Self-Assembling Materials

The smaller, more complex machines of the future cannot be built with current methods: they must almost make themselves

by George M. Whitesides

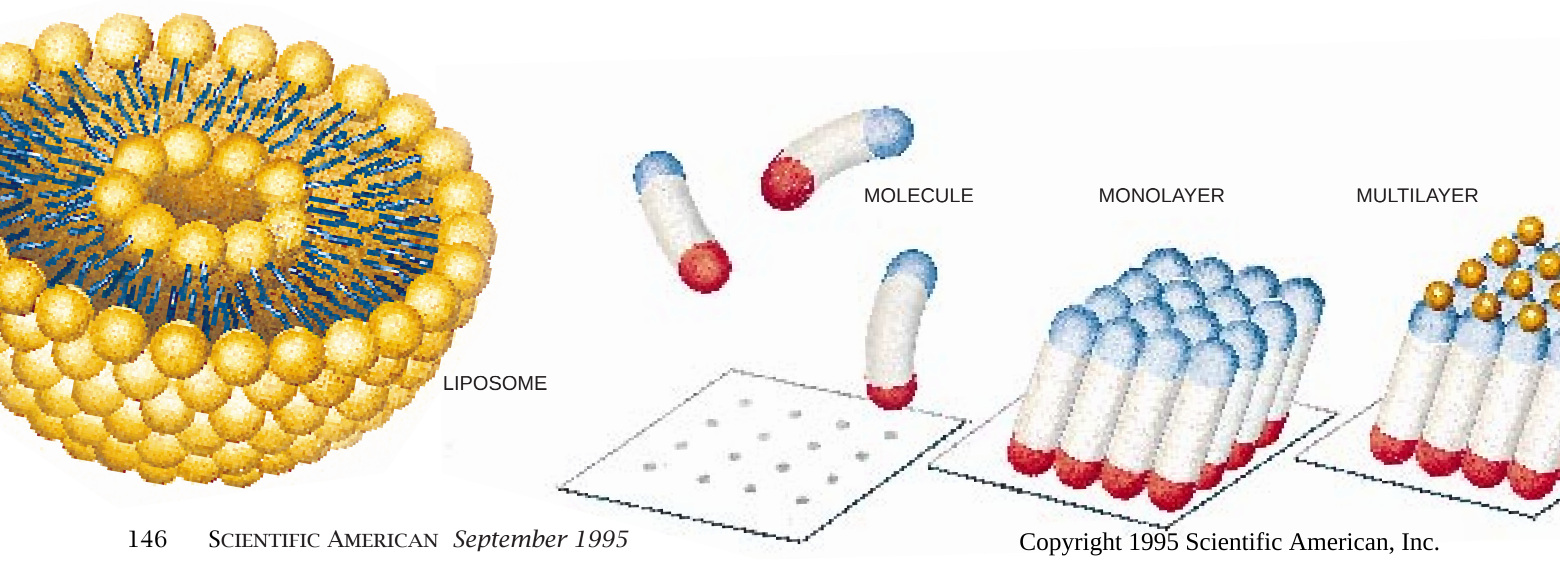
Our world is populated with machines, nonliving entities assembled by human beings from components that humankind has made. Our automobiles, computers, telephones, toaster ovens and screwdrivers far outnumber *us.* Despite this proliferation, no machine can reproduce itself without human agency. Yet.

