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Self-Assembly and Nanostructured Materials

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“Nanostructured materials” are those having properties defined by features smaller than 100 nm. This class of materials is interesting for the reasons: i) They include *most* materials, since a broad range of properties—from fracture strength to electrical conductivity—depend on nanometer-scale features. ii) They may offer *new* properties: The conductivity and stiffness of buckytubes, and the broad range of fluorescent emission of CdSe quantum dots are examples. iii) They can mix classical and quantum behaviors. iv) They offer a bridge between classical and biological branches of materials science. v) They suggest approaches to “materials-by-design”. Nanomaterials can, in principle, be made using both top-down and bottom-up techniques. Self-assembly bridges these two techniques and allows materials to be designed with hierarchical order and complexity that mimics those seen in biological systems. Self-assembly of nanostructured materials holds promise as a low-cost, high-yield technique with a wide range of scientific and technological applications.

9.1. INTRODUCTION

9.1.1. *Materials*

Materials are what the world is made of. They are hugely important, and hugely interesting. They are also intrinsically complicated. Materials comprise, in general, large numbers of atoms, and have properties determined by complex, heterogeneous structures. Historically, the heterogeneity of materials—regions of different structure, composition,

and properties, separated by interfaces that themselves have nanometer-scale dimensions and that may play crucial roles in determining properties¹—have been determined largely empirically, and manipulated through choice of the compositions of starting materials and the conditions of processing.

The phrase “nanostructured materials,” implies two important ideas: i) that at least some of the property-determining heterogeneity in materials occurs in the size range of nanostructures (~ 1 –100 nm), and ii) that these nanostructures might be synthesized and distributed (or organized), at least in part, by design. The idea of “nanostructured materials” thus focuses on four key questions: i) What nanostructures are interesting? ii) How can they be synthesized? iii) How can they be introduced into materials? iv) How can the relationships between their structures and compositions, their matrices, and their interfaces control the properties of the materials that incorporate them? The last question is an old one: “materials by design” has been a goal of materials science since its inception². It remains, however, a difficult one—sufficiently difficult, in fact, that the majority of research still focuses on the first three, where progress is easier to achieve and recognize.

Two broad strategies are commonly employed for generating nanostructures. The first is “bottom-up^{3,4}”: that is, to use the techniques of molecular synthesis⁴, colloid chemistry⁵, polymer science⁶, and related areas to make structures with nanometer dimensions. These nanostructures are formed in parallel and can sometimes be nearly identical, but usually have no long-range order when incorporated into extended materials. The second strategy is “top-down⁷”: that is, to use the various methods of lithography to pattern materials. Currently, the maximum resolution of these patterns is significantly coarser than the dimensions of structures formed using bottom-up methods. Materials science needs an accessible strategy to bridge these two methods of formation, and to enable the fabrication of materials with the fine resolution of bottom-up methods and the longer-range and arbitrary structure of top-down processes. This bridging strategy is “self-assembly^{7–9}”: that is, to allow structures (in principle, structures of any size, but especially nanostructures) synthesized bottom-up to organize themselves into regular patterns or structures by using local forces to find the lowest-energy configuration, and to guide this self assembly using templates fabricated top-down.

The literature contains many examples of self-assembly bridging top-down and bottom-up structures¹⁰: photolithography can be used to direct the phase separation of block copolymers into patterns¹¹; (an example of top-down control constraining a self-assembling system); or alkanethiols can form self-assembled monolayers (SAMs) on gold colloids^{5,12} (an example of self-assembly increasing the complexity of a bottom-up structure). Self-assembly is particularly useful because it allows the aggregation of structures too small to be manipulated individually (or manipulated *conveniently*) into the ordered arrays or patterns that often give function to materials. The development of hierarchically ordered structures—structures in which self-assembly has been at work at different scales, each bringing a different property—is one that permeates biology, but is just beginning to be exploited consciously and rationally in synthetic materials^{13–15} (although, of course, the concept that underlies composite materials is hierarchical structure). Self-assembly can also both generate structures with true three-dimensional order, and do so in bulk and inexpensively. An example is the self-assembly of atoms and molecules into stable crystalline CdSe nanoparticles, and the subsequent self-assembly of the nanoparticles into three-dimensional photonic crystals¹⁶.

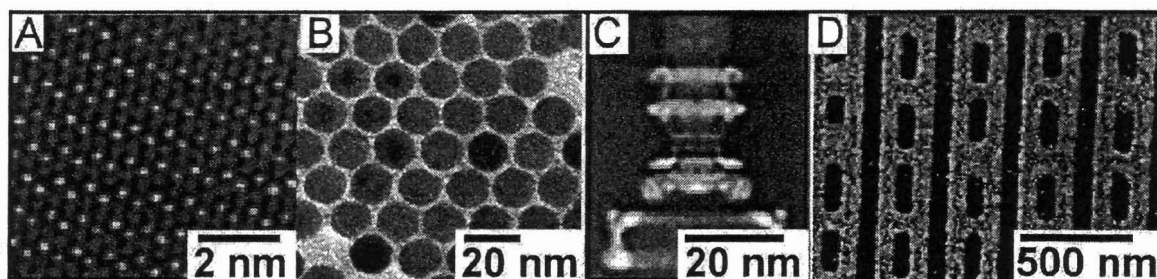


FIGURE 9.1. Examples of different nanostructures. A) Molecular: an STM image of the surface of a SAM of alkanethiolates¹⁷. B) Colloidal: TEM image of self-assembled iron oxide nanoparticles. C) Biological: rotationally averaged electron microscope image of a flagellar motor⁶⁰. D) Microfabricated: SEM image of a pattern generated lithographically⁴⁴.

