

Nanoscience, Nanotechnology, and Chemistry**

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What is Nanoscience?

“Nanoscience” is the emerging science of objects that are intermediate in size between the largest molecules and the smallest structures that can be fabricated by current photolithography; that is, the science of objects with smallest dimensions ranging from a few nanometers to less than 100 nanometers.^[1–3] In chemistry, this range of sizes has historically been associated with colloids, micelles, polymer molecules, phase-separated regions in block copolymers, and similar structures—typically, very large molecules, or aggregates of many molecules. More recently, structures such as buckytubes, silicon nanorods, and compound semiconductor quantum dots have emerged as particularly interesting classes of nanostructures. In physics and electrical engineering, nanoscience is most often associated with quantum behavior, and the behavior of electrons and photons in nanoscale structures. Biology and biochemistry also have a deep interest in nanostructures as components of the cell; many of the most interesting structures in biology—from DNA and viruses to subcellular organelles and gap junctions—can be considered as nanostructures.^[4,5]

These very small structures are intensely interesting for many reasons. First, many of their properties mystify us. How *does* the flagellar motor of *E. coli* run?^[6,7] How *do* electrons move through organometallic nanowires?^[8] Second, they are challenging to make. Molecules are easily synthesized in large quantities, and can be characterized thoroughly. Colloids and micelles and crystal nuclei have always been more difficult to prepare (in fact, most can only be made as mixtures—a characteristic that contributes to the difficulty of colloid science) and to characterize; developing a “synthetic chemistry” of colloids that is as precise as that used to make molecules is a wonderful challenge for

chemistry.^[9,10] Synthesizing or fabricating ordered arrays and patterns of colloids poses a different and equally fascinating set of problems.^[11]

Third, because many nanoscale structures have been inaccessible and/or off the beaten scientific track, studying these structures leads to new phenomena.^[12–14] Very small particles, or large, ordered, aggregates of molecules or atoms, are simply not structures that science has been able to explore carefully. Fourth, nanostructures are in a range of sizes in which quantum phenomena—especially quantum entanglement and other reflections of the wave character of matter—would be expected to be important (and important at room temperature!). Quantum phenomena are, of course, the ultimate basis of the properties of atoms and molecules, but are largely hidden behind classical behavior in macroscopic matter and structures.^[15] Quantum dots and nanowires have already been prepared and demonstrated to show remarkable electronic properties; there will, I am certain, be other nanoscale materials, and other properties, to study and exploit.

Fifth, the nanometer-sized, functional structures that carry out many of the most sophisticated tasks of the cell are one frontier of biology. The ribosome (Figure 1), histones and chromatin, the Golgi apparatus, the interior structure of the mitochondrion, the flagellar micromotor, the photosynthetic reaction center, and the fabulous ATPases that power the cell are all nanostructures we have only just begun to understand.^[16,17] Sixth, nanostructures will be the basis of nanoelectronics and -photonics.^[18,19]

The single most important fabrication technology of our time is, arguably, microlithography: its progeny—the microprocessors and memories that it generates—are the basis for the information technology that has so transformed society in the last half-century (Figure 2). Microelectronic technology has relentlessly followed a single law—Moore’s law—for almost 50 years; the popular expression of this law is “smaller is cheaper and faster”.^[20,21] Enthusiasm for “smaller” as the guiding ideology in circuit design has recently cooled, and other features—heat dissipation, power distribution, clock synchronization, intrachip communication—have become increasingly important. Still, technical evolution in the semiconductor industry has brought the components of