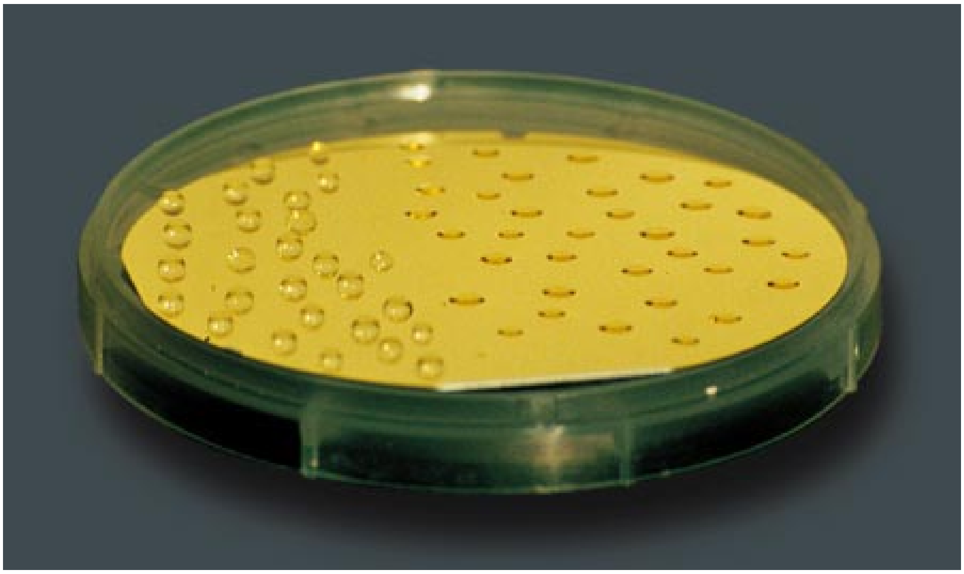
In the 21st century, scientists will introduce a manufacturing strategy based on machines and materials that virtually make themselves. Called self-assembly, it is easiest to define by what it is not. A self-assembling process is one in which humans are *not* actively involved, in which atoms, molecules, aggregates of molecules and components arrange themselves into ordered, functioning entities without human intervention. In contrast, most current methods of manufacturing involve a considerable degree of human direction. We, or machines that we pilot, control many important elements of fabrication and assembly. Self-assembly omits the human hand from the building. People may design the process, and they may launch it, but once under way it proceeds according to its own internal plan, either toward an energetically stable form or toward some system whose form and function are encoded in its parts.

The concept of self-assembly is not new. It was inspired by nature, where entities as simple as a raindrop or as complex as a living cell arise from physical principles or instructions implicit in their components [*see box on page 148*]. And it is already exploited in the manufacture of a number of common products. Most window glass, for example, is so-called float glass, made by floating molten glass on a pool of molten metal. The metal tends to minimize its surface area by becoming smooth and flat; consequently, the glass on top becomes optically smooth and uniformly flat as well. It is much less expensive to produce float glass than it is to grind and polish glass produced by other processes, and the quality of the float-glass surface is higher. Similarly, conventional manufacturing methods cannot specify the placement of the silicon and dopant atoms in a semiconductor crystal. The growth of the crystal from a melt of silicon is dictated by thermodynamic principles, not human presumption.

Such examples illustrate the potential of self-assembly. Those materials were arrived at almost by accident. In the next few decades, however, materials scientists will begin deliberately to design machines and manufacturing systems explicitly incorporating the principles of self-assembly. The approach could have many advantages. It would allow the fabrication of materials with novel properties. It would eliminate the error and expense introduced by human

SELF-ASSEMBLING MATERIALS, such as the liposome at the left, are generating increasing interest. The liposome represents an early success among these materials: the microscopic capsules are in clinical trials as a drug-delivery system within the body. Current research focuses on self-assembling layers built from sausage-shaped molecules. At one end of each molecule is an atom that interacts strongly with a surface; at the other end, a variety of other atomic groupings. These molecules can organize themselves on one surface, thereby creating at their other end a surface with different properties. Such monolayers are being used to guide the growth of living cells, to study wetting, adhesion and friction, and to form microstructures. Additional layers can be built onto the monolayer; these self-assembling multilayers are being explored as coatings to control reflection in devices that use light in communications.





GEORGE M. WHITESIDES

GOLD-COATED SILICON WAFER is often used in studying self-assembled monolayers. In this experiment the left half was covered with a monolayer having a hydrophobic surface, the right half with one presenting a hydrophilic surface. Drops of water flattened on the hydrophilic side but formed round beads that minimized contact with the surface on the hydrophobic side. The behavior shows that the outermost part of the self-assembled monolayer controls the wettability of the surface. The same strategy can be used to control adhesion, friction and corrosion.

labor. And the minute machines of the future envisioned by enthusiasts of so-called nanotechnology would almost certainly need to be constructed by self-assembly methods.