Whatever the method of synthesis or fabrication, there is general agreement for the moment that the most inclusive definition of “nanostructures” is that they are structures with smallest dimensions less than 100 nm. Further differentiation of the field is, however, useful in considering strategies for integrating nanoscience and materials science. The types of nanostructures can be organized into groups based on their size, function, and structure; this organization will help to define some of the potential of the field.

9.1.2. Nanostructured Materials by Size

We introduce the question of “size” by examining several classes of nanostructures, grouped according to the methods by which they were formed (Figure 9.1).

Molecules (1–6 nm) The most sophisticated and structurally complex nanostructures are molecules¹⁷. Chemists have, albeit unwittingly, been doing nanoscience since the beginning of chemistry. One important task and competence of chemistry is to place atoms into molecular or extended structures with atomic-level precision. The art of chemical synthesis—especially synthesis of organic and organometallic molecules—is one of the most sophisticated in all of science. It has been most highly developed in making functional materials—especially drugs¹⁸, but also a wide variety of polymers¹⁹, adhesives^{20,21}, dyes²², detergents²³, explosives²⁴, and other materials.

Because most organic molecules are not electrically conducting, chemistry has historically been connected with information technology (IT)—the area of nanotechnology that is commercially most important—only insofar as it has contributed passive components^{25–27} such as insulators, adhesives, structural materials, and bulk starting materials, such as single-crystal silicon and doping gases. Since it is now clear that organic compounds can be conductors²⁸ and semiconductors^{29,30} in addition to insulators, one of the opportunities in nanomaterials science is to use organic synthesis and molecular design to make electronically useful structures starting with organic molecules.

Colloids, small crystals, and aggregates (1–100 nm) The chemistry of colloids and small aggregates (nanocrystals³¹, micelles³², small particles of synthetic polymers^{33–36}, and phase-separated polymers^{37,38}) also has a rich background and history, but only recently an association with nanoscience. Nanoscale objects have always been difficult to work with: they cannot be characterized by molecular techniques; they are too small to see optically; and they are usually heterogeneous in size and properties (at least compared to molecular

synthesis). As their potential as components in materials science has become clear, however, they are increasingly attractive objectives for research³⁹. There is great interest in understanding and developing new synthetic routes^{40–42} to materials in this regime whether by synthesis, phase-separation, self-assembly, or some other route.

Micro/nanofabricated structures (currently, 70 nm and up) Microelectronics is the technology that has focused attention on the economic importance of nanoscience. This technology has evolved steadily over its history to smaller and smaller structures. Current methods of photolithography can generate structures well into the <100 nm regime^{43,44}. With the addition of difficult but well-understood extensions based on phase-shifting methods⁴⁵ and immersion optics^{46,47}, that limit can certainly be extended to 70 nm in practical processes^{47,48}, and probably to still smaller dimensions. By moving to shorter wavelengths (deep- or extreme-UV photolithography⁴⁹) and front-surface optics⁵⁰, it may be possible to generate features as small as 10 nm^{51–53}. Electron beam lithography⁵² and perhaps other methods (x-ray lithography⁵⁴ and scanning probe lithography⁵⁵) can also generate structures in this size range. There is, thus, a substantial overlap in sizes that the methods of lithography and of colloid and molecular synthesis can access. An important difference is, however, that lithographically fabricated structures are ordered, but are expensive and largely limited to small, planar patterns, whereas bottom-up methods often generate nanostructures with little or no long-range order, but can do so in large quantities and inexpensively.

Biological structures (2 nm and up) One of the inspirations for nanoscience is biology⁵⁶. There are many descriptions of a cell, one of which is, “an ensemble of functional nanostructures, enclosed in a molecule- and ion-selective, semi-permeable membrane, that replicates itself.” These functional structures—proteins and nucleic acids, often associated into aggregates, modified with oligosaccharides, and associated with lipids, are the most sophisticated nanostructures known⁵⁷. These structures, from the simplest small RNA molecules⁵⁸, to functional organelles such as ribosomes⁵⁹ or flagellar nanomotors^{60,61}, to viruses⁶² and complete cells, are all, of course, self-assembled: no hand—robotic or human—places their components together. The myriad examples of functional, self-assembled nanostructures found in biology provide an encyclopedia of demonstrations and strategies for those wishing to learn how to use self-assembly of molecules at the nanoscale to generate complex function.

Although much of the interest in biological nanostructures has focused on relatively complex functionality, cells and organisms themselves can be considered as a collection of self-assembled *materials*: lipid bilayers, the extracellular matrix, tendon and connective tissue, skin, spider silk, cotton fiber, wood, and bone are all self-assembled biological materials, with an internal structure hierarchically ordered from the molecular to the macroscopic scale.