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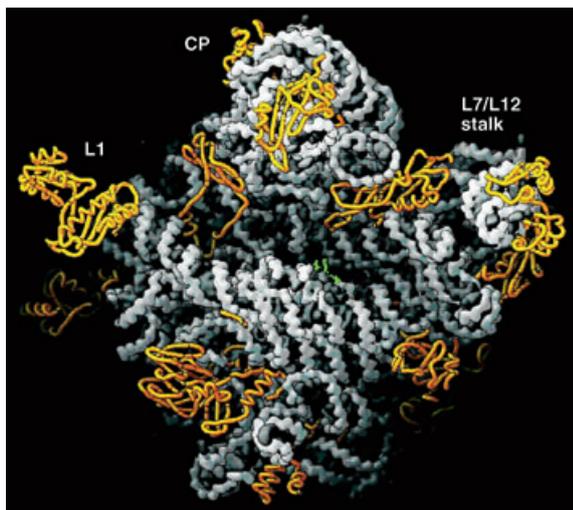


Figure 1. The *H. marismortui* large ribosomal subunit. RNA is shown in gray, the protein backbones are rendered in gold. The particle is approximately 25 nm across.^[78] The macromolecular structures that populate the cell are functional nanostructures—“nanomachines”—with a sophistication much greater than that of the nanostructures now available by synthesis and/or fabrication. The principles by which these three-dimensional structures are generated rely heavily on self-assembly, starting with linear precursors, and are very different from those familiar in microelectronics or materials science.

commercial semiconductor devices to sizes close to 100 nm, and miniaturization continues unabated. Understanding the behaviors of matter in <100 nm structures is, and will continue to be, a part of this evolution, as microelectronics becomes nanoelectronics.

The combination of the promise of new phenomena—new *science*—with an extension of an extremely important *technology* is the force that drives nanoscience. There is also a less rational form of propulsion: Nanoscience and nanotechnology have become a playground for futurists—people who imagine how the future might be—and of science fictionists; sometimes the two overlap.^[22–26] The imaginative



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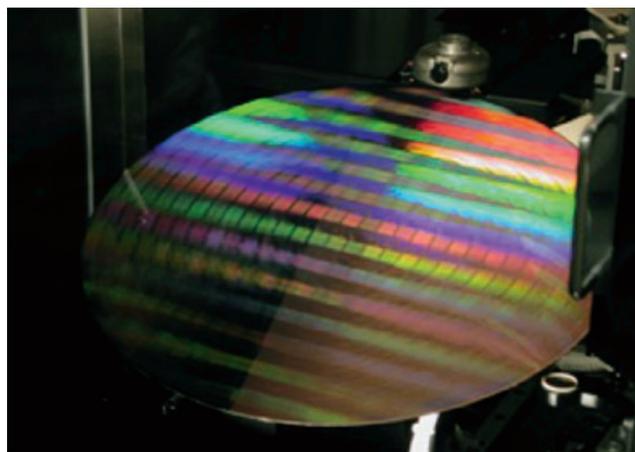


Figure 2. An optical modulator made entirely out of a silicon wafer.^[79] The evolutionary extension of the technology for micrometer-scale fabrication into the sub-100-nm range guarantees that “nanotechnology” will happen.

projection of nanoscience into the future—sometimes with little constraint on the imagination of those projecting—has produced ideas both exciting and terrifying. And, sometimes, downright silly. These ideas—transmitted through the media, in fiction, and through groups concerned with protecting society from thoughtless or unethical technology—have captured public interest, and nanoscience has become one icon for the future of physical science. It is both exhilarating and disquieting, and that contrast arouses both enthusiasm and concern.^[27,28]

Is There a Nanotechnology?

Nanoscience has now been with us for a decade. Technologies growing from it are still few, and the rate at which they have emerged has seemed (although it may not be) slower than that in areas such as biotechnology. The immediate question is: “Is there, or will there be, a nanotechnology?” The answer is: “Absolutely yes!” The next questions are “What is it? When will it appear? And in what form? And will there be *one* or *two* or *many* nanotechnologies?”

There will certainly be—in fact, there already *is*—an *evolutionary* nanotechnology, based on products that already exist, and that have micro- and nanometer-scale features. Commercial “nanotechnology” exists, and is in the robust health of early childhood.^[29] The more interesting question is whether there will be *revolutionary* nanotechnologies, based on fundamentally new science, with products that we cannot presently imagine. I suspect so, but I do not know; if so, they will probably emerge—as do most new technologies—only gradually.

