



Self-Assembled Materials

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Any intelligent fool can make things bigger, more complex, and more violent. It takes a touch of genius—and a lot of courage—to move in the opposite direction.

Albert Einstein (1879–1955)

Doing engineering is practicing the art of the organized forcing of technological change.

Gordon Spencer Brown
Electronics; Engineer-Scientist (p. 53)
Volume 32, Number 47
20 November 1959

Self-assembled materials in the 21st century may represent building blocks comparable to those of alloys, plastics, and semiconductors in the 20th century. These materials are formed from interatomic and intermolecular interactions other than the traditional covalent, ionic, and metallic bonding forces. Opportunities offered by self-assembled materials are becoming a significant factor in current research directions. Biological life forms demonstrate an intricate pattern of macroscopic structures and functions formed through a hierarchical series of forces. A consequence of this “intelligent self-assembly” is the functional utility of self-replication and self-repair.

Until recently, the term “self-assembly” was applied almost exclusively to biological structures. Research publications today reveal a host of important self-assembled materials beyond those in biology. Figure 1 displays the number of times that the term “self-assembly” appears in titles of articles cataloged by Science Citation Index over the past 26 years. These data include only those articles that have the term in the title; many additional publications include self-assembly concepts. Clearly, a great deal of interest has been generated in the subject recently.

Self-assembly involves forces such as hydrogen bonding, dipolar forces, other van der Waals forces, hydrophilic or hydrophobic interactions (all frequently referred to as “supramolecular interactions”), chemisorption, surface tension, and gravity. Forces involving ions and ligands (the “coordinate-covalent bond”) have resulted in supramolecular structures. These interactions lead to atomic aggregates that are typically larger than conventional molecular species, are regular in form and appearance, and have some properties unlike either their con-

stituents or bulk properties of similar materials. The assembly of clusters in a “superlattice” is included in this category.

Biological structures formed by self-assembly include membranes, vesicles, tubules, DNA, and a wide variety of structures in a cell. The double helix of DNA, with major contributions by a 1962 Nobel Prize discovery by Watson, Crick, and Wilkins, results from the attraction between two separate molecular strands primarily through hydrogen-bonding interactions. Protein-folding of biological molecular structures results from these hydrogen-bonding forces and other dipolar interactions throughout the molecule, balanced by the potential-energy surfaces associated with changes in molecular conformation. Membrane materials form through the intermolecular attraction of like ends of amphiphilic molecules, forming hydrophilic layers on one side of the aggregated structure and hydrophobic layers on the other. This arrangement of the molecules in a membrane serves to minimize the free energy relative to the many alternative structures that could form.

The 1986 Nobel Prize-winning discovery by Binnig and Rohr for the scanning tunneling microscope served as a stimulus for copious measurements of structures and forces at the nanometer level. These “local probes” are now used for fabrication as well as characterization on the nanoscale. The 1996 Nobel Prize-winning discovery of C₆₀ (Buckminster-

fullerenes) by Curl, Kroto, and Smalley, and the subsequent discovery of the formation of carbon tubules, enhanced the enthusiasm for fabricating and examining self-assembled nanostructures. In these efforts, covalent-bonding forces provided a method for forming rather large uniform nanostructures. Carbon nanotubes have considerable mechanical strength, excellent conductivity, and are a miniature example of carbon fibers already of considerable commercial importance for use in composites. The 1987 Nobel Prize awarded to Cram, Lehn, and Pederson for structure-specific interactions demonstrated many supramolecular structures formed with forces such as hydrogen bonding and coordination complexes. Many new supramolecular structures are being synthesized and characterized by chemists, demonstrating the utility of strategically locating polar substituents involving host-guest interactions.

To demonstrate these principles, recent experiments have used macroscopic structures (about 1 mm in dimension), hand-painted with hydrophilic and hydrophobic surfaces on various segments of geometries such as squares, diamonds, hexagons, and even more complex structures. The manner in which these structures aggregate when suspended and agitated by mechanical means is similar to that formed with thermal agitation at the molecular level. By understanding the opportunities for self-assembly of macroscopic struc-