9.1.3. By Function

Nanostructured materials can also be classed according to their function.

Electronic “Micro” electronics is, without any ground-breaking new technology, on the verge of becoming “nano” electronics. Some structures already have one nanoscale dimension—for example, gate dielectrics in CMOS technology⁶³ and vertical structures in giant magnetoresistive devices⁶⁴. Lateral dimensions of other types of structures—especially those used for information storage—are also shrinking rapidly. IT is highly

developed and technologically sophisticated, and its immediate evolutionary extension well beyond 100 nm-scale structures is inevitable, albeit technically difficult.

There is also a possibility that nanoscience may bring *revolutionary* new technology to IT. Many possibilities have been suggested: buckytubes^{65–67} or silicon nanowires⁶⁸ as transistors; arrays of gold quantum dots as components of cellular automata^{69–71}; random tangles (“spaghetti”) of nanowires as the basis for hyper-defect-tolerant computers; and computers using devices based on single molecules⁷² or single colloid particles⁷³. Most of these possibilities are at the level of “suggestion” and it is not clear if any will ever see commercial reality. Regardless, their exploration is a source of stimulation for the field. In particular, they require an emphasis on the design of properties—electrical and magnetic—that have not conventionally been effectively generated by bottom-up methods.

Optical The importance of optical materials in IT is comparable to that of electronic materials, since most information is shipped optically; there is probably a comparable opportunity for nanostructured materials in optical applications. Photonic bandgap materials—although typically structured with repeat distances larger than 100 nm^{74–76}—are properly considered part of nanotechnology, because the structure is modified with defects that create the desired band-gap properties, and the placement of these defects must be precise on the nanoscale⁷⁷. Self-assembly is an obvious strategy for the fabrication of photonic band-gap materials^{78,79}. Quantum dots⁸⁰—most commonly CdSe nanoparticles having diameters of tens of nm, and with protective (and usually self-assembled) surface coatings¹⁶—are remarkable for their ability to fluoresce over the complete visible spectral range, with the controlling parameter being their size⁸¹. Substrates for surface-enhanced Raman spectroscopy (SERS, a technique with very high sensitivity)—typically silver particles—give the best performance when these particles are engineered into shapes that maximize the electric field gradients that underlie the spectroscopic phenomena⁸². Sub-wavelength optical structures—for example, polarizers⁸³, filters⁸⁴, and superluminescent antennae based on nm-sized holes⁸⁵—all require manipulating materials with optical functionality into structures having nanoscale periodicity.

Magnetic The magnetic properties of materials depend on the structure and interaction of magnetic domains; these domains typically have <100 nm dimensions⁸⁶. Currently these systems are structurally uncomplicated, although even they are often challenging to fabricate. Some examples of these systems include: 2D crystals formed from monodisperse superparamagnetic alloy colloids, with potential use in very dense magnetic storage media⁸⁷; magnetite colloids stabilized against aggregation in a magnetic field by self-assembled dextran coatings and used to increase contrast, *in vivo*, in magnetic resonance imaging^{88,89}; metal nanorods stabilized and functionalized with alkanethiolate SAMs and used to characterize the mechanical properties of living mammalian cells^{90–92}.

9.1.4. By Structure

Certain structural classes are especially relevant to nanoscience.

Surfaces and interfaces As the dimensions of structures become smaller, their ratio of surface-to-volume increases. Molecules are essentially “all surface,” as are the smallest nanostructures. The ability to make materials with high ratios of surface-to-volume by building them from nanostructures is an important opportunity for surface science and technology. The surface is an extremely interesting state of matter: it determines many properties crucial

for materials⁹³—wettability, adhesion, friction, susceptibility to corrosion, some aspects of biocompatibility, and many others. Self-assembly has already made a large contribution to surface science through the introduction of self-assembled monolayers⁹⁴ (SAMs), which allow significant control and tunability of the surface properties. The field of engineered, nanostructured surfaces is still in its infancy, and only a few of the opportunities in this area have been exploited: the great majority of research has focused on SAMs of alkanethiols on gold and silver⁹⁵. The complexity of self-assembling systems can be increased by exploring new components (e.g. complex organic and organometallic molecules) or supramolecular structures (e.g. monodisperse colloids⁹⁶, or proteins⁹⁷). Surfaces and interfaces are intrinsically nanoscale structures that are key in determining the properties and behavior of many important systems. They are, also, uniquely amenable to investigation using the tools already available in nanoscience, especially scanning probe⁹⁸ and particle (electron and ion) beam⁹⁹ devices.

Mechanical properties The mechanical properties of materials are strongly influenced by nanoscale structure. Fracture strength and character, ductility, and various mechanical moduli all depend on the substructure of the materials over a range of scales. This dependence has been extensively exploited throughout the field of structural materials: formation of grains in metallic alloys¹⁰⁰, phase-separation in polymers³⁷ and ceramics¹⁰¹, and toughening of materials with nanoparticle additives^{102–104} (carbon black and silica) are examples. Since much of the development of nanostructured materials has been carried out empirically, the opportunity to redevelop a science of materials that are nanostructured by design is largely open.