The nanotechnology that is already with us is that of microelectronics (where clever engineers have already shown how to extend existing methods for making microelectronic devices to new systems with sub-70-nm wires and components),^[30] materials science (where many of the properties of polymers, metals, and ceramics are determined by 1–100 nm structures),^[31–33] and chemistry (where nanometer-

scale drugs are routinely used to control proteins and signaling complexes, and where macromolecules have dimensions of many nanometers).^[34,35] These technologies are “evolutionary nano” (Figure 3).

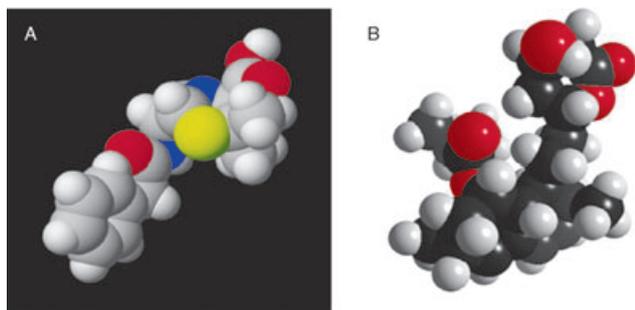


Figure 3. Space-filling molecular models of penicillin (A) and lovastatin (B).^[80,81] Penicillin marked the beginning of rational approaches to the treatment of bacterial disease; lovastatin is equally important in the treatment of cardiovascular disease. Both can be regarded as engineered nanostructures, which act to shut down the activities of larger catalytically functional nanostructures—enzymes—in cells.

The nanotechnology whose form and importance is yet undefined is “revolutionary nano”; that is, technologies emerging from new nanostructured materials (e.g., buckytubes), or from the electronic properties of quantum dots, or from fundamentally new types of architectures—based on nanodevices—for use in computation and information storage and transmission. Nanosystems that use or mimic biology are also intensely interesting.

There is no question that revolutionary nanoscience exists in the laboratories of universities now, and that new forms of nanotechnology will be important; it is just not clear—at the moment—how much of this exciting, revolutionary science will migrate into new technology, and how rapidly this migration will occur. The history of technology suggests, however, that where there is smoke, there will eventually be fire; that is, where there is enough new science, important new technologies will eventually emerge.

Will Chemistry Play a Role in Nanoscience and Nanotechnology?

It should be bracing to chemists to realize that chemistry is already playing a leading role in nanotechnology. In a sense, chemistry *is* (and has always been) the ultimate nanotechnology: Chemists make new forms of matter (and they are really the only scientists to do so routinely) by joining atoms and groups of atoms together with bonds. They carry out this subnanometer-scale activity—chemical synthesis—on megaton scales when necessary, and do so with remarkable economy and safety. Although the initial interest in nanotechnology centered predominantly on nanoelectronics, and on fanciful visions of the futurists, the first new and potentially commercial technologies to emerge from revolutionary nanoscience seem, in fact, to be in materials science; and materials are usually the products of chemical processes. Some examples follow below.

Buckytubes and Buckyballs

Buckyballs were the first of the discrete, graphite-like nanostructures; they have so far been a disappointment in terms of applications. They were, however, followed rapidly by buckytubes—also known as carbon nanotubes—which are long graphite rods. These structures have a range of remarkable properties, including metallic electrical conductivity, semiconductivity with very high carrier mobility, and extraordinary mechanical strength.^[36–38] They are beginning to find commercial uses. Among these uses—surprisingly for such exotic materials—are valuable but relatively mundane applications such as increasing the electrical conductivity of polymers to facilitate electrostatic spray-painting, and to dissipate static. The future may include plasma displays and printed electronics. Buckytubes are, of course, in competition with inexpensive materials such as carbon black and silicon for some of these applications, and cost and safety will determine the winners. Chemistry and chemical engineering play an essential role in developing the catalytic and process chemistry required to make uniform buckytubes at acceptable costs.

