Advanced Nanotechnology

(Research, Applications & Implications)

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Introduction

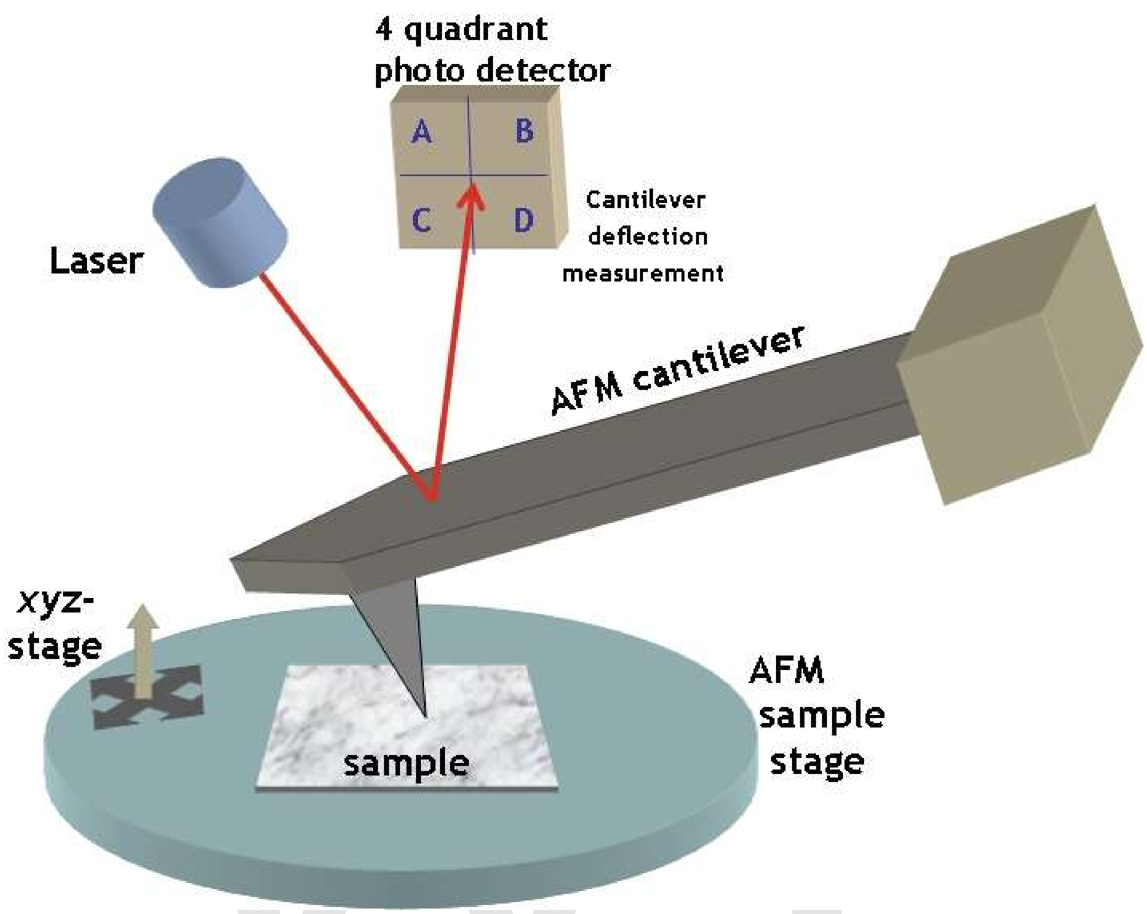
Nanotechnology, shortened to "**nanotech**", is the study of manipulating matter on an atomic and molecular scale. Generally nanotechnology deals with structures sized between 1 to 100 nanometer in at least one dimension, and involves developing materials or devices within that size. Quantum mechanical effects are very important at this scale.

Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to investigating whether we can directly control matter on the atomic scale.

There is much debate on the future implications of nanotechnology. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as with any introduction of new technology, including concerns about the toxicity and environmental impact of nanomaterials, and their potential effects on global economics, as well as speculation about various doomsday scenarios. These concerns have led to a debate among advocacy groups and governments on whether special regulation of nanotechnology is warranted.

Tools and techniques

There are several important modern developments. The atomic force microscope (AFM) and the Scanning Tunneling Microscope (STM) are two early versions of scanning probes that launched nanotechnology. There are other types of scanning probe microscopy, all flowing from the ideas of the scanning confocal microscope developed by Marvin Minsky in 1961 and the scanning acoustic microscope (SAM) developed by Calvin Quate and coworkers in the 1970s, that made it possible to see structures at the nanoscale. The tip of a scanning probe can also be used to manipulate nanostructures (a process called positional assembly). Feature-oriented scanning-positioning methodology suggested by Rostislav Lapshin appears to be a promising way to implement these nanomanipulations in automatic mode. However, this is still a slow process because of low scanning velocity of the microscope. Various techniques of nanolithography such as optical lithography, X-ray lithography dip pen nanolithography, electron beam lithography or nanoimprint lithography were also developed. Lithography is a top-down fabrication technique where a bulk material is reduced in size to nanoscale pattern.



Typical AFM setup. A microfabricated cantilever with a sharp tip is deflected by features on a sample surface, much like in a phonograph but on a much smaller scale. A laser beam reflects off the backside of the cantilever into a set of photodetectors, allowing the deflection to be measured and assembled into an image of the surface.

Another group of nanotechnological techniques include those used for fabrication of nanowires, those used in semiconductor fabrication such as deep ultraviolet lithography, electron beam lithography, focused ion beam machining, nanoimprint lithography, atomic layer deposition, and molecular vapor deposition, and further including molecular self-assembly techniques such as those employing di-block copolymers. However, all of these techniques preceded the nanotech era, and are extensions in the development of scientific advancements rather than techniques which were devised with the sole purpose of creating nanotechnology and which were results of nanotechnology research.

The top-down approach anticipates nanodevices that must be built piece by piece in stages, much as manufactured items are made. Scanning probe microscopy is an important technique both for characterization and synthesis of nanomaterials. Atomic force microscopes and scanning tunneling microscopes can be used to look at surfaces and to move atoms around. By designing different tips for these microscopes, they can be used for carving out structures on surfaces and to help guide self-assembling structures. By using, for example, feature-oriented scanning-positioning approach, atoms can be moved around on a surface with scanning probe microscopy techniques. At present, it is expensive and time-consuming for mass production but very suitable for laboratory experimentation.

In contrast, bottom-up techniques build or grow larger structures atom by atom or molecule by molecule. These techniques include chemical synthesis, self-assembly and positional assembly. Dual polarisation interferometry is one tool suitable for characterisation of self assembled thin films. Another variation of the bottom-up approach is molecular beam epitaxy or MBE. Researchers at Bell Telephone Laboratories like John R. Arthur. Alfred Y. Cho, and Art C. Gossard developed and implemented MBE as a research tool in the late 1960s and 1970s. Samples made by MBE were key to the discovery of the fractional quantum Hall effect for which the 1998 Nobel Prize in Physics was awarded. MBE allows scientists to lay down atomically precise layers of atoms and, in the process, build up complex structures. Important for research on semiconductors, MBE is also widely used to make samples and devices for the newly emerging field of spintronics.

However, new therapeutic products, based on responsive nanomaterials, such as the ultradeformable, stress-sensitive Transfersome vesicles, are under development and already approved for human use in some countries.

Chapter-1

History of Nanotechnology and Fundamental Concepts

History of Nanotechnology

Although nanotechnology is a relatively recent development in scientific research, the development of its central concepts happened over a longer period of time.