9.2. WHY BUILD NANOSTRUCTURES?

“Nanotechnology” has become a word around which a remarkable range of science and engineering is being organized. Why has it emerged into the limelight, while other areas of technology that might have as much potential (“intelligent machines”, the biological/computational interface, sustainable development, and others) have not? The answer to this question is complicated, with components of economic necessity, scientific opportunity, and public engagement. Some of the more technical aspirations of nanotechnology are these:

9.2.1. Unique Properties

A key aspiration of nanotechnology is to demonstrate the proposition that as things become small, they become different. “Different” often translates into “interesting”, and sometimes into “useful and valuable”. There are a number of demonstrations of the emergence of differences in nanostructures. Although buckyballs¹⁰⁵ (among the first of the synthetic nanostructures to catch the interest of both the technical community and the public) have so far fallen in the category of “interesting but not especially useful”, buckytubes (or carbon nanotubes) have genuinely remarkable properties: especially their high electrical conductivity and unique mechanical strength^{106,107}. The properties of surfactant-stabilized colloids are the basis for many bioanalytical systems^{108,109}. Fluorescent CdSe quantum dots,

unlike fluorescent organic dyes, photobleach only slowly (or not at all)¹¹⁰, and show interesting (if annoying) optical phenomena such as “blinking”¹¹¹. SAMs provide an unequaled ability to tailor the properties of surfaces¹¹².

9.2.2. *Quantum Behavior*

Quantum behavior becomes increasingly prominent as structures become smaller. Many of the behaviors of atoms and molecules are, of course, only explicable on the basis of quantum mechanics. The properties of objects and structures larger than a few microns are usually classical. In the intermediate region—the region of nanometer-scale structures—quantum and classical behaviors mix. This mixture offers the promise of new phenomena and/or new technologies. The fluorescent behavior of semiconductor quantum dots can only be explained quantum mechanically¹¹⁰; as can the tunneling currents that characterize scanning tunneling microscopes, and electron emission from the tips of buckytubes¹⁰⁷. The response of electrical resistance to magnetic field in GMR materials is already useful in magnetic information storage^{64,113,114}, and the behavior of spin-polarized electrons in magnetic semiconductors forms one foundation for the emerging field of spintronics¹¹⁵. The ability to make structures in the region where quantum behavior emerges, or where classical and quantum behaviors merge in new ways, is one with enormous opportunity for discovery. And because quantum behavior is fundamentally counterintuitive, there is the optimistic expectation that nanostructures and nanostructured materials will found fundamentally new technologies.

9.2.3. *Microelectronics*

The argument for the development of nanotechnology for use in the microelectronics industry is clear. Information technology (IT) has been the technology that has most changed society in the last 50 years. Its development has not yet subsided, although the progression of dimensions to ever-smaller sizes—described by Moore’s Law¹¹⁶—must inevitably come to an end when these dimensions reach the size of molecules and individual atoms. In between the current structures (~ 100 nm) and the minimum size limit (~ 1 nm), developments of immense economic importance are inevitable.

Beyond evolutionary developments in silicon-based technology, there are a host of possibilities in *new*, but not necessarily fundamentally different, technologies for IT. Will there be important technologies built around organic semiconductors? Will it be possible and practical to take advantage of the high mobility of electrons in semiconducting buckytubes to make new electronic devices? Will some combination of bottom-up synthesis of monodisperse, magnetic colloids, surfactant-assisted crystallization, and materials fabrication generate practical, ultradense magnetic information storage media? Is there a way to use self-assembly of small circuit elements as the basis for a new strategy for fabricating microprocessors, mass storage devices, or displays? It is too early to judge the practical importance of these areas, although they are showing technical feasibility in demonstrations in research laboratories.

In the longer term loom the potentially *revolutionary* technologies, to which nanostructures and nanomaterials may make a contribution: quantum computing^{117–119}, computing

using cellular automata^{120,121}, photonic computing^{122,123}, semiconductor/biological hybrid computing^{124,125}, molecular electronics⁹⁵, and others. The history of predicting revolutions is poor, and it is likely that any revolution will emerge from an unexpected direction. Since, however, nanostructures constrain electrons and photons in new ways, and since nanostructures have been difficult to fabricate, and hence are still relatively unexplored, the possibility that a revolution in IT will appear, unexpectedly, from the exploration of some area of nanoscience is higher than it might be in more familiar areas.

9.2.4. Manufacturing

The relation between manufacturing and nanotechnology is less explored than that in many apparently higher-technology areas. Manufacturing is a field that permeates technology: any successful technology must be transferred from its developer to its users, and most technologies (even software is ultimately housed in hardware) require manufacturing something. There are complex but important relations between nanoscale features of manufacturing systems, the cost of manufacturing processes, and the performance of manufactured objects. Would the performance of ball-bearings in a heavy-duty transmission improve if there were no defects larger than a few nanometers? What would robotic assembly systems be like if every part were identical to within a few nanometers? It is not possible, at present, to answer these and related questions, since nanoscience is just beginning to generate the tools and metrologies necessary to explore them. Nanoscience does, however, have the potential to make important contributions to future manufacturing systems.