Quantum Dots

Quantum dots can be many things, but the initial products that incorporate quantum dots are small grains (a few nanometers in size) of semiconductor materials (for example, cadmium selenide).^[39–41] These grains are stabilized against hydrolysis and aggregation by coating with a layer of zinc oxide and a film of organic surfactant—technologies already familiar to the chemical industry in making paints and washing powders. These first semiconductor quantum dots are fluorescent—they emit colored light when exposed to ultraviolet excitation—and are being tested in displays for computers and mobile telephones, and as inks. These materials are interesting for several reasons: one is that they do not photobleach (that is, lose their color on exposure to light); a second is that a single manufacturing process can make them in a range of sizes, and thus, in a single process, in all colors. Their applications in biology illustrate the difficulties in introducing a new technology. They have been explored as probes in cell biology (Figure 4), but their toxicity, and competition from molecular-scale probes, have made these initial explorations only modestly successful.^[42,43] Nonetheless, small, nontoxic particles are clearly the *right kind of material* to use in characterizing the interior of the living cell.

Phase-Separated Polymers

The chemical industry has used phase-separated copolymers and blends for many years to optimize properties of polymeric materials. Nanoscience is beginning to produce new methods of characterizing the structures of the phase-separated regions (which are often of nanometer dimensions), and thus provide ways of engineering these regions

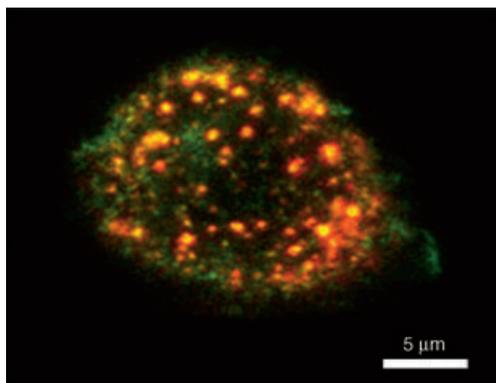


Figure 4. Image of a mammalian cell labeled with fluorescent, surfactant-stabilized, semiconductor quantum dots.^[82] The resistance of these nanostructures to photobleaching makes them attractive in applications in which the sensitivity of molecular fluorophores to the exciting light is a serious impediment to their use.

(and the properties of the polymeric materials) in rational ways.^[44–46] Understanding these relationships between the composition of the polymer, and the properties of the materials made from it, will provide a new approach to engineered materials. Nanoscale, phase-separated block copolymers are also finding uses as materials in microelectronics and photonics.

Self-Assembled Monolayers

These materials (affectionately known as “SAMs” by those who work with them) are formed by allowing appropriate surfactants to assemble on surfaces (again, soap chemistry! See Figure 5).^[47–49] They provide synthetic routes

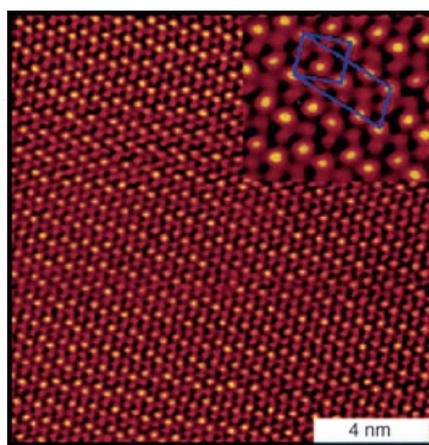


Figure 5. Scanning tunneling microscope image of a self-assembled monolayer (SAM) of decanethiol on gold.^[83] The scanning probe microscopes make it possible to view nanostructures in molecular detail, and have revolutionized surface science. SAMs represent a class of material in which properties such as wetting and biocompatibility can be engineered at the molecular level; many other examples of materials engineered at the nanoscale are now emerging from nanoscience.

to nanometer-thick, highly structured films on surfaces that provide biocompatibility, control of corrosion, friction, wetting, and adhesion, and may offer routes to possible nanometer-scale devices for use in “organic microelectronics”. They have also changed the face of surface science as a research enterprise, moving it from the study of metals and metal oxides in high vacuum to the study of organic materials in circumstances more closely approximating the real world.