From Materials to Machines

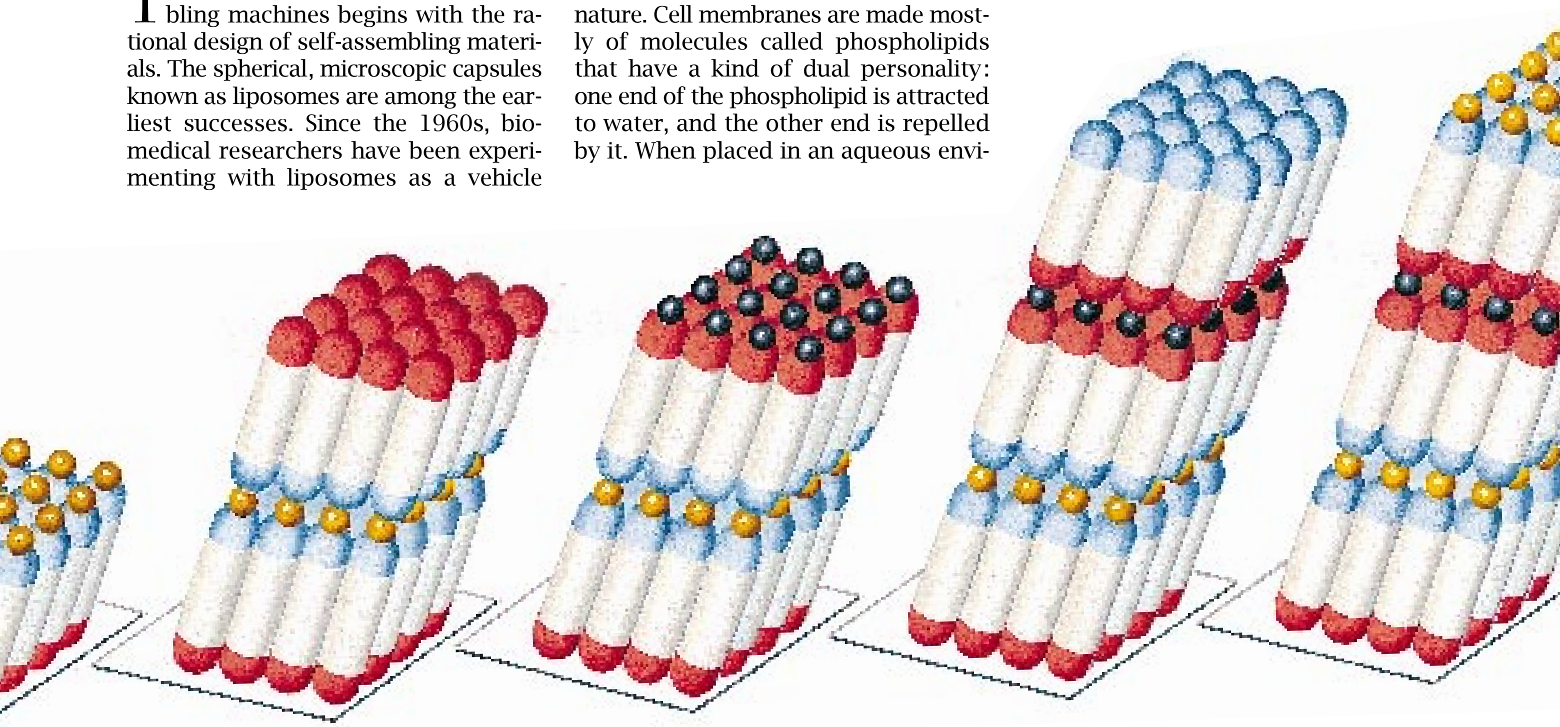
The rational design of self-assembling machines begins with the rational design of self-assembling materials. The spherical, microscopic capsules known as liposomes are among the earliest successes. Since the 1960s, biomedical researchers have been experimenting with liposomes as a vehicle for transporting drugs in the body; because the capsules protect their cargo from degradation by enzymes, a drug contained in a liposome envelope can remain active for longer periods than it would otherwise.

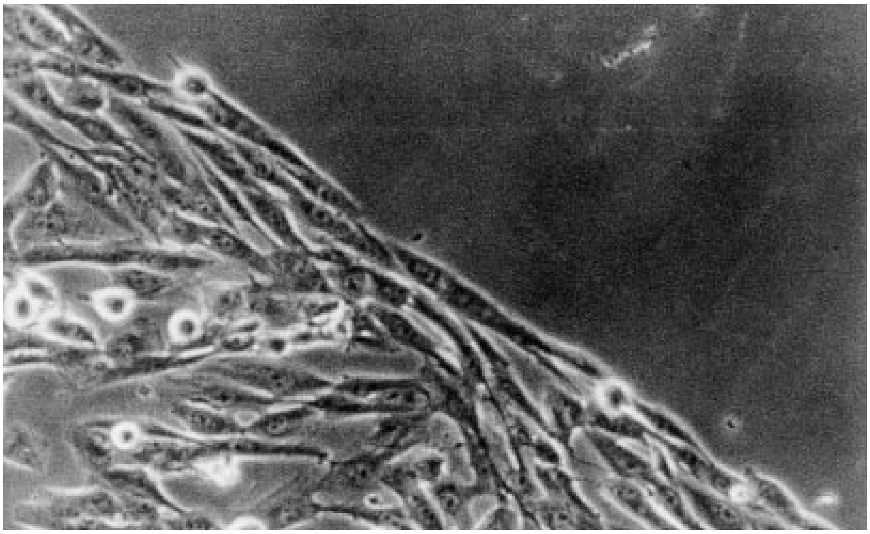
Liposomes were modeled after cell membranes, which are among the most striking examples of self-assembly in nature. Cell membranes are made mostly of molecules called phospholipids that have a kind of dual personality: one end of the phospholipid is attracted to water, and the other end is repelled by it. When placed in an aqueous environment, the molecules spontaneously form a double layer, or bilayer, in which the hydrophilic ends are in contact with the water and the hydrophobic ends point toward one another. Researchers use these same phospholipids to make liposomes. If there are enough molecules, the phospholipid bilayer will grow into a sphere with a cavity large enough to hold drug molecules. The liposomes are then injected into the body, and the drugs are released either by leakage or when a sphere ruptures. Liposome drug-delivery systems are currently in clinical trials.