9.2.5. Fundamental Science

At the foundation, underlying the technologies, is the fundamental science of phenomena at the nanoscale. Nanoscience, in its broad sense, is a new area. We do not know what will develop, but we do know that in order for it to develop, it must have materials, procedures, and tools. Developing new ways of manipulating matter at the smallest scales—scales that bridge between atoms and molecules (chemistry) and mesoscopic matter, (materials science)—is a centrally important part of fundamental scientific inquiry.

9.3. WHY USE SELF-ASSEMBLY TO BUILD NANOSTRUCTURES?

Self-assembly has a special place in nanoscience. Top-down methods of fabrication provide the ability to build patterns, but are capital intensive, two dimensional, and limited in their ability to provide materials in quantity. Bottom-up methods can make large quantities of nanostructures (including nanostructures too small to be made by any top-down method: e.g., molecules), but without pattern or regularity to their arrangement. Self-assembly bridges the two: it provides a strategy that makes possible the patterning (in a broad sense) of nanostructures made by bottom-up synthesis; it can also use patterns generated by top-down fabrication to guide the ordering of nanostructures made by bottom-up methods.

This capability of self-assembly to make ordered arrays of nanostructures is, in essence, nothing new. Crystallization of molecular or atomic species (whether it is the phase transition of liquid water into solid ice, or of liquid silicon into semiconductor-grade silicon crystal) is an example of self-assembly, as are the formation of surfactants in soap bubbles¹²⁶, the crystallization of viruses for x-ray structure determination¹²⁷, and the ordering of liquid crystals in displays¹²⁸. The novelty of self-assembly is in the focus on the formation of matter *structured rationally* at scales less than 100 nm, and the realization that the only practical method of achieving these structure is to have the components assemble themselves spontaneously.

We examine several general areas where self-assembly seems to be the best method (by whatever metric: practicality, cost, order, dimensionality) for building materials with nanodimensional structural regularities.

9.3.1. *Components too Small for Top-Down*

Self-assembly provides the only approach to nanostructured materials that simply cannot be fabricated by current top-down methods. Although top-down methods are versatile⁵³, and can fabricate astonishingly small structures⁵², there are many types of structures that they can not fabricate, the most important and obvious of which are molecules.

The ability of scanning probe devices to arrange atoms on surfaces is a demonstration of the power of these devices, but it is a methodology that is limited in its practicality, and in the complexity of the systems that it can make. A circle of xenon atoms on a surface is a practical target^{129,130}; cholesterol is not. Self-assembly will, thus, be an essential part of the generation of materials starting from their atomic or molecular components. Top-down lithographic methods will, of course continue to be the best for the important, specialized task of making planar structures with arbitrary patterns (e.g. circuits).

9.3.2. *Too Many Components for Conventional Placement*

Self-assembly is a massively parallel process, and can normally involve very large numbers of components (a large crystallization might involve 10^{27} molecules). Robotic pick-and-place methods for placement are limited by the fact that they are serial. Although they can be accelerated by using a number of robotic devices in parallel (for example, the multiple scanning probe heads of the IBM "millipede"¹³¹), they cannot approach the number of molecules in a test tube, for example.

There is no clear understanding at this point of the parameters that dictate the cases for which "self-assembly" will be superior to "externally directed assembly". For numerous, small components, self-assembly will probably always be superior; for unsymmetrical patterns with relatively large components (e.g., microelectronic circuits) top-down fabrication will probably remain superior. In problems involving intermediate sizes and intermediate numbers of components, it remains to be seen which strategy is best. Pick-and-place assembly with 100-nm components will never be straightforward practically, although it may find uses in research.

9.3.3. *Too Many Dimensions*

The technologies for making nm-scale structures by current lithographic methods are largely restricted to planar or quasi-planar geometries. (An array of trenches carved into

silicon by reactive ion etching is formally a 3D structure, but its method of production precludes more complex 3D structures without elaborate stacking and registration.) Self-assembly is not limited to planar surfaces, and may work better in 3D than in 2D in some cases. Crystallization is a good example of 3D self-assembly. In crystallization each atom benefits from bonding interactions with all of its neighboring atoms. While there are some materials that form stable 2D crystals (e.g. SAMs), the majority of materials form solids in three dimensions because of energy minimization through interactions with neighbors.

9.3.4. *Fragility of Biological Systems*

Manipulating biological nanostructures is already a technologically important area. Fabricating DNA and protein arrays^{132,133}, analyzing small quantities of biological materials^{134,135}, and manipulating or examining the cell with nanometer scale probes^{136–138} are examples of problems in which the combination of the small sizes of components, and their sensitivity to damage outside of a narrow range of environmental parameters, requires mild conditions for fabrication and assembly—conditions where self-assembly can work uniquely well.

9.3.5. *Cost*

Because self-assembly is a parallel process, and because it does not involve robotic or other devices to impose order on nanostructures, it will probably, when applicable, ultimately always have an advantage in cost over other methods of fabrication.

