifically designed to glom onto each other.

It's basically an issue of size. Silicon's carefully crafted semiconducting properties are produced after the fact, by shooting boron or other atoms into the finished bulk material. Tomorrow, this scattershot approach won't be good enough. Organic molecules will have to be placed at specific locations with atomic precision. One method might be to insert organics inside the crystalline structure of silicon, so its properties can be chemically tweaked from within. A research team at the University of Toronto, led by chemist Geoffrey A. Ozin, pulled off such a feat late last year. They crammed organic molecules into porous silica, producing an insulating compound that could replace the silicon-dioxide layers on future chips. Circuit lines and insulation will soon shrink to dimensions at which silicon dioxide is no longer an effective insulator.

At the University of Minnesota, a team led by chemist Xiaoyang Zhu tackled another size-related problem by attaching chlorine atoms to silicon atoms. The problem is called stiction—the stickiness that particles exhibit starting in the so-called mesoscale range. This is in between the nano realm of quantum physics and the macro world of chemical events that unfold in test tubes or industrial vats. Stiction kicks in at around 1,000 nanometers. Below that, surface forces "really dominate everything else," says Zhu. Even fluids have a hard time moving, not to mention the components in microelectromechanical systems, or MEMS—little machines carved into silicon chips. But a coating of chlorine that's one, and only one, atom thick can create a lubricating film that will make it easier for MEMS designs to include parts that move across the surface.



RAINBOW'S END

The romance of rainbow colors gives way to mathematical formulas in the nano world. Researchers at MIT developed a polymer-semiconductor composite that can emit different colors–in fact, all visible colors. The material could yield nano-size light-emitting diodes (LEDs) for wallpaper-thin computer displays and TV screens.

The nano world has its own size-related surprises. For example, researchers at Massachusetts Institute of Technology discovered that semiconductor nano particles sandwiched between one polymer that conducts negative charges and another that conducts positive charges can create light-emitting diodes (LEDs) that emit colors spanning the visible spectrum. The same structure produces a rainbow of hues depending on the size of the particles. Green light is emitted by 1.8-nanometer particles, while 7.5-nanometer particles glow red when they're illuminated with ultraviolet light. This makes for more than a pretty light show. Diodes like these could provide the color in those fold-up displays for pocket computers—or for "wallpaper" TV screens in homes.

Similarly, the bulk properties of materials often change dramatically with nano or meso ingredients. Composites made from particles of nano-size ceramics or metals smaller than 100 nanometers can suddenly become much stronger than predicted by existing materials-science models, says Richard W. Siegel, chief nanotechnologist at Rensselaer Polytechnic Institute. For example, metals with a so-called grain size of around 10 nanometers are as much as seven times harder and tougher than

NEW DREAMS With a bottom-up approach, scientists can fashion materials that traditional chemistry could never create

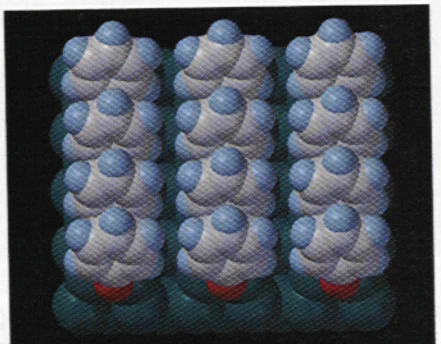
(TOP TO BOTTOM) PHOTOGRAPHS COURTESY NASA/AMES RESEARCH CENTER; FELICE FRANKEL/MIT/CENTER FOR MATERIALS SCIENCE AND ENGINEERING their ordinary counterparts with grain sizes in the hundreds of nanometers.

The causes of these drastic changes stem from the weird world of quantum physics, says Thomas N. Theis, IBM's director of physical science. The bulk properties of any material, he explains, are merely the average of all the quantum forces affecting all the atoms. "But as you chop things smaller and smaller, you eventually reach a point where the averaging no longer works."

Associated changes in electrical properties have grabbed the attention of the U.S. Air Force, says John Kieffer, an inorganic chemist at the University of Illinois. The radar "signature" of a jet plane coated with nano compounds could be smaller and stealthier. Mesoscale particles may turn up in car paints. Andreas Stein, a Minnesota chemist, is working on photonic crystals that could be tuned to reject green light. Green light carries the most energy of any color. Block it with special paints, and the interior of cars parked in the sunlight wouldn't get so hot. Or the paint could include tough ceramic particles smaller than the wavelengths of visible light—making them transparent, so they wouldn't affect the color of the paint. But the particles could provide a virtually scratchproof surface.

CHAMELEON. For materials scientists, all these strange new potentials are inspiring new dreams. At the University of California at Los Angeles, chemist James R. Heath envisions building unique materials from "artificial atoms." These actually are small clusters of atoms dubbed quantum dots. With a bottom-up approach, Heath predicts, it will be possible to create materials that could never be produced with traditional chemistry. To prove it, his research group recently hatched a chameleon material that responds to electrical signals by switching back and forth from being a metal to being an insulator.