Overview

In 1965, Gordon Moore, one of the founders of Intel Corporation, made the outstanding prediction that the number of transistors that could be fit in a given area would double every 18 months for the next ten years. This it did and the phenomenon became known as Moore's Law. This trend has continued far past the predicted 10 years until this day, going from just over 2000 transistors in the original 4004 processors of 1971 to over 700,000,000 transistors in the Core 2. There has, of course, been a corresponding decrease in the size of individual electronic elements, going from millimeters in the 60's to hundreds of nanometers in modern circuitry.

At the same time, the chemistry, biochemistry and molecular genetics communities have been moving in the other direction. Over much the same period, it has become possible to direct the synthesis, either in the test tube or in modified living organisms.

Finally, the last quarter of a century has seen tremendous advances in our ability to control and manipulate light. We can generate light pulses as short as a few femtoseconds ($1\ fs = 10^{-15}\ s$). Light too has a size and this size is also on the hundred nanometer scale.

Thus now, at the beginning of a new century, three powerful technologies have met on a common scale — the nanoscale — with the promise of revolutionizing both the worlds of electronics and of biology. This new field, which we refer to as biomolecular nanotechnology, holds many possibilities from fundamental research in molecular biology and biophysics to applications in biosensing, biocontrol, bioinformatics, genomics, medicine, computing, information storage and energy conversion.HI

Historical background

Humans have unwittingly employed nanotechnology for thousands of years, for example in making steel, paintings and in vulcanizing rubber. Each of these processes rely on the properties of stochastically-formed atomic ensembles mere nanometers in size, and are distinguished from chemistry in that they don't rely on the properties of individual molecules. But the development of the body of concepts now subsumed under the term nanotechnology has been slower...

The first mention of some of the distinguishing concepts in nanotechnology (but predating use of that name) was in 1867 by James Clerk Maxwell when he proposed as a thought experiment a tiny entity known as Maxwell's Demon able to handle individual molecules.

The first observations and size measurements of nano-particles was made during the first decade of the 20th century. They are mostly associated with Richard Adolf Zsigmondy who made a detailed study of gold sols and other nanomaterials with sizes down to 10 nm and less. He published a book in 1914. He used ultramicroscope that employes the *dark field* method for seeing particles with sizes much less than light wavelength. Zsigmondy was also the first who used **nanometer** explicitly for characterizing particle size. He determined it as 1/1,000,000 of millimeter. He developed the first system classification based on particle size in the nanometer range.

There have been many significant developments during the 20th century in characterizing nanomaterials and related phenomena, belonging to the field of interface and colloid science. In the 1920s, Irving Langmuir and Katharine B. Blodgett introduced the concept of a monolayer, a layer of material one molecule thick. Langmuir won a Nobel Prize in chemistry for his work. In the early 1950s, Derjaguin and Abrikosova conducted the first measurement of surface forces.

There have been many studies of *periodic colloidal structures* and principles of molecular self-assembly that are overviewed in the paper. There are many other discoveries that serve as the scientific basis for the modern nanotechnology which can be found in the "Fundamentals of Interface and Colloid Science by H.Lyklema.

Conceptual origins

The topic of nanotechnology was again touched upon by "There's Plenty of Room at the Bottom," a talk given by physicist Richard Feynman at an American Physical Society meeting at Caltech on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and Van der Waals attraction would become more important, etc. This basic idea appears feasible, and exponential assembly enhances it with parallelism to produce a useful quantity of end products. At the meeting, Feynman announced two challenges, and he offered a prize of $1000 for the first individuals to solve each one. The first challenge involved the construction of a nanomotor, which, to Feynman's surprise, was achieved by November 1960 by William McLellan. The second challenge involved the possibility of scaling down letters small enough so as to be able to fit the entire Encyclopedia Britannica on the head of a pin; this prize was claimed in 1985 by Tom Newman.

In 1965 Gordon Moore observed that silicon transistors were undergoing a continual process of scaling downward, an observation which was later codified as Moore's law. Since his observation transistor minimum feature sizes have decreased from 10 micrometers to the 45-65 nm range in 2007; one minimum feature is thus roughly 180 silicon atoms long.

The term "nanotechnology" was first defined by Norio Taniguchi of the Tokyo Science University in a 1974 paper as follows: "'Nano-technology' mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or one molecule." Since that time the definition of nanotechnology has generally been extended to include features as large as 100 nm. Additionally, the idea that nanotechnology embraces structures exhibiting quantum mechanical aspects, such as quantum dots, has further evolved its definition.

Also in 1974 the process of atomic layer deposition, for depositing uniform thin films one atomic layer at a time, was developed and patented by Dr. Tuomo Suntola and co-workers in Finland.

In the 1980s the idea of nanotechnology as deterministic, rather than stochastic, handling of individual atoms and molecules was conceptually explored in depth by Dr. K. Eric Drexler, who promoted the technological significance of nano-scale phenomena and devices through speeches and the books Engines of Creation: The Coming Era of Nanotechnology and *Nanosystems: Molecular Machinery, Manufacturing, and Computation,* (ISBN 0-471-57518-6). Drexler's vision of nanotechnology is often called "Molecular Nanotechnology" (MNT) or "molecular manufacturing," and Drexler at one point proposed the term "zettatech" which never became popular.

In 2004 Richard Jones wrote a book called Soft Machines (nanotechnology and life), is a book about nanotechnology for the general reader, published by Oxford University. In this book he describes radical nanotechnology as a deterministic/mechanistic idea of nano engineered machines that does not take into account the nanoscale challenges such as wetness, stickness, brownian motion, high viscosity (Drexler view). He also explains what is soft nanotechnology or more appropriatelly biomimetic nanotechnology which is the way forward, if not the best, to design functional nanodevices that can cope with all the problems at nanoscale. One can think of soft nanotechnology as the development of nanomachines that uses the lessons learned from biology on how things work, chemistry to precisely engineer such devices and stochastic physics to model the system and its natural processes in detail.