9.4. WHAT ARE TARGETS FOR THE FIELD OF NANOSTRUCTURED MATERIALS BY SELF-ASSEMBLY?

The field of nanotechnology is in its infancy, and it is too early to identify targets with any certainty. Some systems are, however, obvious candidates for research and development, either because there is a clear economic imperative requiring their exploration in order to have options on future technologies as they emerge, or because they hold promise for exploratory research (Figure 9.2).

9.4.1. *Information Technology (IT): Electronics and Electronic Components; Photonic Materials—Magnetic Materials*

IT is an area in which it is already clear that emerging nanotechnologies will be centrally important; the only question is “Which ones?”

Electron transport in organic molecules The ultimate electronic nanotechnology—single molecule electronics—has had a checkered start, with the concern that a number of the initial experiments that stimulated interest in the field are not reproducible, or over-interpreted, or in one unfortunate set of experiments, fraudulent. This field has yet to sort itself out—one *goal* for the field of self-assembled nanomaterials in electronics is to build a set of experiments that provides a believable basis for estimating its potential^{139,140}, either as the object of fundamental science, or, perhaps, for commercialization.

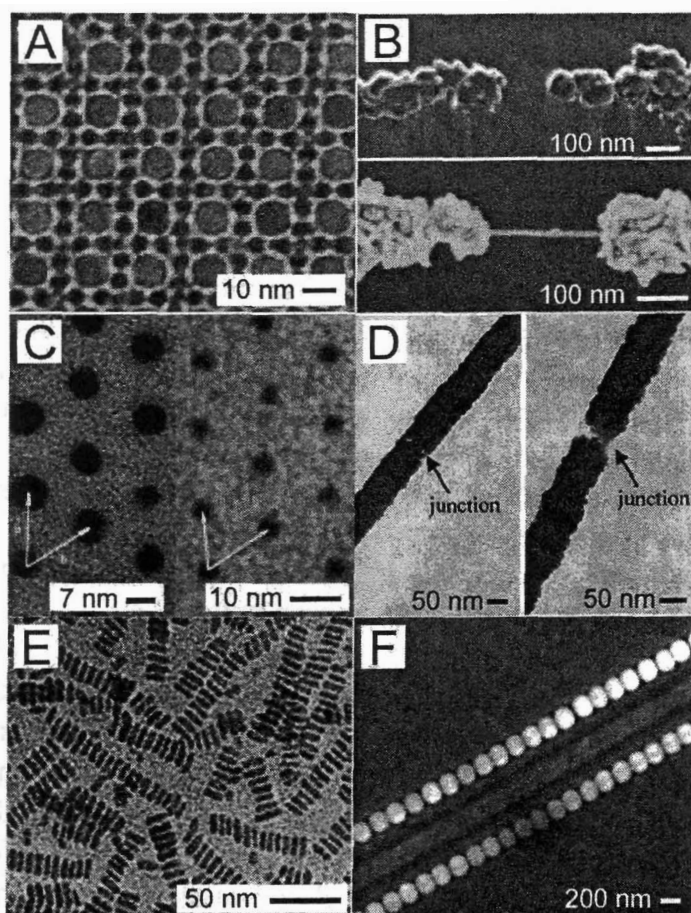


FIGURE 9.2. Examples of self-assembled nanostructures: A) Close packed binary nanoparticle superlattice¹⁸⁵. B) DNA templated carbon nanotube transistor, (top) single nanotube, (bottom) carbon nanotube bundle¹⁷⁰. C) Nanoparticles on S-layer protein lattices¹⁷¹. D) Molecular junctions in nanowires¹⁴⁰. E) Self-assembled chains of prismatic BaCrO₄ nanoparticles on a TEM grid¹⁸⁶. F) Template-assisted self-assembly of colloids on a photoresist pattern¹⁸³.

The most reliable current method for examining the mechanism of electron transport through *single* molecules is probably to incorporate the molecule of interest in a SAM, and probe it with an STM¹⁴¹. This system has two advantages: i) it involves making one chemical contact—at the end where the thiol-metal bond forms; ii) it allows examination of a large number of molecules, and hence the accumulation of useful statistics on the variation in measured properties. It has the disadvantage that the molecule of interest is in a matrix of other molecules in the SAM, but the one through which electron transport occurs is often located at a “special” site (a site where the exchange of molecules with the solution is relatively rapid and the surface structure is distinct and less well characterized)⁹⁵. The results from STM-based examinations are in general agreement with results from experiments in which the junction consists of a SAM in contact with a mercury drop covered with a second SAM¹⁴², or even a SAM onto which a second electrode is formed by evaporation of metal^{143,144}. Similar results are also obtained from electrochemical studies of SAMs¹⁴².

Although these SAM-based systems have been studied extensively in terms of electron transport, and although self-assembly plays a crucial role in determining the degree of order in these systems, there remain a number of uncertainties. i) It is now clear that the

structures of SAMs—although generally ordered—contain many defects, due to steps and grain boundaries in the metal substrate, vacancies and domain walls in the SAM, and other details of structure^{17,95,145}. ii) The SAM-metal interface is not well defined, and in circumstances where there is a second, contacting electrode formed by evaporation, the structure of *this* interface is only just beginning to be understood^{146,147}. iii) There is a concern that the structure of the junction may change when potential is applied across it: formation of metal filaments by electromigration, followed by burnout of these filaments at high currents, is a matter of particular concern¹⁴⁸.