SAMs

The example of nature has helped to illuminate liposome research, but many investigations of self-assembling behavior must start almost from scratch. A self-assembled monolayer—affectionately referred to as SAMs by those who work with them—is a simple prototype that exemplifies the design principles materials researchers are exploring. A SAM is a one- to two-nanometer-thick film of organic molecules that form a two-dimensional crystal on an adsorbing substrate. The molecules in a SAM are sausage-shaped, being longer than they are wide. At one end is an atom or

GEORGE V. KELVIN





CELL PATTERNING reveals the boundary between two different types of self-assembled monolayers. One side was designed to promote, the other to prevent, the adhesion of mammalian cells. The ability to control the attachment of living cells is being used to understand how cells interact with man-made surfaces and with surfaces that mimic those in living organisms and to improve the performance of devices that will be implanted in the body.

group of atoms that interacts strongly with the surface; at the other, chemists can affix a variety of atomic groupings, thereby altering the properties of the new surface formed by the SAM.

The most extensively studied system of SAMs is made of molecules called alkanethiols, long hydrocarbon chains with a sulfur atom at one terminus. The sulfur adsorbs well onto a substrate of gold or silver. When, say, a glass plate coated with a thin film of gold is dipped into a solution of alkanethiol, the sulfur atoms attach to the gold. The distance between the sulfur atoms adsorbed on the surface is about the same as the cross-sectional diameter of the rest of the molecule (hence the sausage shape), and the alkanethiols pack together, generating what is essentially a two-dimensional crystal.

The thickness of this crystal can be controlled by varying the length of the hydrocarbon chain, and the properties of the crystal's surface can be modified with great precision. By attaching different terminal groups, for example, the surface can be made to attract or repel water, which in turn can affect its adhe-

Two Types of Self-Assembly

RAINDROPS on a leaf illustrate thermodynamic self-assembly.

Nature abounds with examples of self-assembly. Consider a raindrop on a leaf. The liquid drop has a smooth, curved surface of just the kind required for optical lenses. Grinding a lens of that shape would be a major undertaking. Yet the liquid assumes this shape spontaneously, because molecules at the interface between liquid and air are less stable than those in the interior. The laws of thermodynamics require that a raindrop take the form that maximizes its energetic stability. The smooth, curved shape does so by minimizing the area of the unstable surface.

This type of self-assembly, known as thermodynamic self-assembly, works to construct only the simplest structures. Living organisms, on the other hand, represent the extreme in complexity. They, too, are self-assembling: cells reproduce themselves each time they divide. Complex molecules inside a cell direct its function. Complex subcomponents help to sustain cells. The construction of a cell's complexity is balanced thermodynamically by energy-dissipating structures within the cell and requires complex molecules such as ATP. An embryo, and eventually new life, can arise from the union of two cells, whether or not human beings attend to the development.

The kind of self-assembly embodied by life is called coded self-assembly because instructions for the design of the system are built into its components. The idea of designing materials with a built-in set of instructions that will enable them to mimic the complexity of life is immensely attractive. Researchers are only beginning to understand the kinds of structures and tasks that could exploit this approach. Coded self-assembly is truly a concept for the next century.