Experimental advances

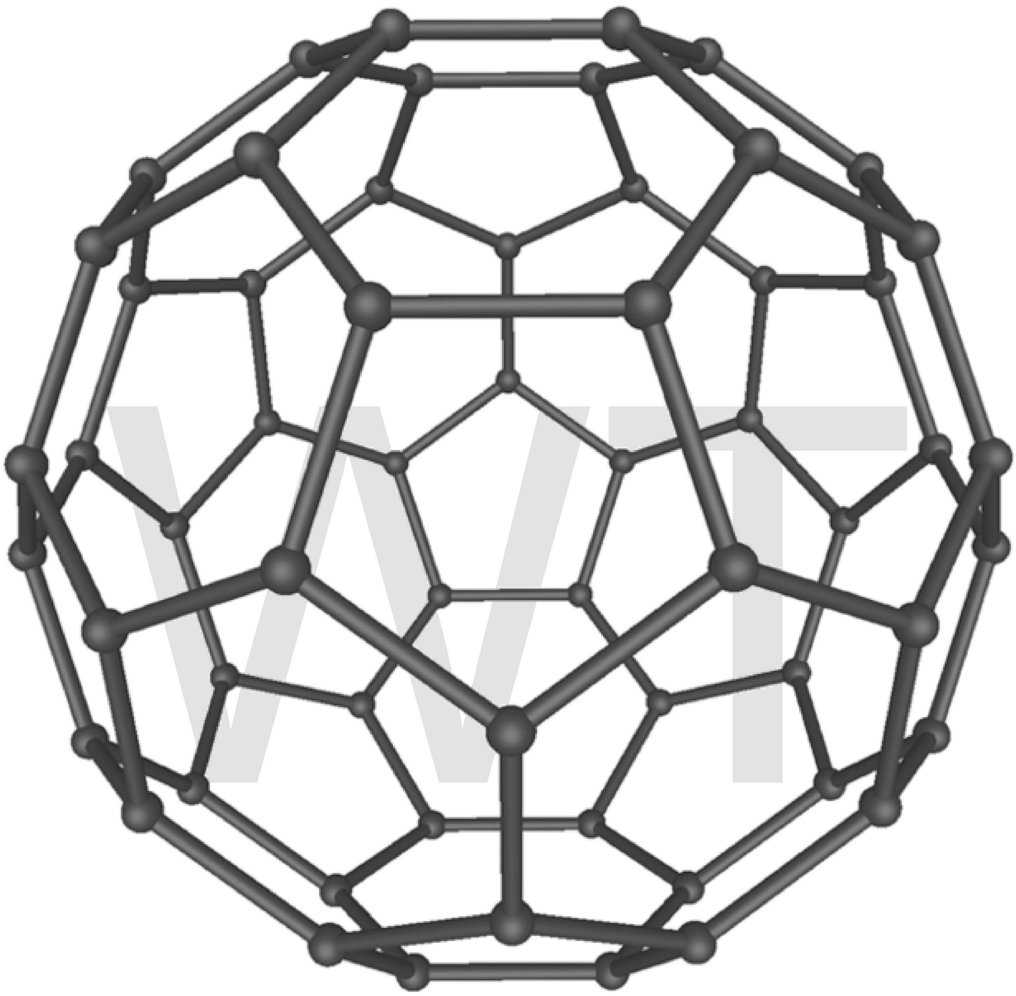
Nanotechnology and nanoscience got a boost in the early 1980s with two major developments: the birth of cluster science and the invention of the scanning tunneling microscope (STM). This development led to the discovery of fullerenes in 1985 and the structural assignment of carbon nanotubes a few years later. In another development, the synthesis and properties of semiconductor nanocrystals were studied. This led to a fast increasing number of semiconductor nanoparticles of quantum dots.

In the early 1990s Huffman and Kraetschmer, of the University of Arizona, discovered how to synthesize and purify large quantities of fullerenes. This opened the door to their characterization and functionalization by hundreds of investigators in government and industrial laboratories. Shortly after, rubidium doped C_{60} was found to be a mid temperature (Tc = 32 K) superconductor. At a meeting of the Materials Research Society in 1992, Dr. T. Ebbesen (NEC) described to a spellbound audience his discovery and characterization of carbon nanotubes. This event sent those in attendance and others downwind of his presentation into their laboratories to reproduce and push those discoveries forward. Using the same or similar tools as those used by Huffman and Kratschmere, hundreds of researchers further developed the field of nanotube-based nanotechnology.

At present in 2007 the practice of nanotechnology embraces both stochastic approaches (in which, for example, supramolecular chemistry creates waterproof pants) and deterministic approaches wherein single molecules (created by stochastic chemistry) are manipulated on substrate surfaces (created by stochastic deposition methods) by deterministic methods comprising nudging them with STM or AFM probes and causing simple binding or cleavage reactions to occur. The dream of a complex, deterministic molecular nanotechnology remains elusive. Since the mid 1990s, thousands of surface scientists and thin film technocrats have latched on to the nanotechnology bandwagon and redefined their disciplines as nanotechnology. This has caused much confusion in the field and has spawned thousands of "nano"-papers on the peer reviewed literature. Most of these reports are extensions of the more ordinary research done in the parent fields.

For the future, some means has to be found for MNT design evolution at the nanoscale which mimics the process of biological evolution at the molecular scale. Biological evolution proceeds by random variation in ensemble averages of organisms combined with culling of the less-successful variants and reproduction of the more-successful variants, and macroscale engineering design also proceeds by a process of design evolution from simplicity to complexity as set forth somewhat satirically by John Gall: "A complex system that works is invariably found to have evolved from a simple system that worked. . . . A complex system designed from scratch never works and can not be patched up to make it work. You have to start over, beginning with a system that works." A breakthrough in MNT is needed which proceeds from the simple atomic ensembles which can be built with, e.g., an STM to complex MNT systems via a process of design evolution. A handicap in this process is the difficulty of seeing and manipulation at the nanoscale compared to the macroscale which makes deterministic selection of successful trials difficult; in contrast biological evolution proceeds via action of what Richard Dawkins has called the "blind watchmaker" comprising random molecular variation and deterministic reproduction/extinction.

Origins



Buckminsterfullerene C_{60}, also known as the buckyball, is a representative member of the carbon structures known as fullerenes. Members of the fullerene family are a major subject of research falling under the nanotechnology umbrella.

The first use of the concepts found in 'nano-technology' (but pre-dating use of that name) was in "There's Plenty of Room at the Bottom", a talk given by physicist Richard Feynman at an American Physical Society meeting at Caltech on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, and so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and van der Waals attraction would become increasingly more significant, etc. This basic idea appeared plausible, and exponential assembly enhances it with parallelism to produce a useful quantity of end products. The term "nanotechnology" was defined by Tokyo Science University Professor Norio Taniguchi in a 1974 paper as follows: "'Nano-technology' mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule." In the 1980s the basic idea of this definition was explored in much more depth by Dr. K. Eric Drexler, who promoted the technological significance of nano-scale phenomena and devices through speeches and the books Engines of Creation: The Coming Era of Nanotechnology (1986) and *Nanosystems: Molecular Machinery, Manufacturing, and Computation*, and so the term acquired its current sense. Engines of Creation: The Coming Era of Nanotechnology is considered the first book on the topic of nanotechnology. Nanotechnology and nanoscience got started in the early 1980s with two major developments; the birth of cluster science and the invention of the scanning tunneling microscope (STM). This development led to the discovery of fullerenes in 1985 and carbon nanotubes a few years later. In another development, the synthesis and properties of semiconductor nanocrystals was studied; this led to a fast increasing number of metal and metal oxide nanoparticles and quantum dots. The atomic force microscope (AFM or SFM) was invented six years after the STM was invented. In 2000, the United States National Nanotechnology Initiative was founded to coordinate Federal nanotechnology research and development and is evaluated by the President's Council of Advisors on Science and Technology.

Fundamental Concept

One nanometer (nm) is one billionth, or 10^{-9}, of a meter. By comparison, typical carbon-carbon bond lengths, or the spacing between these atoms in a molecule, are in the range 0.12–0.15 nm, and a DNA double-helix has a diameter around 2 nm. On the other hand, the smallest cellular life-forms, the bacteria of the genus Mycoplasma, are around 200 nm in length.

To put that scale in another context, the comparative size of a nanometer to a meter is the same as that of a marble to the size of the earth. Or another way of putting it: a nanometer is the amount an average man's beard grows in the time it takes him to raise the razor to his face.

Two main approaches are used in nanotechnology. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control.

Areas of physics such as nanoelectronics, nanomechanics, nanophotonics and nanoionics have evolved during the last few decades to provide a basic scientific foundation of nanotechnology.