Nanofabrication

As the critical dimensions in microelectronics have shrunk, the complex technologies necessary to circumvent the limitations on size imposed by optical diffraction has made photolithography increasingly complicated and expensive. Surprisingly, technologies that are very familiar in chemistry—printing, molding, and embossing—have emerged (in the forms of soft lithography and nanoimprint lithography) as potential competitors for (or complements to) photolithography.^[50,51] The intrinsic limitations to the sizes of the patterns that can be replicated using printing and molding is set by van der Waals interactions, and perhaps by the granularity of matter at the molecular scale, but certainly not by optical diffraction. Self-assembly—a strategy best understood and most highly developed in chemistry—is also offering an appealing strategy for fusing “bottom-up” and “top-down” fabrication, and leading to hierarchical structures of the types so widely found in nature (Figure 6).^[52–54] Electrochemistry in the pores of membranes provides a widely useful route to nanoscale rods.

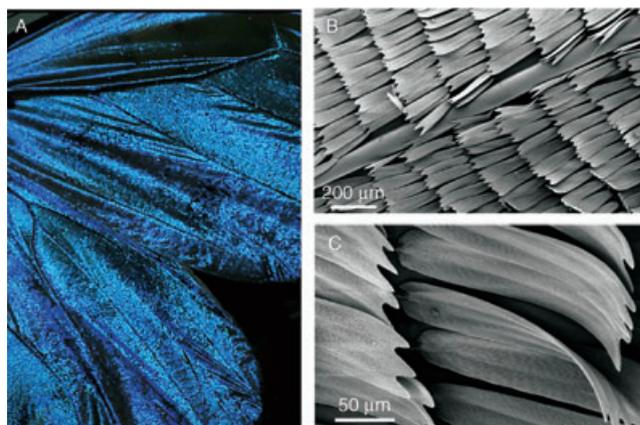


Figure 6. Photograph (A) and SEM images (B,C) of the wing of the *morpho* butterfly (images by Felice Frankel). The brilliant blue reflection from the wing of this butterfly is due to the operation of a remarkable, optically sophisticated photonic bandgap structure, which not only is wavelength selective, but also reflects over a broad range of angles of incidence and observation. Biology presents examples of functional nanostructures of a wide range of types, and has much to teach nanoscience and nanotechnology.

Applied Quantum Behavior

One of the areas in which *revolutionary* nanoscience might emerge is in applications of quantum behaviors: entanglement, the wave nature of molecules, and quantum teleportation. The small size of molecules, and the ability of chemists to engineer their electronic states, has seemed a possible entry into chemical approaches to structures with quantum electrical functionality. The recent fall from grace of molecular electronics has been a setback for this area,^[55] but understanding and exploiting the movement of electrons in molecules is potentially so important—in areas ranging from redox enzymology to quantum electronics—that research into the quantum behavior in molecular matter will certainly continue vigorously.

Nanobiomedicine

Understanding the cell—that is, understanding life—is one of the great unanswered questions in science. The cell is the quantum of biology—the smallest and most fundamental unit—the one from which the rest is built. The cell is a system of molecules and remarkable nanoscale “machines”—functional molecular aggregates of great complexity. Understanding these molecular nanostructures in their full, mechanistic, molecular complexity is vital to a reductionist understanding of the cell. Doing so will require new methods of examining these systems: in isolation, in the cell, and in the organism. The methods that emerge from this research will help us to move closer to understanding human life and health, and thus toward “nanomedicine”. Nanostructures may also be useful in delivering drugs, as imaging agents, and in clinical analysis.^[56–58]

What Are the Scientific Opportunities for Chemistry?