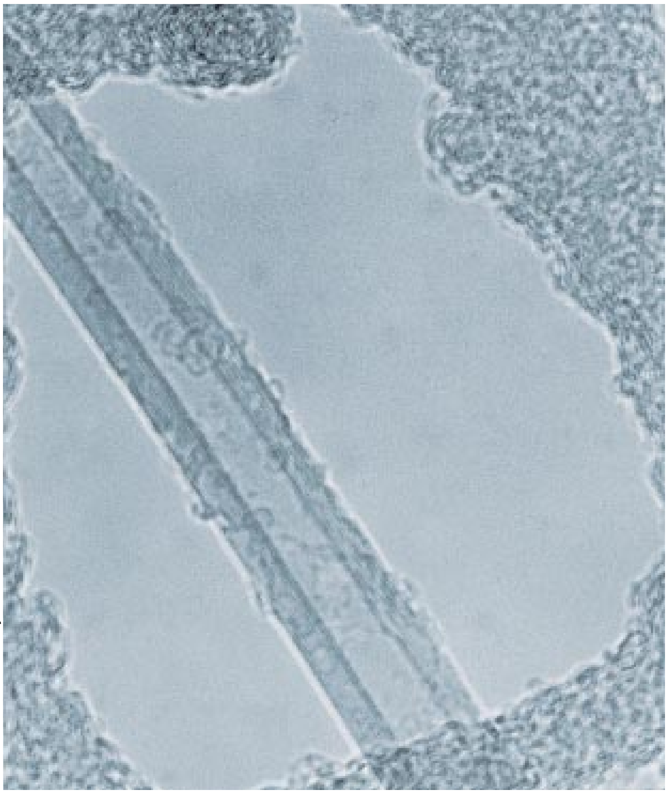
EMBRYO exemplifies coded self-assembly.

sion, corrosion and lubrication. If the alkanethiols are stamped onto the gold in a particular pattern, they can be used to investigate the growth of cells on different organic substrates or to construct diffraction gratings for optical instruments. In contrast to most procedures for surface modification, all these operations are simple and inexpensive, requiring neither high-vacuum equipment nor lithography.

Buckytubes

Self-assembly has also produced tiny graphite tubes that are among the smallest electrical "wires" ever made. These tubes are called buckytubes, because they are structurally similar to the carbon buckyballs named for their resemblance to the geodesic domes of Buckminster Fuller. Buckytubes consist of several nested, concentric cylinders with nanometer-scale diameters, and because they are made of graphite—the most thermodynamically stable form of carbon at atmospheric pressure—they tend to form under conditions that allow carbon to move toward thermodynamic equilibrium.

In one process, a small drop of liquid metal is exposed at high temperature to a carbon source, such as benzene. The carbon dissolves on one face of the metal droplet and, for reasons no one quite understands, precipitates on the other. As it precipitates, it forms a circular tube of graphite whose diameter is fixed by the size of the metal drop. The tube grows from the drop continuously as carbon is fed to it. Because supports holding millions of metal drops are simple to prepare, millions of buckytubes can be grown simultaneously in a single reactor. The tubes are good conductors of electricity; although it is still not clear how to assemble them into coherent structures, chemists hope to use the tubes as dopants to increase electrical conductivity in polymers and other nonconducting materials and someday to build circuits with them.



YUAN LU *Harvard University*

BUCKYTUBES are among the smallest "wires" ever made. The electron micrograph shows in cross section the multiple layers of graphite of which they are composed. These nanometer-scale tubes are good conductors of electricity and may find use as dopants that increase conductivity in polymers and improve the performance of batteries.

Indeed, buckytubes might be part of a more ambitious approach to self-assembly embodied in what materials researchers call a crystal memory: a self-assembling, three-dimensional version of the planar memories that are used in microelectronic devices today. At present, the crystal memory is purely conceptual: not one of its components has been demonstrated in the laboratory, even in principle. But they can be imagined.

The smallest unit of a crystal memory might be a silicon chip or some other semiconducting material that would be capable of carrying out a variety of microelectronic operations and that would have embedded in it instructions on how to behave when activated by signals from similar chips. These units would aggregate spontaneously, or crystallize, into a single larger unit, much as a liposome or SAM forms from smaller components. In their new configuration, the chips would stimulate one another and form electrical connections; signals from those connections would then trigger the units to begin differentiation, according to their embedded programming, into specialized roles: input or output units, switches, memory cells and so on.

If such a device seems improbable, consider that the process just described has many precedents in nature; in fact, all forms of life issue from simple subunits communicating among themselves. A microelectronic memory device could someday be able to build itself by the crystallization of smaller parts, thus ushering in a new era in manufacturing.

The Author

GEORGE M. WHITESIDES is Mallinckrodt Professor of Chemistry at Harvard University. He received his Ph.D. in 1964 from the California Institute of Technology and taught at the Massachusetts Institute of Technology for almost 20 years before joining the chemistry department at Harvard in 1982. His interest in both materials science and biology and, in particular, his fascination with smaller and smaller structures drew him toward investigations of self-assembly.

Further Reading

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