Larger to smaller: a materials perspective

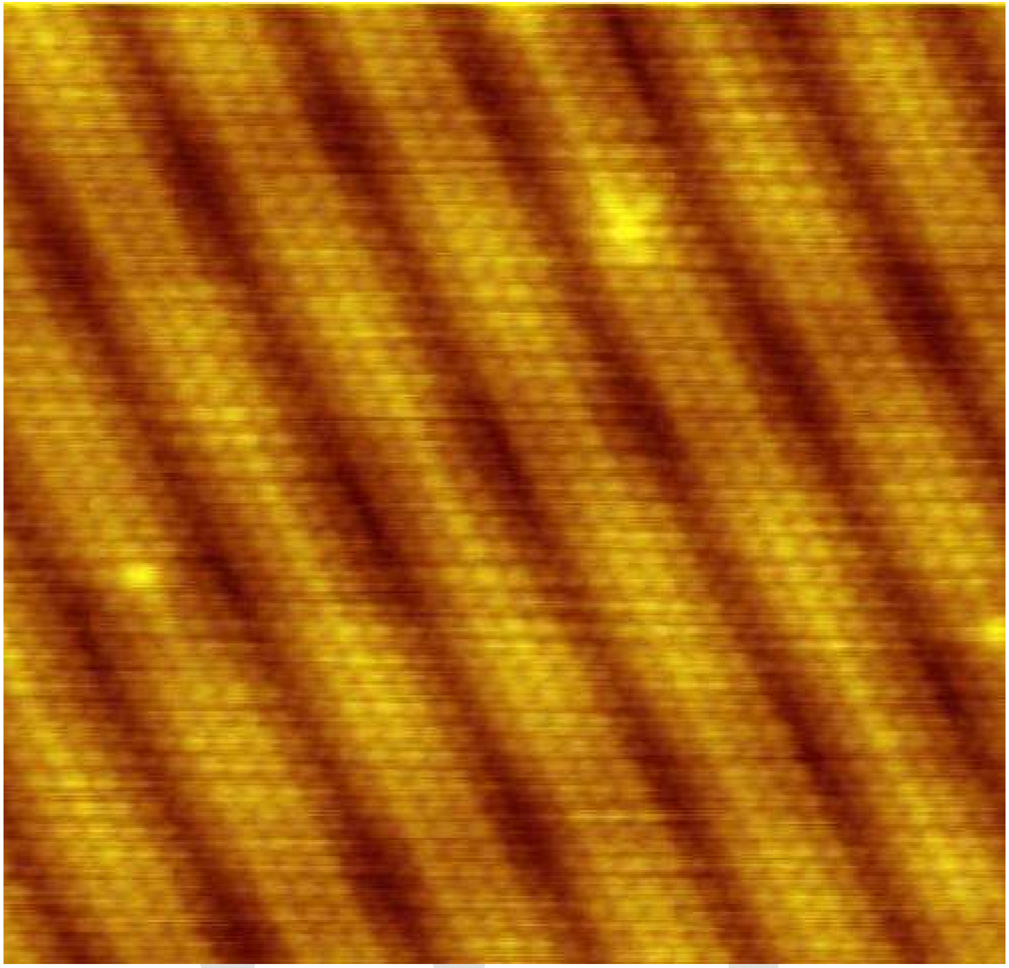


Image of reconstruction on a clean Gold(100) surface, as visualized using scanning tunneling microscopy. The positions of the individual atoms composing the surface are visible.

A number of physical phenomena become pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, for example the "quantum size effect" where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, quantum effects become dominant when the nanometer size range is reached, typically at distances of 100 nanometers or less, the so called quantum realm. Additionally, a number of physical (mechanical, electrical, optical, etc.) properties change when compared to macroscopic systems. One example is the increase in surface area to volume ratio altering mechanical, thermal and catalytic properties of materials. Diffusion and reactions at nanoscale, nanostructures materials and nanodevices with fast ion transport are generally referred to nanoionics. *Mechanical* properties of nanosystems are of interest in the nanomechanics research. The catalytic activity of nanomaterials also opens potential risks in their interaction with biomaterials.

Materials reduced to the nanoscale can show different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper); stable materials turn combustible (aluminum); insoluble materials become soluble (gold). A material such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nanoscale.

Simple to complex: a molecular perspective

Modern synthetic chemistry has reached the point where it is possible to prepare small molecules to almost any structure. These methods are used today to manufacture a wide variety of useful chemicals such as pharmaceuticals or commercial polymers. This ability raises the question of extending this kind of control to the next-larger level, seeking methods to assemble these single molecules into supramolecular assemblies consisting of many molecules arranged in a well defined manner.

These approaches utilize the concepts of molecular self-assembly and/or supramolecular chemistry to automatically arrange themselves into some useful conformation through a bottom-up approach. The concept of molecular recognition is especially important: molecules can be designed so that a specific configuration or arrangement is favored due to non-covalent intermolecular forces. The Watson–Crick basepairing rules are a direct result of this, as is the specificity of an enzyme being targeted to a single substrate, or the specific folding of the protein itself. Thus, two or more components can be designed to be complementary and mutually attractive so that they make a more complex and useful whole.

Such bottom-up approaches should be capable of producing devices in parallel and be much cheaper than top-down methods, but could potentially be overwhelmed as the size and complexity of the desired assembly increases. Most useful structures require complex and thermodynamically unlikely arrangements of atoms. Nevertheless, there are many examples of self-assembly based on molecular recognition in biology, most notably Watson–Crick basepairing and enzyme-substrate interactions. The challenge for nanotechnology is whether these principles can be used to engineer new constructs in addition to natural ones.

Molecular nanotechnology: a long-term view

Molecular nanotechnology, sometimes called molecular manufacturing, describes engineered nanosystems (nanoscale machines) operating on the molecular scale. Molecular nanotechnology is especially associated with the molecular assembler, a machine that can produce a desired structure or device atom-by-atom using the principles of mechanosynthesis. Manufacturing in the context of productive nanosystems is not related to, and should be clearly distinguished from, the conventional technologies used to manufacture nanomaterials such as carbon nanotubes and nanoparticles.

When the term "nanotechnology" was independently coined and popularized by Eric Drexler (who at the time was unaware of an earlier usage by Norio Taniguchi) it referred to a future manufacturing technology based on molecular machine systems. The premise was that molecular scale biological analogies of traditional machine components demonstrated molecular machines were possible: by the countless examples found in biology, it is known that sophisticated, stochastically optimised biological machines can be produced.

It is hoped that developments in nanotechnology will make possible their construction by some other means, perhaps using biomimetic principles. However, Drexler and other researchers have proposed that advanced nanotechnology, although perhaps initially implemented by biomimetic means, ultimately could be based on mechanical engineering principles, namely, a manufacturing technology based on the mechanical functionality of these components (such as gears, bearings, motors, and structural members) that would enable programmable, positional assembly to atomic specification. The physics and engineering performance of exemplar designs were analyzed in Drexler's book *Nanosystems*.

In general it is very difficult to assemble devices on the atomic scale, as all one has to position atoms on other atoms of comparable size and stickiness. Another view, put forth by Carlo Montemagno, is that future nanosystems will be hybrids of silicon technology and biological molecular machines. Yet another view, put forward by the late Richard Smalley, is that mechanosynthesis is impossible due to the difficulties in mechanically manipulating individual molecules.

This led to an exchange of letters in the ACS publication Chemical & Engineering News in 2003. Though biology clearly demonstrates that molecular machine systems are possible, non-biological molecular machines are today only in their infancy. Leaders in research on non-biological molecular machines are Dr. Alex Zettl and his colleagues at Lawrence Berkeley Laboratories and UC Berkeley. They have constructed at least three distinct molecular devices whose motion is controlled from the desktop with changing voltage: a nanotube nanomotor, a molecular actuator, and a nanoelectromechanical relaxation oscillator.

An experiment indicating that positional molecular assembly is possible was performed by Ho and Lee at Cornell University in 1999. They used a scanning tunneling microscope to move an individual carbon monoxide molecule (CO) to an individual iron atom (Fe) sitting on a flat silver crystal, and chemically bound the CO to the Fe by applying a voltage.