The opportunities for chemistry to make important contributions to nanoscience abound. My favorite five are as follows: 1) *Synthesis of Nanostructures*: Chemistry is unique in the sophistication of its ability to synthesize new forms of matter. The invention of new kinds of nanostructures will be crucial to the discovery of new phenomena. In nanoscience, chemistry can be on the streets at the beginning of the revolution if it has the courage to do so; 2) *Materials*: Materials science and chemistry are, over much of their shared border, indistinguishable. Chemistry has contributed (and will continue to contribute) to the invention and development of materials whose properties depend on nanoscale structure. Chemistry and chemical engineering will, ultimately, be important in producing these materials reproducibly, economically, and in quantity; 3) *Molecular Mechanisms in Nanobiology*: By understanding the molecular mechanisms of functional nanostructures in biology—the light-harvesting apparatus of plants, ATPases, the ribosome, the structures that package DNA—ultimately, the cell is an area where chemistry, with its singular understanding of mo-

lecular mechanism, can make unique contributions (Figure 7); 4) *Tools and Analytical Methods*: The scanning probe microscope—invented by Binnig and Rohrer at the IBM laboratory in Zurich—is the instrument that ignited the explosion of nanoscience.^[59,60] Developing new nano-

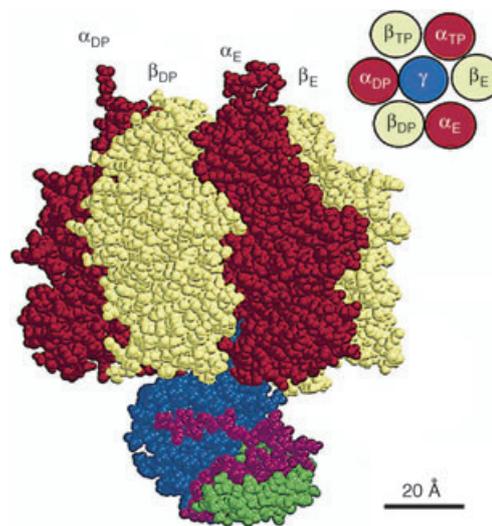


Figure 7. The crystal structure of the central stalk in bovine F1-ATPase at 2.4-Å resolution.^[84] This structure represents a biological solution to a rotary machine. Although it superficially resembles a conventional electrical motor in that it has a rotating “shaft” and a “stator”, its mechanism of operation depends on conformational changes in proteins and ion currents rather than on magnetic fields and electrical currents.

structures requires knowing what they are. Physical and analytical chemistry will help to build the tools that define these structures; 5) *Risk Assessment and Evaluation of Safety*: Understanding the risks of nanostructures and nanomaterials will require cooperation across disciplines that range from chemistry to physiology, and from molecular medicine to epidemiology.^[61,62]

What Are the Commercial Opportunities for Chemistry?

Nanotechnology also offers the chemical industry at least six particular opportunities: 1) *Tools for Research*: The first of these opportunities—and one already well established—is to produce new tools and equipment for research (and increasingly for development and manufacturing). “Instruments for nanoscience” is a growing commercial area; 2) *New Materials*: Materials will be a commercially important class of nanostructures. Examples include structural and electrically/magnetically/optically functional polymers, particles, and composites for a range of applications, from spray-painted automobile bumpers and nanoscale bar-coded rods,^[63] to the printed organic electronics of electronic newspapers and smart shipping labels.^[64] In these applications, chemistry and chemical-process technology will probably be key to commercial realization of the value of the technolo-

gy; 3) *New Processes for Fabrication*: Nanomaterials can only be commercialized if they can be produced. The importance of vapor/liquid/solid catalytic growth of buckytubes over nanoparticles of iron to the development of “nanotubes” illustrates this point.^[65] The development of new processes to make new materials is an activity in which the chemical industry has always excelled; 4) *Nanoelectronics*: The development of new photoresists and processes with which to fabricate structures with the sub-50-nm dimensions required by nanoelectronics will present immediate opportunities for materials science and chemistry;^[66,67] 5) *Nanoparticle Technology*: Specialized kinds of nanoparticles will become important in a wide range of applications—from hydrophobic drugs generated and formulated in nanoparticulate form to improve bioavailability, to electrodes and lumiphores for new kinds of graphic displays; 6) *The Revolutionary Unknown*: A final class—and the one that is the most exciting—comprises the revolutionary ideas, for example, nano-CDs (read by an array of parallel atomic force microscope tips known as the “centipede”),^[68,69] quantum computers, and biocompatible nanoparticles able to reach, recognize, and report presymptomatic disease.

