Perspectives

MATERIALS SCIENCE

Some Assembly Required

Sharon C. Glotzer

Self-assembly—the spontaneous organization of matter into ordered arrangements—is a governing principle by which materials form (*1*). The patterns arising from self-assembly are ubiquitous in nature, from the opalescent inner surface of the abalone shell to the internal compartments of a living cell. Much of materials science and soft condensed-matter physics in the past century involved the study of self-assembly of fundamental building blocks (typically atoms, molecules, macromolecules, and colloidal particles) into bulk thermodynamic phases. Today, the extent to which these building blocks can be engineered has undergone a quantum leap. We are on the verge of a materials revolution in which entirely new classes of "supermolecules" and particles will be designed and fabricated with desired features, including programmable instructions for assembly. These new building blocks will be the "atoms" and "molecules" of tomorrow's materials, self-assembling into novel structures made possible solely by their unique design.

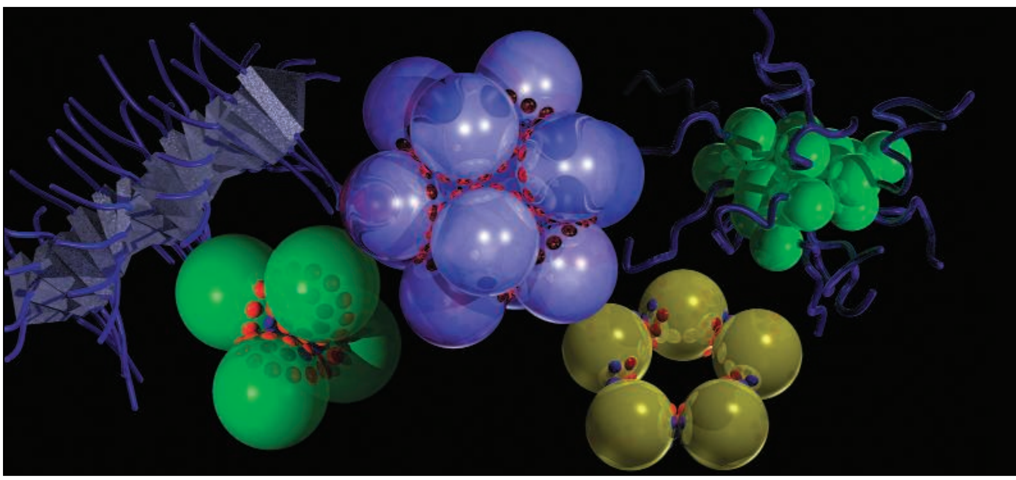
What happens when traditional atoms and molecules are replaced with these new building blocks? What types of ordered structures are possible, and what unique properties do they have?

Colloidal polyhedra (*2*), nanocrystals in the form of tetrapods (*3*) and triangles (*4*), and tiny cubes of molecular silica (*5*) are just a few examples of new building blocks being made today. In most cases, these building blocks may not naturally assemble into any desired structures. One emerging approach to confer upon nanoparticles and colloids predetermined "instructions" for assembly is to decorate the surface of the particles with "sticky patches," made, for example, of synthetic organic or biological molecules. This strategy takes its inspiration in part from biology, where the precision of self-assembled structures such as viruses and organelles originates in the selectivity of the interactions between their constituents. According to computer simulations, synthetic "patchy particles" should self-assemble under the right conditions into structures atypical of traditional materials (*6*) (see the figure).

On macroscopic scales, millimeter-sized plastic wedges patterned with patches of solder and hydrophobic lubricant self-assemble under surface tension when dispersed in water to form tiny electronic devices whose structure resembles that of the tobacco mosaic virus (*7*). Making patchy particles with precise patterns of interactions on nanometer scales is much more challenging, but exciting developments are being reported. For example, Stellacci and co-workers (*8*) recently synthesized gold and silver particles 4 nm in diameter, using organic molecules to control the size of the nanoparticles. Although the use of organic stabilizing layers is commonplace in nanoparticle synthesis, these researchers used a mixture of ligands that, on flat surfaces, would tend to phase separate into bulk phases or random domains. Instead, the ligands self-organized on the nanoparticle surface into repeating patterns of stripes and dots with spacings as small as 0.5 nm, imparting a controllable, precise, and unprecedentedly small pattern of attractive and repulsive patches to the surfaces of the particles. Striped spheres and spheres with polar patches were obtained, providing a striking demonstration of the role of curvature in pattern formation (*9*). This method suggests an exciting strategy for controlling the symmetry of nanoparticle assemblies through anisotropic interactions achieved by patterning. In another example, Mokari *et al.* recently patterned semiconductor tetrapods and nanorods with gold patches on the tips (*10*), potentially providing a new way to assemble components for nanocomputing devices.

Genetic engineering of biomolecules like DNA and proteins opens up further possibilities for conferring recognition (*11*) and chemical specificity to particles, creating building blocks that are potentially capable of assembling into hierarchically arranged structures. In a recent twist, a new patchy particle was synthesized by precisely positioning gold particles onto specific sites on the surface of the cowpea mosaic virus, creating a new type of building block with the potential for self-assembly (*12*).