Chapter-2

Molecular Nanotechnology & Molecular Self-assembly

Molecular Nanotechnology

Molecular nanotechnology (MNT): a technology based on the ability to build structures to complex, atomic specifications by means of mechanosynthesis. This is distinct from nanoscale materials. Based on Richard Feynman's vision of miniature factories using nanomachines to build complex products (including additional nanomachines), this advanced form of nanotechnology (or *molecular manufacturing*) would make use of positionally-controlled mechanosynthesis guided by molecular machine systems. MNT would involve combining physical principles demonstrated by chemistry, other nanotechnologies, and the molecular machinery of life with the systems engineering principles found in modern macroscale factories.

Introduction

While conventional chemistry uses inexact processes obtaining inexact results, and biology exploits inexact processes to obtain definitive results, molecular nanotechnology would employ original definitive processes to obtain definitive results. The desire in molecular nanotechnology would be to balance molecular reactions in positionally-controlled locations and orientations to obtain desired chemical reactions, and then to build systems by further assembling the products of these reactions.

A roadmap for the development of MNT is an objective of a broadly based technology project led by Battelle (the manager of several U.S. National Laboratories) and the Foresight Institute. The roadmap was originally scheduled for completion by late 2006, but was released in January 2008. The Nanofactory Collaboration is a more focused ongoing effort involving 23 researchers from 10 organizations and 4 countries that is developing a practical research agenda specifically aimed at positionally-controlled diamond mechanosynthesis and diamondoid nanofactory development. In August 2005, a task force consisting of 50+ international experts from various fields was organized by the Center for Responsible Nanotechnology to study the societal implications of molecular nanotechnology.

Projected applications and capabilities

Smart materials and nanosensors

One proposed application of MNT is so-called smart materials. This term refers to any sort of material designed and engineered at the nanometer scale for a specific task. It encompasses a wide variety of possible commercial applications. One example would be materials designed to respond differently to various molecules; such a capability could lead, for example, to artificial drugs which would recognize and render inert specific viruses. Another is the idea of self-healing structures, which would repair small tears in a surface naturally in the same way as self-sealing tires or human skin.

A MNT nanosensor would resemble a smart material, involving a small component within a larger machine that would react to its environment and change in some fundamental, intentional way. A very simple example: a photosensor might passively measure the incident light and discharge its absorbed energy as electricity when the light passes above or below a specified threshold, sending a signal to a larger machine. Such a sensor would supposedly cost less and use less power than a conventional sensor, and yet function usefully in all the same applications — for example, turning on parking lot lights when it gets dark.

While smart materials and nanosensors both exemplify useful applications of MNT, they pale in comparison with the complexity of the technology most popularly associated with the term: the replicating nanorobot.

Replicating nanorobots

MNT nanofacturing is popularly linked with the idea of swarms of coordinated nanoscale robots working together, a popularization of an early proposal by Drexler in his 1986 discussions of MNT, but superseded in 1992. In this early proposal, sufficiently capable nanorobots would construct more nanorobots in an artificial environment containing special molecular building blocks.

Critics have doubted both the feasibility of self-replicating nanorobots and the feasibility of control if self-replicating nanorobots could be achieved: they cite the possibility of mutations removing any control and favoring reproduction of mutant pathogenic variations. Advocates address the first doubt by pointing out that the first macroscale autonomous machine replicator, made of Lego blocks, was built and operated experimentally in 2002. While there are sensory advantages present at the macroscale compared to the limited sensorium available at the nanoscale, proposals for positionally controlled nanoscale mechanosynthetic fabrication systems employ dead reckoning of tooltips combined with reliable reaction sequence design to ensure reliable results, hence a limited sensorium is no handicap; similar considerations apply to the positional assembly of small nanoparts. Advocates address the second doubt by arguing that bacteria are (of necessity) evolved to evolve, while nanorobot mutation could be actively prevented by common error-correcting techniques. Similar ideas are advocated in the

Foresight Guidelines on Molecular Nanotechnology, and a map of the 137-dimensional replicator design space recently published by Freitas and Merkle provides numerous proposed methods by which replicators could, in principle, be safely controlled by good design.

However, the concept of suppressing mutation raises the question: How can design evolution occur at the nanoscale without a process of random mutation and deterministic selection? Critics argue that MNT advocates have not provided a substitute for such a process of evolution in this nanoscale arena where conventional sensory-based selection processes are lacking. The limits of the sensorium available at the nanoscale could make it difficult or impossible to winnow successes from failures. Advocates argue that design evolution should occur deterministically and strictly under human control, using the conventional engineering paradigm of modeling, design, prototyping, testing, analysis, and redesign.

In any event, since 1992 technical proposals for MNT do not include self-replicating nanorobots, and recent ethical guidelines put forth by MNT advocates prohibit unconstrained self-replication.

Medical nanorobots

One of the most important applications of MNT would be medical nanorobotics or nanomedicine, an area pioneered by Robert Freitas in numerous books and papers. The ability to design, build, and deploy large numbers of medical nanorobots would, at a minimum, make possible the rapid elimination of disease and the reliable and relatively painless recovery from physical trauma. Medical nanorobots might also make possible the convenient correction of genetic defects, and help to ensure a greatly expanded healthspan. More controversially, medical nanorobots might be used to augment natural human capabilities. However, mechanical medical nanodevices would not be allowed (or designed) to self-replicate inside the human body, nor would medical nanorobots have any need for self-replication themselves since they would be manufactured exclusively in carefully regulated nanofactories.

Utility fog

Diagram of a 100 micrometer foglet

Another proposed application of molecular nanotechnology is "utility fog" — in which a cloud of networked microscopic robots (simpler than assemblers) would change its shape and properties to form macroscopic objects and tools in accordance with software commands. Rather than modify the current practices of consuming material goods in different forms, utility fog would simply replace many physical objects.

Phased-array optics

Yet another proposed application of MNT would be phased-array optics (PAO). However, this appears to be a problem addressable by ordinary nanoscale technology. PAO would use the principle of phased-array millimeter technology but at optical wavelengths. This would permit the duplication of any sort of optical effect but virtually. Users could request holograms, sunrises and sunsets, or floating lasers as the mood strikes. PAO systems were described in BC Crandall's *Nanotechnology: Molecular Speculations on Global Abundance* in the Brian Wowk article "Phased-Array Optics."

Potential social impacts

Benefits

Nanotechnology (or molecular nanotechnology to refer more specifically to the goals discussed here) will let us continue the historical trends in manufacturing right up to the fundamental limits imposed by physical law. It will let us make remarkably powerful molecular computers. It will let us make materials over fifty times lighter than steel or aluminium alloy but with the same strength. We'll be able to make jets, rockets, cars or even chairs that, by today's standards, would be remarkably light, strong, and inexpensive. Molecular surgical tools, guided by molecular computers and injected into the blood stream could find and destroy cancer cells or invading bacteria, unclog arteries, or provide oxygen when the circulation is impaired.

Nanotechnology will replace our entire manufacturing base with a new, radically more precise, radically less expensive, and radically more flexible way of making products. The aim is not simply to replace today's computer chip making plants, but also to replace the assembly lines for cars, televisions, telephones, books, surgical tools, missiles, bookcases, airplanes, tractors, and all the rest. The objective is a pervasive change in manufacturing, a change that will leave virtually no product untouched. Economic progress and military readiness in the 21st Century will depend fundamentally on maintaining a competitive position in nanotechnology.

Despite the current early developmental status of nanotechnology and molecular nanotechnology, much concern surrounds MNT's anticipated impact on economics and on law. Some conjecture that MNT would elicit a strong public-opinion backlash, as has occurred recently around genetically modified plants and the prospect of human cloning. Whatever the exact effects, MNT, if achieved, would tend to upset existing economic structures by reducing the scarcity of manufactured goods and making many more goods (such as food and health aids) manufacturable.