One of the advantages of junctions based on SAMs and containing organic molecules is the ability to design the structure of these junctions by using organic molecules of different structures. This type of study has, so far, been constrained to relatively simple systems (for example, n-alkanethiolates¹³⁹, or simple biphenyls¹⁴⁹). More complex structures have been incorporated as SAMs in the junctions of cross-bar structures using nanowires¹⁵⁰, but the structure of the SAMs in these junctions are so uncertain, and the values of the processes that determine the electronic phenomena so unclear, that it will be impossible to interpret these experiments until they have been reproduced.

Very low cost, medium performance printed electronics A less controversial area is printed (or organic) electronics. The objective in this rapidly developing field is to develop alternatives to silicon and conventional photolithography as the basis for electronic systems^{151–153}. Initially, the devices produced using this technology would have relatively low performance, but very low cost. These devices would be directed toward applications (for example, RF ID tags¹⁵⁴) where one-time use would dictate cost and performance.

The economics of these kinds of systems will probably require that patterns be produced by printing. Although it is not likely that the active electronic systems produced by printing methods would have nm-scale features, microcontact printing of SAMs—ultimately, probably, by reel-to-reel printing—is being explored for forming metal features^{155,156}.

Low-cost, high-performance electronics A more ambitious challenge is that of developing a technology for fabricating high-performance (>GHz clock rate) electronics. There are several methods being considered for this type of technology. One method would use high-mobility materials such as carbon nanotubes⁶⁵ or silicon nanowires⁶⁸, and orient these materials in the gate region by self-assembly^{157,158}. A second would use lower-mobility materials (e.g., organic semiconductors²⁹ or amorphous silicon) and fabricate very narrow gates by self-assembly¹⁵⁹.

9.4.2. Sensors and Analytical Systems

The ability to fabricate small cantilevers, tips, and wires¹⁶⁰ (and to cross the wires, in some circumstances), opens the possibility of making nanoscale sensors¹⁶¹. A number of these systems have been demonstrated in laboratory experiments; in most cases, SAMs have provided the functionality that gives the systems their selectivity for particular analytes^{162,163}.

This area is clearly an interesting one for exploratory research. An important question is: "For what applications does one *need* nanoscale sensors?" Maximization of surface area is one consideration, and nanoscale devices have the advantage of being largely surface. The list of potential applications that exploit this advantage is, however, not currently long. One potential use may exist in the study of individual cells (either intact, or after lysis); in this application, the quantity of sample is very limited, and sensing regions should ideally

be sufficiently small that they do not to deplete materials present on the cell membrane, or in solution¹⁶⁴.

9.4.3. *Structural and Multifunctional Materials: Controlled Heterogeneity*

The development of composite structural materials based on ordered nanostructures in a matrix material has been surprisingly difficult to accomplish, and has only proved successful in a few cases¹⁶⁵. Part of the difficulty is that the surface chemistry of the nanostructures must be controlled carefully so that the structure truly *is* a composite and that the nanostructured phase in the matrix is ordered. Given the importance of nano-scale heterogeneity in determining the mechanical properties of materials, this area is one of great theoretical and practical interest.

9.4.4. *Surfaces*

Surface science has been one of the first beneficiaries of self-assembled nanostructures (in the form of SAMs). Self-assembly is a very general strategy for forming molecularly tailored interfaces, and, other than the few systems that have formed the basis for the majority of work in SAMs, almost none of the obvious opportunities to use self-assembly to build ordered, nanostructured interfaces have been examined. The preparation of more sophisticated structures based on molecules with complex structures, on self-assembled colloids; on multilayered polymers formed by electrostatic interactions between charged groups^{166,167}, or on biologically derived structures is just beginning^{168–171}.

A number of other types of processes that can be considered a form of self-assembly at surfaces are just beginning to appear. The selective oxidation of silicon, followed by etching of the silicon dioxide, as a route to silicon nanowires is an example¹⁷²; the galvanic deposition of platinum on selenium nanostructures, followed by removal of the selenium, to make nanowalls with complex shapes is a second^{173,174}.

9.4.5. *Structured Colloids and Other Mesoscale Systems*

One of the most successful areas of early-stage nanotechnology is the preparation of structured colloids, and the modification of the structures and properties of these systems. Examples include: i) the formation of nanorods by electrodeposition, followed by selective formation of SAMs on regions of these nanorods^{140,175}; ii) the formation of liquid crystal structures from these nanorods¹⁷⁶; iii) the formation of metallic nanopores, and the modification of the interior surface of these pores with SAMs (and the remarkable demonstration of ion selectivity of the resulting nanochannels^{177,178}); iv) the formation of a wide variety of colloids, some with remarkable structures^{179–181}; v) the self-assembly of small spheres into wells, and the use of this templating to make ordered aggregates of these spheres^{182–184}; and vi) the formation of colloids, and their use as the basis for the formation of more complex structures by self-assembly^{185,186}.