To Colin Humphreys, a materials expert at Britain's Cambridge University, such feats indicate that materials



MIX AND MELD

Organic coatings consisting of one-atom-thick layers may be silicon's ticket to new jobs. Here, nitrogen atoms (red) link a silicon substrate and a coating of carbon atoms capped with hydrogen (blue). The University of Minnesota is developing a range of coatings for inorganic silicon.

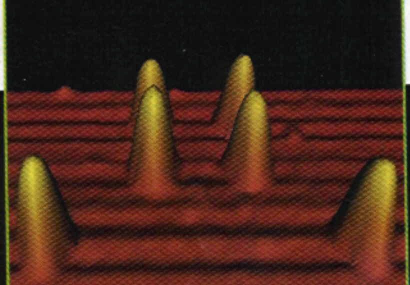
science is now reaching a point analagous to genetic engineering in biology: Molecules will be engineered at the atomic level, then replicated with biologically modeled processes to produce bulk quantities. That's why many labs are working to harness biological principles, often focusing on DNA-like molecules that can direct the self-assembly of new materials. DNA is the leader of the body's chemical orchestra, directing it to turn out the 200-odd types of cells that make up human bodies.

Chipmakers salivate at the thought of a DNA-type process for creating circuits. Actually, it will soon be necessary, says Aristides A. G. Requicha, head of the Laboratory for Molecular Robotics at the University of Southern California. "We've got to break away from traditional silicon technology," he says, "because it's about to price itself out of the market." The cost of new chip factories has climbed above $2 billion, with no end in sight. In 10 years, it could hit $15 billion. Moreover, silicon physics is due to hit a brick wall around 2010 to 2015, when circuit lines shrink to 0.01 micron and fall prey to the weird effects of quantum physics. So the search is on for new ways to fabricate transistors and wires. This is the main driver behind nanotech advances.

This year, a research group at the University of Illinois, led by electrical engineer Joseph W. Lyding, pulled off a neat trick. They attached buckyballs and other carbon molecules to precise points on the surface of silicon, where the silicon transistors would normally be. The carbon atoms were attached in such a way that they could spin like tops, at speeds of trillions of times a second. If Lyding's team can create nano circuits to regulate the direction of spin, their carbon transistors might switch on and off a thousand times faster than silicon. The Defense Advanced Research Projects Agency (DARPA), the Pentagon's venture capitalist, is cultivating that potential. It has launched a $10 million "spintronics" research program headed by the University of Buffalo.

In another thrust, DARPA's Moletronics program aims to lay the foundations for molecular electronics. While molecular biologists can manipulate electrical charges in protein channels very accurately, this knowhow has been patched together empirically. The mathematical formulas that engineers would need to translate the biological processes into computer circuits don't exist. "We're getting the hang of designing molecules to have specific electrical properties, not just chemical properties," says Christie R. K. Marrian, manager of DARPA's Moletronics program. How to wire such molecular switches together is now the main roadblock, he adds, but a DNA-type mechanism for self-assembly could be a solution.

If scientists harness DNA for materials, the results would be amazing. Kieffer at Illinois envisions engineers spelling out what a material needs to do, and a computer program doping out the possible structures and the procedures for growing them. For NASA, creating superstrong, ultralight materials on de-



ATOMIC SKYSCRAPERS Researchers can use exotic tools such as atomic-force microscopes to nudge individual atoms into place. Until recently the atoms were just rolled across a surface. Now scientists at the University of Southern California are building upward, erecting structures that look like tall ant hills—two, three, and four molecules high.

(TOP) PHOTOGRAPHS COURTESY PROFESSOR ZHU/UNIVERSITY OF MINNESOTA; COURTESY LABORATORY FOR MOLECULAR ROBOTICS/UNIVERSITY OF SOUTHERN CALIFORNIA mand would be just what the doctor ordered. "NASA has the world's biggest weight-watchers program," says Meyya Meyyapan, chief nanotechnologist at NASA's Ames Research Center. "Every pound we try to lift to LEO [low-earth orbit] costs $10,000—and to Mars, it's $100,000 a pound." The ultimate goal: a robotic spacecraft tipping the scales at 22 pounds. Here on earth, Dow Chemical Co. is working on nano composites for cars that could slash U.S. gasoline consumption by 4 billion gallons for each model year they're used. In turn, that would cut carbon-dioxide emissions by 11 billion pounds.