It is generally considered that future citizens of a molecular-nanotechnological society would still need money, in the form of unforgeable digital cash or physical specie (in special circumstances). They might use such money to buy goods and services that are unique, or limited within the solar system. These might include: matter, energy, information, real estate, design services, entertainment services, legal services, fame, political power, or the attention of other people to ones political/religious/philosophical message. Furthermore, futurists must consider war, even between prosperous states, and non-economic goals.

If MNT were realized, some resources would remain limited, because unique physical objects are limited (a plot of land in the real Jerusalem, mining rights to the larger near-earth asteroids) or because they depend on the goodwill of a particular person (the love of a famous person, a live audience in a musical concert). Demand will always exceed supply for some things, and a political economy may continue to exist in any case. Whether the interest in these limited resources would diminish with the advent of virtual reality, where they could be easily substituted, is yet unclear; one reason why it might not is a hypothetical preference for "the real thing".

MNT should make possible nanomedical capabilities able to cure any medical condition not already cured by advances in other areas. Good health would be common, and poor health of any form would be as rare as smallpox and scurvy are today. Even cryonics would be feasible, as cryopreserved tissue could be fully repaired.

Risks

Molecular nanotechnology is one of the technologies that some analysts believe could lead to a Technological Singularity. Some feel that molecular nanotechnology would have daunting risks. It conceivably could enable cheaper and more destructive conventional weapons. Also, molecular nanotechnology might permit weapons of mass destruction that could self-replicate, as viruses and cancer cells do when attacking the human body. Commentators generally agree that, in the event molecular nanotechnology were developed, mankind should permit self-replication only under very controlled or "inherently safe" conditions.

A fear exists that nanomechanical robots, if achieved, and if designed to self-replicate using naturally occurring materials (a difficult task), could consume the entire planet in their hunger for raw materials, or simply crowd out natural life, out-competing it for energy (as happened historically when blue-green algae appeared and outcompeted earlier life forms). Some commentators have referred to this situation as the "grey goo" or "ecophagy" scenario. K. Eric Drexler considers an accidental "grey goo" scenario extremely unlikely and says so in later editions of *Engines of Creation*.

In light of this perception of potential danger, the Foresight Institute (founded by K. Eric Drexler to prepare for the arrival of future technologies) has drafted a set of guidelines for the ethical development of nanotechnology. These include the banning of free-foraging self-replicating pseudo-organisms on the Earth's surface, at least, and possibly in other places.

Technical issues and criticism

The feasibility of the basic technologies analyzed in *Nanosystems* has been the subject of a formal scientific review by U.S. National Academy of Sciences, and has also been the focus of extensive debate on the internet and in the popular press.

Study and recommendations by the U.S. National Academy of Sciences

In 2006, U.S. National Academy of Sciences released the report of a study of molecular manufacturing as part of a longer report, *A Matter of Size: Triennial Review of the National Nanotechnology Initiative* The study committee reviewed the technical content of *Nanosystems*, and in its conclusion states that no current theoretical analysis can be considered definitive regarding several questions of potential system performance, and that optimal paths for implementing high-performance systems cannot be predicted with confidence. It recommends experimental research to advance knowledge in this area:

"Although theoretical calculations can be made today, the eventually attainable range of chemical reaction cycles, error rates, speed of operation, and thermodynamic efficiencies of such bottom-up manufacturing systems cannot be reliably predicted at this time. Thus, the eventually attainable perfection and complexity of manufactured products, while they can be calculated in theory, cannot be predicted with confidence. Finally, the optimum research paths that might lead to systems which greatly exceed the thermodynamic efficiencies and other capabilities of biological systems cannot be reliably predicted at this time. Research funding that is based on the ability of investigators to produce experimental demonstrations that link to abstract models and guide long-term vision is most appropriate to achieve this goal."

Assemblers versus nanofactories

A section heading in Drexler's *Engines of Creation* reads "Universal Assemblers", and the following text speaks of assemblers which could hypothetically "build almost anything that the laws of nature allow to exist." Drexler's colleague Ralph Merkle has noted that, contrary to widespread legend, Drexler never claimed that assembler systems could build absolutely any molecular structure. The endnotes in Drexler's book explain the qualification "almost": "For example, a delicate structure might be designed that, like a stone arch, would self-destruct unless all its pieces were already in place. If there were no room in the design for the placement and removal of a scaffolding, then the structure might be impossible to build. Few structures of practical interest seem likely to exhibit such a problem, however."

In 1992, Drexler published *Nanosystems: Molecular Machinery, Manufacturing, and Computation*, a detailed proposal for synthesizing stiff covalent structures using a table-top factory. Diamondoid structures and other stiff covalent structures, if achieved, would have a wide range of possible applications, going far beyond current MEMS technology. An outline of a path was put forward in 1992 for building a table-top factory in the absence of an assembler. Other researchers have begun advancing tentative, alternative proposed paths for this in the years since Nanosystems was published.

The Smalley-Drexler debate

Several researchers, including Nobel Prize winner Dr. Richard Smalley (1943–2005), attacked the notion of universal assemblers, leading to a rebuttal from Drexler and colleagues, and eventually to an exchange of letters. Smalley argued that chemistry is extremely complicated, reactions are hard to control, and that a universal assembler is science fiction. Drexler and colleagues, however, noted that Drexler never proposed universal assemblers able to make absolutely anything, but instead proposed more limited assemblers able to make a very wide variety of things. They challenged the relevance of Smalley's arguments to the more specific proposals advanced in *Nanosystems*. Also, Smalley argued that nearly all of modern chemistry involves reactions that take place in a solvent (usually water), because the small molecules of a solvent contribute many things, such as lowering binding energies for transition states. Since nearly all known chemistry requires a solvent, Smalley felt that Drexler's proposal to use a high vacuum environment was not feasible. However, Drexler addresses this in Nanosystems by showing mathematically that well designed catalysts can provide the effects of a solvent and can fundamentally be made even more efficient than a solvent/enzyme reaction could ever be.

The feasibility of the proposals in *Nanosystems*

The feasibility of Drexler's proposals largely depends, therefore, on whether designs like those in *Nanosystems* could be built in the absence of a universal assembler to build them and would work as described. Supporters of molecular nanotechnology frequently claim that no significant errors have been discovered in *Nanosystems* since 1992. Even some critics concede that "Drexler has carefully considered a number of physical principles underlying the 'high level' aspects of the nanosystems he proposes and, indeed, has thought in some detail" about some issues.

Other critics claim, however, that *Nanosystems* omits important chemical details about the low-level 'machine language' of molecular nanotechnology. They also claim that much of the other low-level chemistry in *Nanosystems* requires extensive further work, and that Drexler's higher-level designs therefore rest on speculative foundations. Recent such further work by Freitas and Merkle is aimed at strengthening these foundations by filling the existing gaps in the low-level chemistry.

Drexler argues that we may need to wait until our conventional nanotechnology improves before solving these issues: "Molecular manufacturing will result from a series of advances in molecular machine systems, much as the first Moon landing resulted from a series of advances in liquid-fuel rocket systems. We are now in a position like that of the British Interplanetary Society of the 1930s which described how multistage liquid-fueled rockets could reach the Moon and pointed to early rockets as illustrations of the basic principle." However, Freitas and Merkle argue that a focused effort to achieve diamond mechanosynthesis (DMS) can begin now, using existing technology, and might achieve success in less than a decade if their "direct-to-DMS approach is pursued rather than a more circuitous development approach that seeks to implement less efficacious nondiamondoid molecular manufacturing technologies before progressing to diamondoid".

To summarize the arguments against feasibility: First, critics argue that a primary barrier to achieving molecular nanotechnology is the lack of an efficient way to create machines on a molecular/atomic scale, especially in the absence of a well-defined path toward a self-replicating assembler or diamondoid nanofactory. Advocates respond that a preliminary research path leading to a diamondoid nanofactory is being developed.