High-performance functional nanomaterials are an opportunity for the chemical industry. They will, however, pose a dilemma, in that, at least initially, and perhaps perpetually, the volumes required will be low. Nanotechnology will confront the chemical industry—in a world that no longer needs new, billion-dollar chemical plants, and in which agility is absolutely required to succeed in seizing technical opportunity—with the choice of trying to manage businesses that make small amounts of boutique materials, or trying to move downstream—in principle into competition with traditional customers—to capture some of the value of the systems of which the materials become a part.^[70,71]

What are the Risks of Nanotechnology?

A new technology sparks conflict between those wishing to exploit it as rapidly as possible and those wishing to wait—forever, if necessary—to have it proved absolutely safe. Nanotechnology is new; although parts of it are quite familiar, parts are unfamiliar, and it is not a surprise that the public is wary of its potential for harm, as well as excited by its potential for good.

The “Assembler” and “Grey Goo”

One concern is that nanotechnology will go out of control. This concern is based on an idea put forward by several futurists (Drexler, Joy, and others),^[22,24] and adopted gleefully by science fiction writers:^[23] that is, the idea of small machines that can replicate themselves (“assemblers”) and that escape the laboratory and eat the earth. Any statement about the future is, of course, always personal opinion. I, personally, see no way that such devices can exist. The idea of small, self-replicating machines has always seemed not

impossible—after all, bacteria exist—but developing such machines *de novo*—a task close to developing a new form of life—has seemed to me to be intractably difficult; it continues to seem so.^[72] I do not believe that self-replicating nanomachines that resemble the larger machines with which we are familiar can be built. So, in my opinion, this type of concern can be dismissed, at least until and unless scientific inventions—in self-replication, and in artificial life—appear that will *far* exceed nanoscience in their importance.

Effects of Nanoparticles on Health

Here public concern has a legitimate basis. We do not, in fact, understand the interaction of small particles with cells and tissues, but there *are* diseases associated with a few of them: silicosis, asbestosis, “black lung”.^[73,74] Most nanomaterials are probably safe: there is no reason to expect fundamentally new kinds of toxicity from them, and in any event, they are common in the environment. Moreover, in commerce, most would be made and used in conditions in which the nanomaterial was relatively shielded from exposure to society (an example would be buckytubes compounded into plastics). Still, we do not know how nanoparticles enter the body, how they are taken up by the cell, how they are distributed in the circulation, or how they affect the health of the organism. If the chemical industry intends to make a serious entry into nanostructured materials, it would be well advised to sponsor arms-length, careful, and entirely dispassionate studies on the effects of existing and new nanoparticles and nanomaterials on the behavior of cells and on the health of animals. This particular aspect of public health will, in any event, be examined in detail by regulatory agencies concerned with the effects of nanoparticulates from other sources (especially carbon nanoparticles in the exhaust from diesel engines) on health.

Privacy and Civil Liberties

In my opinion, the most serious risk of nanotechnology comes, not from hypothetical *revolutionary* materials or systems, but from the uses of *evolutionary* nanotechnologies that are already developing rapidly. The continuing extension of electronics and telecommunications—fast processors, ultradense memory, methods for searching databases, ubiquitous sensors, electronic commerce and banking, commercial and governmental record keeping—into most aspects of life is increasingly making it possible to collect, store, and sort enormous quantities of data about people.^[75] These data can be used to identify and characterize individuals; and the ease with which they can be collected and manipulated poses a direct threat to historical norms of individual privacy. “Universal surveillance”—the observation of everyone and everything, in real time, everywhere; a concept suggested by those most concerned with terrorism—is not a technology that I would wish to see cloak a free society, no matter how protectively intended.^[76]

The risk (and promise; good and evil are not always easy to separate in technology) of new information technologies emerges naturally and almost invisibly from an existing technology with which society is already comfortably familiar, and in which there is no fundamentally “new” concept, and nothing uniquely associated with “nano”. There is, however, no question that information technology has already (and to a far greater extent than biotechnology) transformed the world. I believe that it will continue to do so, and that that transformation is more pervasive and deep-seated than anything that will come from “revolutionary” nanotechnology in the foreseeable future.