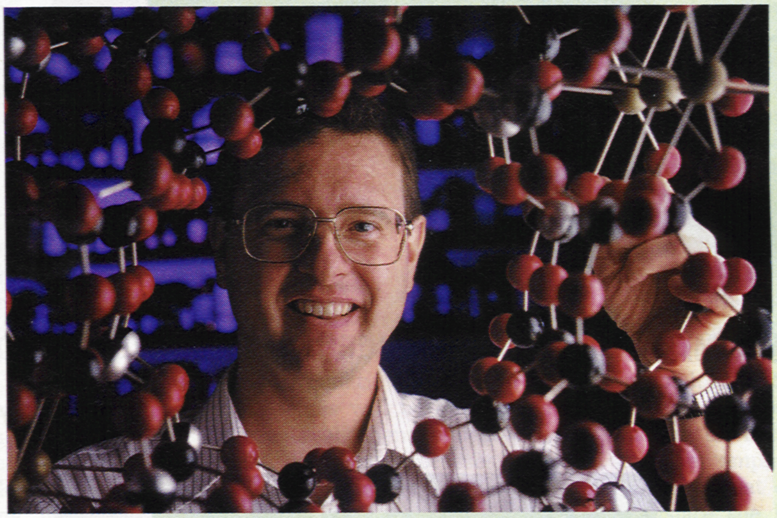
PAYOFFS. Researchers at the California Institute of Technology think they're close to cracking Nature's codes. William A. Goddard III, head of Caltech's Materials & Process Simulation Center, says software has been devised for the Army that predicts the structure necessary to create a supersensitive sniffer. "We're now in the process of designing modified olfactory receptors sensitive to very small concentrations of the products that come off land mines—and off nerve gases," says Goddard. Still, many questions remain, he admits. For example, when a molecule binds to an olfactory receptor, the receptor signals nerve cells by releasing calcium. "We don't know enough about that to mimic it artificially," so for now the sniffer will sound the alarm with silicon circuits. But in a year or two, he predicts, Caltech will know how to do a far broader imitation of life.

Some scientists smell commercial payoffs and are forming companies. Earlier this year, Smalley of Rice teamed up with Bob G. Gower, former chairman of Lyondell Petrochemical Co., to create Carbon Nanotechnologies Inc. in Houston to produce nanotubes. Minnesota's Stein recently co-founded MicroSurfaces Inc. in Minneapolis to market mesoscale coatings. And at North Carolina, physicist Otto Z. Zhou has a prototype product: an iron-polymer nano composite battery with "double the lifetime per unit weight" of lithium-ion batteries—plus several manufacturers haggling for the rights to build it.

The new century is off to a good start in nanotech. It will be years before nanotubes and nanocomposites become as familiar as silicon. But the Nano Age should be in full swing around 2010.

FROM A VOLCANO TO YOUR WASHING MACHINE—AND BEYOND

Look at the ingredients listed on a box of laundry detergent, says Andreas Stein, a chemist at the University of Minnesota. "You may find 'aluminosilicates as water softeners.' These are zeolites." The tiny porous crystals function as sponges for the calcium and magnesium atoms that make water "hard." Recently, zeolites emerged as a hot area of so-called meso-scale research. This is the field of materials science that studies structures and processes involving things bigger than atoms and molecules but smaller than the clumps of bulk materials in traditional test tubes and vats.



CRYSTAL GAZING
Chemist Andreas Stein envisions oil-grabbing crystals that can clean up spills

CATALYSTS. Nature's zeolites, found in volcanic rocks, were first introduced to industry in the 1950s. Because they're even more porous than sponges, zeolites have an enormous surface area—hundreds of square meters per gram. And the aluminum atoms studding the cavern walls of the silicon dioxide-based crystals can serve as catalysts to trigger chemical reactions. Led by ExxonMobil Corp., the petrochemical industry has been refining oil with zeolite catalysts since the early 1960s. Today, most oil and many polymers are processed with zeolites, although the crystals are now largely man-made. Their pores are carefully tailored to admit molecules up to a certain size, but no bigger. Zeolites with slightly different pore sizes produce gasoline with different octane ratings by separating petroleum molecules of different sizes—larger molecules packing more energy.

What sparked the latest round of research was Mobil's development in 1992 of a new kind of zeolite crystal. By modifying the basic inorganic structure with organic molecules, Mobil stretched the pore openings and channels, enlarging them enough to admit even the "bottom-of-the-barrel" gunk that until then had defied processing with zeolites. But the bigger pore sizes also opened the door to other exciting applications, including pharmaceuticals. Researchers at several schools—including Pennsylvania State University, Georgia Institute of Technology, and the Universities of Rochester, Toronto, and Wisconsin—began exploring the potentials of inorganic-organic hybrids. Late last year, a team of chemists from Arizona State University and the University of Michigan announced a metal-organic "framework" that can be used at temperatures up to 300C—highly unusual for a structure containing organic components, so even more applications may arise.

Back in Minneapolis, one of Stein's pet projects is aimed at a variation of zeolite water softeners. He wants to create a meso sponge that sops up oil. Someday, when an oil spill washes ashore, the cleanup crew may sprinkle Stein's oil-grabbing crystals on the water to get rid of the oil below the surface while it collects the thick stuff floating on top.

By Otis Port in New York

JONATHAN CHAPMAN