A second difficulty in reaching molecular nanotechnology is design. Hand design of a gear or bearing at the level of atoms might take a few to several weeks. While Drexler, Merkle and others have created designs of simple parts, no comprehensive design effort for anything approaching the complexity of a Model T Ford has been attempted. Advocates respond that it is difficult to undertake a comprehensive design effort in the absence of significant funding for such efforts, and that despite this handicap much useful design-ahead has nevertheless been accomplished with new software tools that have been developed, e.g., at Nanorex.

A third difficulty in achieving molecular technology is separating successful trials from failures, and elucidating the failure mechanisms of the failures. Unlike biological evolution, which proceeds by random variations in ensembles of organisms combined with deterministic reproduction/extinction as a selection process to achieve great complexity after billions of years, deliberate design and building of nanoscale mechanisms requires a means other than reproduction/extinction to winnow successes from failures in proceeding from simplicity to complexity. Such means are difficult to provide (and presently non-existent) for anything other than small assemblages of atoms viewable by an atomic force microscope (AFM) or scanning tunneling microscope (STM). Advocates agree this is a valid constraint using current technology, but they insist that this is not a fundamental constraint imposed by the laws of physics. They assert that, once mechanosynthetic tooltips and similar future positionally-controlled molecular tools are fabricated, the same technology could permit prototyping, testing, and rework of failed designs. However, both critics and advocates agree that this expectation remains to be proven and further research will be required to resolve the issue.

In the latest report *A Matter of Size: Triennial Review of the National Nanotechnology Initiative* put out by the National Academies Press in December 2006 (roughly twenty years after Engines of Creation was published), no clear way forward toward molecular nanotechnology could yet be seen, as per the conclusion on page 108 of that report: "Although theoretical calculations can be made today, the eventually attainable range of chemical reaction cycles, error rates, speed of operation, and thermodynamic efficiencies of such bottom-up manufacturing systems cannot be reliably predicted at this time. Thus, the eventually attainable perfection and complexity of manufactured products, while they can be calculated in theory, cannot be predicted with confidence. Finally, the optimum research paths that might lead to systems which greatly exceed the thermodynamic efficiencies and other capabilities of biological systems cannot be reliably predicted at this time. Research funding that is based on the ability of investigators to produce experimental demonstrations that link to abstract models and guide long-term vision is most appropriate to achieve this goal." This call for research leading to demonstrations is welcomed by groups such as the Nanofactory Collaboration who are specifically seeking experimental successes in diamond mechanosynthesis. The "Technology Roadmap for Productive Nanosystems" aims to offer additional constructive insights.

It is perhaps interesting to ask whether or not most structures consistent with physical law can in fact be manufactured. Such a question is a great deal more difficult to answer than, for example, the four-color map theorem which was proposed in 1852 and proven in 1976, and it is conceptually impossible to prove the negative of this question since no proof by counter-example can be provided. Advocates assert that to achieve most of the vision of molecular manufacturing it is not necessary to be able to build "any structure that is compatible with natural law." Rather, it is necessary to be able to build only a sufficient (possibly modest) subset of such structures—as is true, in fact, of any practical manufacturing process used in the world today, and is true even in biology. In any event, as Richard Feynman once said, "It is scientific only to say what's more likely or less likely, and not to be proving all the time what's possible or impossible."

Existing work on diamond mechanosynthesis

There is a growing body of peer-reviewed theoretical work on synthesizing diamond by mechanically removing/adding hydrogen atoms and depositing carbon atoms (a process known as mechanosynthesis). This work is slowly permeating the broader nanoscience community and is being critiqued. For instance, Peng et al. (2006) (in the continuing research effort by Freitas, Merkle and their collaborators) reports that the most-studied mechanosynthesis tooltip motif (DCB6Ge) successfully places a C_2 carbon dimer on a C(110) diamond surface at both 300 K (room temperature) and 80 K (liquid nitrogen temperature), and that the silicon variant (DCB6Si) also works at 80 K but not at 300 K. Over 100,000 CPU hours were invested in this latest study. The DCB6 tooltip motif, initially described by Merkle and Freitas at a Foresight Conference in 2002, was the first complete tooltip ever proposed for diamond mechanosynthesis and remains the only tooltip motif that has been successfully simulated for its intended function on a full 200-atom diamond surface.

The tooltips modeled in this work are intended to be used only in carefully controlled environments (e.g., vacuum). Maximum acceptable limits for tooltip translational and rotational misplacement errors are reported in Peng et al. (2006) -- tooltips must be positioned with great accuracy to avoid bonding the dimer incorrectly. Peng et al. (2006) reports that increasing the handle thickness from 4 support planes of C atoms above the tooltip to 5 planes decreases the resonance frequency of the entire structure from 2.0 THz to 1.8 THz. More importantly, the vibrational footprints of a DCB6Ge tooltip mounted on a 384-atom handle and of the same tooltip mounted on a similarly constrained but much larger 636-atom "crossbar" handle are virtually identical in the non-crossbar directions. Additional computational studies modeling still bigger handle structures are welcome, but the ability to precisely position SPM tips to the requisite atomic accuracy has been repeatedly demonstrated experimentally at low temperature, constituting a basic existence proof for this capability.

Further research to consider additional tooltips will require time-consuming computational chemistry and difficult laboratory work.

A working nanofactory would require a variety of well-designed tips for different reactions, and detailed analyses of placing atoms on more complicated surfaces. Although this appears a challenging problem given current resources, many tools will be available to help future researchers: Moore's Law predicts further increases in computer power, semiconductor fabrication techniques continue to approach the nanoscale, and researchers grow ever more skilled at using proteins, ribosomes and DNA to perform novel chemistry.

Works of fiction

- In The Diamond Age by Neal Stephenson diamond can be constructed by simply building it out of carbon atoms. Also all sorts of devices from dust size detection devices to giant diamond zeppelins are constructed atom by atom using only carbon, oxygen, nitrogen and chlorine atoms.

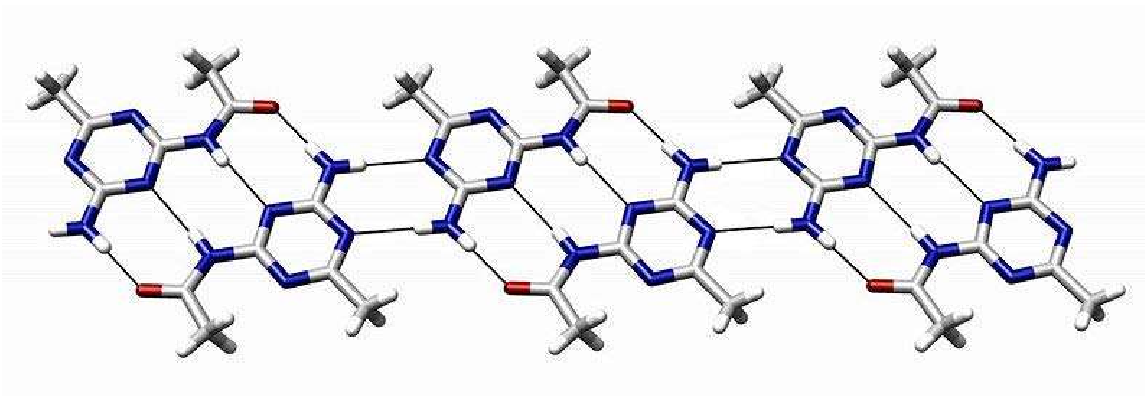
- In the novel *Tomorrow* by Andrew Saltzman (ISBN 1-4243-1027-X), a scientist uses nanorobotics to create a liquid that when inserted into the bloodstream, renders one nearly invincible given that the microscopic machines repair tissue almost instantaneously after it is damaged.