Patchy particles are but one example of "shape amphiphiles"—building blocks of potentially complex shapes with competing interactions that expand the range of self-assembled structures beyond those exhibited by traditional amphiphiles such as surfactants and block copolymers. By attaching polymeric "tethers" to nanoparticles, another new class of shape amphiphile may be fabricated (*13*). These building blocks can



Predicted self-assembled structures for model building blocks. When selective interactions are introduced to particle surfaces through patterning of ligands or polymeric tethers, competing interactions can cause the particles to self-organize into complex structures (*6*, *13*). **(Left)** Twisted wire of tethered triangular nanoparticles; **(middle)** tetrahedron, icosahedron, and ring self-assembled from spherical patchy particles; **(right)** micelle of tethered nanospheres. To fabricate rings from patchy particles, selective sticky patches are placed anisotropically on the equatorial plane at a relative angle of <180°. The diameter of the rings is controlled by the angle between the patches. Tetrahedra and icosahedra form from particles with selective, ringlike patches shifted off the equatorial plane.

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form structures that combine the features of self-assembling surfactant or block copolymer systems with the intricate ordered phases of liquid crystals (see the figure). Patterning techniques such as that described above may provide a means to position tethers at specific locations on the particle surface. If this can be achieved, simulations predict that the combination of forces, particle shapes, and building-block topology will provide a means for assembling the particles into wires, sheets, tubes, and other structures. Examples of tethered building blocks already synthesized include poly(ethylene glycol)–tethered CdTe quantum dots (*14*), poly(ethylene oxide)–tethered fullerenes (*15*), and PEG-tethered silica cubes (*16*). Many more are sure to follow.

In contrast to traditional materials, where materials are selected, rather than designed, for specific applications, the next generation of materials will benefit from the a priori design of novel building blocks, programmed for assembly and synthesized with particular needs in mind. With the rapid pace of developments in this field, humankind's newest atoms and molecules are just around the corner.

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17. Supported by the NSF (grants CTS-0210551 and DMR-0103399) and U.S. Department of Energy (grants DE-FG02-02ER46000 and DE-FG02-03-ER46094).

ECOLOGY AND CONSERVATION

Space—The Final Frontier for Economists and Elephants

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At the Convention on International Trade in Endangered Species this month (*1*), Namibia is asking for an annual quota for the sale of ivory that is "accumulated from natural and management-related mortalities." The discussion is likely to be steeped in controversy, not least because of the complexity of the economic and ecological arguments involved. Managing elephant populations and evaluating the sustainability of the ivory trade require not only detailed economic analyses, but also recognition of the ecological complexities that influence decisions about elephant management.

Enhanced online at www.sciencemag.org/cgi/content/full/306/5695/420

Understanding the economics of natural resources is crucial in such policy deliberations. So-called bioeconomic modeling—which describes interactions between commodity markets and biological populations such as elephant populations—has provided useful insights into two principal aspects of the ivory trade. First, bioeconomic modeling has shown that poaching and legal harvesting of ivory are not independent, although the nature of this interrelationship is still disputed. Some economists argue that banning a legal ivory trade might give an impetus to the black market and boost poaching (*2*). Others suggest that legal harvesting and trade may facilitate the "laundering" of illegal products—a potentially important but untested hypothesis (*3*). Second, economists have debated the effects that revenues from the ivory trade might have on conservation. On the one hand, it can be argued that ivory sales might provide incentives for governments to carefully manage the resource. For example, governments may be encouraged to invest in the monitoring of elephant populations, to enforce laws against illegal hunting and poaching, and to set aside land as elephant habitat [the species "earns its way" (*4*)]. In the absence of such revenues, with growing elephant and human populations competing for land, it has been pointed out that wildlife may be exploited unsustainably, and that habitat will be converted to other more lucrative purposes by local people or investors. Conversely, recent developments in political economics emphasize that high commodity prices for ivory may be bad for conservation. High prices may unleash forms of "rent seizing" and patronage politics whereby vested interests seek to dismantle the protective institutions that limit their ability to grab the resource (*5*). Notwithstanding these contributions and the conflicting signals they send, economic models of elephant management and the ivory trade have failed to capture several essential elements.

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From an economic standpoint, the simplified treatment of the roles played by national and international institutions and the fact that most ivory trade models ignore feedback from other land and labor sectors of national economies suggest that these models are incomplete. These are important omissions. A recent study reveals an association among poor governance, corruption, and declining elephant populations (*6*). Brander and Taylor (*7*) emphasize that incompletely enforced property rights (as is evidently the case for many elephant populations) and a relaxation of ivory trade controls may not only be detrimental for conservation, but also may reduce human welfare in countries where elephants roam (the "range states"). In particular, given that resuming legal trade may have uncertain effects on ivory market prices, it is unclear how incentives to poach will be affected in range states that export ivory and possibly in range states that do not trade in either African or Asian elephant products (an external effect).

Large-bodied species like elephants have slow population growth rates and are particularly at risk from overexploitation. As benefits from tourism are positively affected by the size of elephant populations and negatively affected by poaching mortality and the enforcement costs needed to protect elephants, the net benefits of resuming the ivory trade are inherently uncertain. Regulated

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