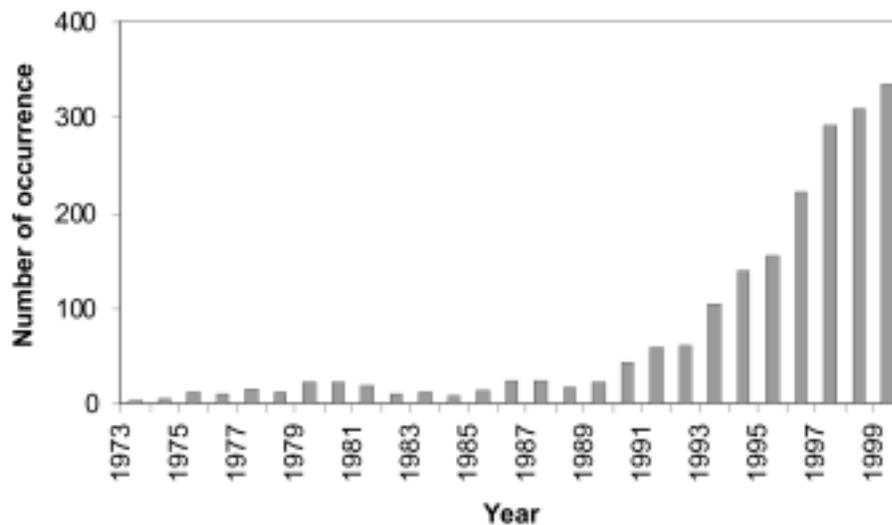


Figure 1. Frequency of occurrence of “self-assembly” in titles.

tures, it may be possible to introduce self-assembly in manufacturing technology for the fabrication of complex structures with minimum cost as well as to shed light on behavior at the molecular level.

The fundamental principle of "like dissolves like" is demonstrated with many solvents and solutes and represents an important driving force for many self-assembled structures today. Block copolymers result from two reactant oligomer species that form polymer chains having segments (or "blocks") A and B that are not mutually soluble (or attracted to one another). The consequent solid material contains domains of A or B adjacent to one another. These domains frequently form in surprisingly regular patterns, representing a superstructure having repeat distances of a few to hundreds of nanometers, depending on conditions. By including silicon in the backbone structure of one component of a block copolymer, and by subsequent removal of the carbon backbone after block-copolymer formation, a regular array of silicon particles may be produced. Chemically removing or etching one component selectively results in a porous array. The size of these arrays may be tailored by the conditions of polymerization, thus introducing a wealth of materials for use in separation technology, catalysis, insulators, and materials with unique optical properties.

Superlattice structures having many repetition lengths may be formed with quantum dots that are uniform (within a few percent) in size. A key element is a highly uniform, monodisperse sample, a building block that is not always readily available. Nanostructures that have been stabilized (as a sol, for example) and condensed to form a solid array frequently demonstrate superlattice structures. The interactions leading to these formations are largely the weaker van der Waals forces, which are relatively more important for larger particles. Such formations may be useful where the bulk properties of a regular array are significantly different from those of the individual particles (particularly true with electromagnetic effects).

The use of templates represents yet another approach to fabricating nanostructures. One template used frequently involves cylindrical tubes in disks of alumina formed by etching the tracks of radioactive particles that have passed through the plates. These tracks serve as templates for the formation of tubular nanostructures. When the alumina support is dissolved by various methods, the remaining tubes are available for subsequent study.

Epitaxial mismatch of two different

crystalline surfaces may result in fairly uniform nanostructures. When the crystalline lattice of the surface layer does not match that of a support layer, the surface layer deforms into various shapes, including regularly spaced domains (similar to the observation of matching regions in a moiré pattern). In this manner, regularly spaced nanostructures may be formed on surfaces using the lattice mismatch.

The possibility that self-assembly may be a factor in manufacturing technology raises opportunities for industrial interest and a desire to explore the principles and the ramifications for mass production.

Steps in manufacturing technology have used techniques of self-assembly, demonstrated with the placement of vertical-cavity surface-emitting lasers (VCSELs) on an etched-silicon substrate. Mechanical agitation of a fluid dispersion of the VCSELs provided the opportunity for contact with etch pits matching the VCSEL size and geometry. The possibility that self-assembly may be a factor in manufacturing technology raises opportunities for industrial interest and a desire to explore the principles and the ramifications for mass production.

Some self-assembled materials have been used in manufacturing technology for years. Nature provided the formation of whiskers long before commercial use was introduced (and before the term self-assembly came into vogue). Composites made of whiskers embedded in a suitable matrix demonstrate superior mechanical properties. Composite materials are likely to have components involving nanostructures in future markets. The example of whiskers for high-strength composites is already recognized. Carbon tubules represent one such approach to new composite materials based on the same principles as current carbon-matrix or carbon-carbon composites today, but with substantially smaller fibers. A general principle enhancing the mechanical strength of a composite material is the Hall-Petch relationship, illustrating greater strength for alloys and ceramics having smaller crystallite sizes (with limits to the strength observed).

Optical properties of nanostructures are of importance due to (1) limited scattering

by particles much smaller than the wavelength of light, (2) major interactions with materials having structures on the order of a wavelength, and (3) the tunability of energy levels to match selected light frequencies. Nanostructures that are well characterized, particularly for particle-size monodispersivity and emission wavelengths, offer opportunities for filters, light-emitting diodes, and for possible laser gain media. Optical cavities and waveguides may be of importance, especially for nonlinear effects that are magnified by higher electromagnetic fields associated with resonance. Optical bandgaps with block-copolymer materials are being demonstrated today. Confinement effects shift the electronic energy levels of particles smaller than about 50 nm. Attachment of different molecules on different-sized clusters can serve as a "signaling device," indicating attractions between matching molecular structures (such as antibodies/antigens) with the simple tool of fluorescence.