9.4.6. *Manufacturing Processes*

There has been relatively little work on the relationship between nanoscience and non-microelectronic (or MEMS) manufacturing. The development of the scanning probe

microscope as a relatively inexpensive instrument with which to measure surface properties is beginning to be used in industrial research laboratories,^{187,188} but not yet in manufacturing process control.

9.5. OPPORTUNITIES, CHALLENGES, AND PROBLEMS

Self-Assembly Works! An important conclusion from the early phase of nanoscience and nanotechnology is that self-assembly provides a useful and general strategy for organizing simple nanostructures—molecules or colloid particles (or other particles that are colloidal in size, such as viruses)—into more ordered structures. The final measure of success in nanoscience will be *function*—regardless of whether as a tool or substrate in fundamental science. Since simple nanoparticles usually have relatively little independent function, the formation of more complex aggregates and structured aggregates will be a constitutive part of nanoscience and nanotechnology. Self-assembly is the only general strategy at this time for accomplishing this type of organization.

9.5.1. *Biology and Biomimetics*

Biologically derived materials carry with them a special set of problems. They are often thermally unstable, scarce, impure, and difficult to manipulate. Certain of the problems of biological materials are being addressed: developing strategies for designing surfaces that will not adsorb proteins is one example¹⁸⁹. Others—for example, designing nanostructures that are compatible with the interior of the cell, and capable of reporting information about this interior—are still at early stages of investigation^{5,109}.

Biomimetic systems also hold much promise. Self-assembly offers, in principle, the opportunity to make materials showing multiple levels of structural organization, and, in principle, multiple contributions to properties. This type of hierarchical self-assembly and self-organization is used throughout biology, but to a relatively low degree in nanoscience^{13–15,190–192}. Another interesting characteristic of self-assembly in biology is that it is usually *dynamic*¹⁹³: that is, self-assembly proceeds only while there is a flux of energy through the system. Understanding dynamic self-assembly (as opposed to the equilibrium or steady-state self-assembly normally practiced in chemistry and materials science) will, in the long term, lead to new concepts^{194,195}.

Biology, on the whole, offers an incredible range of functional nanoscale structures, and processes for forming these structures. Man-made processes almost never resemble the biological ones, in strategy (or often in quality of product). Exploration, understanding, and exploitation of processes mimicking those used in biology are exciting areas of fundamental science, and may eventually contribute to technology.

9.5.2. *Materials and Engineering*

The key to self-assembly is the components that are involved: the information required for efficient self-assembly must, in general, be embedded in these components. The first step toward the capability to design and synthesize nanostructures for self-assembly is simply to expand the range of syntheses and methods of fabrication that lead to nanostructures. For the

most part, the requirements of self-assembly will necessitate that these syntheses generate highly homogeneous (both structurally and functionally) nanostructures. The polydispersity that characterizes most syntheses of colloids, for example, is sufficient to make uniform crystallization impossible without purification^{78,196–198}.

Regardless of the homogeneity of the components, self-assembled structures will always have some level of defects. In a three-dimensional colloidal crystal, for example, a single vacancy will not largely affect the gross optical properties of the structure^{196,198}. Multiple vacancies or cracks can, however, affect the performance of such a crystal. Defects in SAMs can be equally deleterious, for example, to electronic properties. Characterizing these types of defects, and then designing the systems in which the nanostructured materials are to be used, may be a minor task (inspecting the assembled structure to find the occasional defective one, if defects are rare) or a major one (if defects are relatively common). The repair of defective structures is also important, and can be difficult.

For certain types of functional structures—especially for those to be used in information processing and storage—the interface between the nanoscopic world and the macroscopic world of pins, solder pads, and optical fibers may be as important as the nanostructures themselves. Understanding, in a particular case, if this problem of interfacing nanostructures with the macroscopic world can be solved by some application of conventional technology, or if it will require some new solution, is a key part of the problem.

As with any system in materials science, self-assembled nanostructures are unlikely to be useful on a larger scale until they can be generated reproducibly and on a large scale. Developing a *strategy* for applying nanomaterials, nanofabrication, and nano-scale metrology to manufacturing—especially in precision manufacturing outside the area of microelectronics—remains to be done.

9.5.3. *The Fundamentals of Self-Assembly*

If one accepts the premise that self-assembly will be an important component of the formation of nanomaterials, it is clearly important to understand it as a process (or, better, class of processes). The fundamental thermodynamics, kinetics, and mechanisms of self-assembly are surprisingly poorly understood. The basic thermodynamic principles derived for molecules may be significantly different for those that apply (or do not apply) to nanostructures: the numbers of particles involved may be small; the relative influence of thermal motion, gravity, and capillary interactions may be different; the time required to reach equilibrium may be sufficiently long that equilibrium is not easily achieved (or never reached); the processes that determine the rates of processes influencing many nanosystems are not defined.

Putting together a fundamental science of nanostructures and self-assembly will probably take many years. We should not assume that because there is a rich base of information about molecules and their reactions, that there is a closely analogous or equally detailed body of information about nanostructures and self-assembly. Along the same vein, although the combination of top-down patterning and self-assembly promises to be a powerful one, the development of general strategies, based on a sound understanding of the relationship between the template and the self-assembled nanoscale components, remains to be worked out.

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