The “Right Size”

One final word: Nanoscience is now an important, central thread in fundamental research, and it will soon become an important part of technology. In our enthusiasm for “nano”, we must not forget “micro”, or more generally, “small”.^[56] For many applications, microtechnology is more important than nanotechnology. For example, if one wishes to make assay systems based on mammalian cells for use in developing drugs (a promising direction for commercialization of microfluidic technologies), nanotechnology is not very useful: a mammalian cell is an object that is a few micrometers (not nanometers) in size, and any channel containing it must be larger than it is (Figure 8). Research and

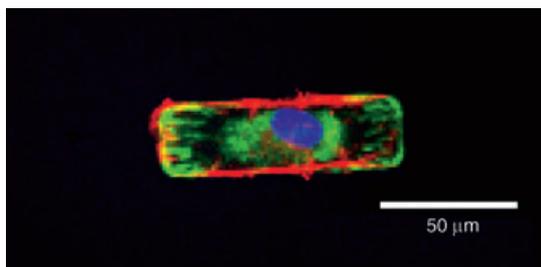


Figure 8. Single human umbilical artery endothelial cells confined on a surface in a rectangular shape using two SAMs on palladium.^[85] One SAM allows proteins to adsorb; the second prevents proteins from adsorbing. Microcontact printing of the “adsorbing” SAM defines the rectangle. Proteins adsorb from the cell-culture medium to this adsorbing surface; the cell attaches to specific peptide sequences in these adsorbed proteins using specialized multiprotein aggregates in its membrane. The colors (fluorescent dyes) define structures in the cell: the blue is the nucleus; red is filamentous actin; green is fibronectin. The scale of the structures used in this type of research on cells is micrometers, since that is their intrinsic size; for this work, “nano” is too small.

development must be focused on the development of science and technology at the *right* size—and that size may range from nanometers to millimeters (for the technologies of small things): “nano” is not always the best or only answer.

Nanoscience is now a thread woven into many fields of science. Nanotechnology—certainly evolutionary, and perhaps revolutionary—will emerge from it. Chemistry will

play a role; whether this role is supporting or leading will depend in part on how the field develops and what opportunities emerge, and in part on how imaginative and aggressive chemists and chemical engineers are, or become, in finding their place in it.

The chemical industry faces particularly interesting choices, since taking full advantage of the opportunities of nanotechnology will require it to behave in new ways.^[77] Few nanomaterials will be commodities, and few processes for making nanofabricated structures will be carried out in facilities having the scale of those used in the production of commodity chemicals. The value of nanomaterials and nanostructures will come in their *function*, and in the systems in which they are embedded. Time will tell whether chemical companies will choose to make photonic devices in order to exploit their ability to produce photonic bandgap (PBG) materials, or whether telecommunications companies will choose to make PBG materials in order to exploit the functions that they provide in their devices and systems. Regardless, it seems inevitable that chemical companies active in nanotechnology will find themselves competing with their customers in the areas of high-valued, functional materials, components, and systems.

Since there are few new, high-margin markets open to the chemical industry, it may need to move downstream—uncomfortable though it may be to do so—in nanotechnology (or other emerging areas) if it is not to stagnate technically and financially. Competition in new markets requires agility, and the ability to move quickly to capture new opportunities is always a difficult trick. It will be particularly difficult for an industry that, for some decades, has not been rewarded for embracing new ideas or for accomplishing new tricks, and that, through lack of practice, has become unaccustomed to doing so.

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