Research in microelectronics has led to the lithographic fabrication of submicron features in commercial computers today. Projections for 50-nm microelectronic structures appear to offer favorable opportunities, and dimensions as small as 5 nm appear to offer some advantage. Alternative computer architectures may be necessary to properly use these smaller features, however. Anticipated advances involve variations using x-rays, electrons, and self-assembly. Just where the various laws of physics and economics converge to an optimum for these future fabrication technologies is a fascinating unanswered question. As the ability to fabricate structures of nanometer dimensions is being achieved lithographically, the ability to fabricate large molecular structures or material superlattices through self-assembly is being demonstrated. Material aggregates of 10–100 nm in dimension are being fabricated by both the "top-down" and "bottom-up" approaches. At some point in the trend toward smaller features in microelectronics, alternatives to optical lithography are likely to be chosen. Self-assembly offers attractive features that may prove advantageous.

As far as self-assembled molecular computers are concerned, biological sources have presented us with proof that such structures may be "self-assembled" through the process of life. However, although the "software" in such logical units appears to demonstrate superior capabilities for such operations as pattern recognition, it is not clear that such units will compete favorably with semiconductor computers for many other desirable features. We have much to learn about the

functions that are “wired” into the brains of living species.

Biological species may sense the presence of certain molecular species with extreme sensitivity and selectivity. Many laboratory schemes have demonstrated the detection of similar interactions at the nanometer level (or between large molecules). Sensor schemes utilizing such interactions are plentiful and important adjuncts for biological research. Biomimetic approaches for improved sensors follow these schemes found initially in nature. By utilizing the attraction between molecular fragments and complementary segments on neighboring materials, attractive forces between the two may be quite substantial. With tools such as scanning probes, changes in the index of refraction, or agglutination methods, the formation of such attractions may be detected, in some cases with single-molecule sensitivity. This opens the door to such remarkable detectors as sensitive and selective as those used by a male moth that can detect pheromones emitted by a female moth with a sensitivity of only a few molecules.

Biomimetics is a field that fabricates materials similar to those found in nature, with a hope of generating improved materials. Some biological deposits provide surprisingly strong materials. A crustacean shell is composed of interspersed layers of inorganic oxides and organic “glue.” This material has been an inspiration for synthetic pathways for many years. More recently, it has been found that alternate inorganic/organic nanolayers result by introducing suitable concentration gradients in appropriate reactant mixtures. Bone is a material involving domains of hydroxyapatite crystals in a collagen matrix.

Forthcoming medical applications for nanostructured materials represent a vast opportunity. By emulating the formation of cell walls, synthetic materials having the function of skin or other organs are being fabricated. By encapsulating drugs or other medicines in suitable membrane materials containing specific molecular structures,

drug delivery may be tailored to a specific site in a living species. Synthetic bone, organs, vessels, and so on are on the verge of being produced. It may seem somewhat presumptuous to assume that important functions of life may be produced by synthesis from available inorganic and organic materials. However, initial forays into this field of medicine have been successful, and there is every reason to expect many important breakthroughs in the future as this field of materials is explored.

The field of chemistry evolved by understanding the consequences of bonding forces, leading to a vast array of materials today. An extension of the same approach to these weaker forces is envisioned.

Theoretical developments in this area show promise. Materials formation involves a balance of energetic forces, entropy, and the effects of agitation (thermal, mechanical, etc.). Since the forces used in self-assembly are generally weaker than those of the chemical bond, the frequency of imperfections is greater. Superstructures based on these weaker forces are unlikely to form perfect lattices for as many repeat distances as those found with covalent or ionic materials, or in metals. Although general thermodynamic principles apply here, there has been little in the way of model development to predict limitations such as the size of a domain lattice or the occurrence of vacancies and imperfections in superstructures. Mathematical models used to simulate this behavior include simulated annealing or genetic algorithms to find global minima; the challenge of avoiding local minima is equally important in both mathematical models and the physical world. Much is to be accomplished when the models are devel-

oped and form important tools by which the characteristics of self-assembled materials may be modeled prior to fabrication.

In conclusion, as self-assembled materials become more generally recognized for their manifold uses, and the principles of fabrication are understood, materials having properties not heretofore available may be expected. The field of chemistry evolved by understanding the consequences of bonding forces, leading to a vast array of materials today. An extension of the same approach to these weaker forces is envisioned. A set of weaker forces is responsible for new frontiers for materials based on principles yet to be fully understood. Elucidating and documenting these principles is currently taking place at the same time as innovative applications are being found. This is exactly how exciting materials development should proceed; this field promises a bright future for materials research with new products emerging for years to come.

Acknowledgment

Many stimulating discussions with B.B. Rath are acknowledged, for inspiration as well as critical evaluation of many ideas herein.

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what will form the fabric of our homes, offices, and roads?



After Cars and Airplanes,
what materials will carry us from place to place?

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