- In the manga series Battle Angel Alita the scientist Desty Nova has specialized in molecular nanotechnology.

- In the roleplaying game Splicers by Palladium Books, humanity has succumbed to a "nanobot plague" that causes any object made of a non-precious metal to twist and change shape (sometimes into a type of robot) moments after being touched by a human. The object will then proceed to attack the human. This has forced humanity to develop "biotechnological" devices to replace those previously made of metal.

- On the television show Mystery Science Theater 3000, the Nanites (voiced variously by Kevin Murphy, Paul Chaplin, Mary Jo Pehl, and Bridget Jones) - are self-replicating, bio-engineered organisms that work on the ship, they are microscopic creatures that reside in the Satellite of Love's computer systems. (They are similar to the creatures in *Star Trek: The Next Generation* episode "Evolution", which featured "nanites" taking over the *Enterprise*.) The Nanites made their first appearance in season 8. Based on the concept of nanotechnology, their comical *deus ex machina* activities included such diverse tasks as instant repair and construction, hairstyling, performing a Nanite variation of a flea circus, conducting a microscopic war, and even destroying the Observers' planet after a dangerously vague request from Mike to "take care of [a] little problem". They also ran a microbrewery.

Molecular Self-Assembly



An example of a molecular self-assembly through hydrogen bonds

Molecular self-assembly is the process by which molecules adopt a defined arrangement without guidance or management from an outside source. There are two types of self-assembly, **intramolecular** self-assembly and **intermolecular** self-assembly. Most often the term molecular self-assembly refers to intermolecular self-assembly, while the intramolecular analog is more commonly called folding.

Supramolecular systems

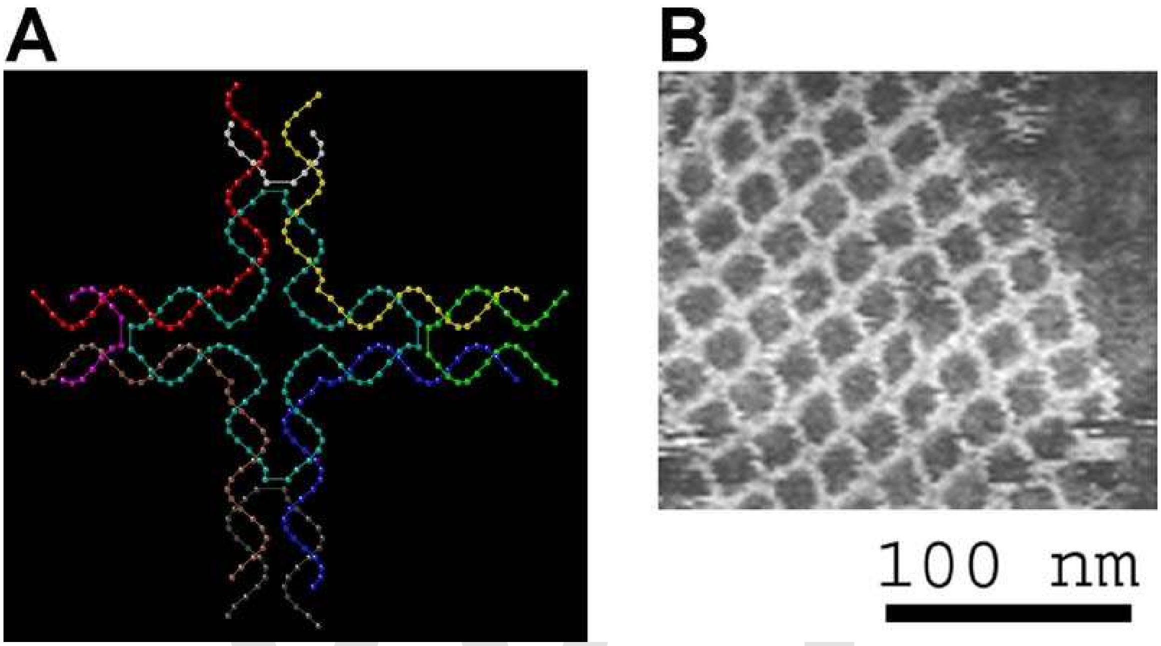
Molecular self-assembly is a key concept in supramolecular chemistry since assembly of the molecules is directed through noncovalent interactions (e.g., hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π-π interactions, and/or electrostatic) as well as electromagnetic interactions. Common examples include the formation of micelles, vesicles, liquid crystal phases, and Langmuir monolayers by surfactant molecules. Further examples of supramolecular assemblies demonstrate that a variety of different shapes and sizes can be obtained using molecular self-assembly.

Molecular self-assembly has allowed the construction of challenging molecular topologies. An example are Borromean rings, interlocking rings wherein removal of one ring unlocks each of the other rings. DNA has been used to prepare a molecular analog of Borromean rings. More recently, a similar structure has been prepared using non-biological building blocks.

Biological systems

Molecular self-assembly is crucial to the function of cells. It is exhibited in the self-assembly of lipids to form the membrane, the formation of double helical DNA through hydrogen bonding of the individual strands, and the assembly of proteins to form quaternary structures. Molecular self-assembly of incorrectly folded proteins into insoluble amyloid fibers is responsible for infectious prion-related neurodegenerative diseases.

Nanotechnology



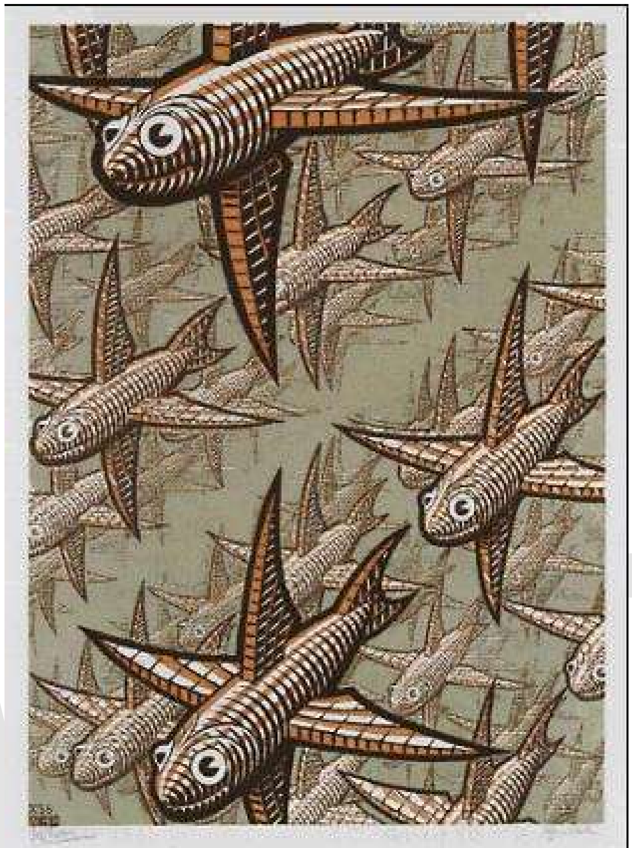
The DNA structure at left (schematic shown) will self-assemble into the structure visualized by atomic force microscopy at right. Image from Strong.

Molecular self-assembly is an important aspect of bottom-up approaches to nanotechnology. Using molecular self-assembly the final (desired) structure is programmed in the shape and functional groups of the molecules. Self-assembly is referred to as a 'bottom-up' manufacturing technique in contrast to a 'top-down' technique such as lithography where the desired final structure is carved from a larger block of matter. In the speculative vision of molecular nanotechnology, microchips of the future might be made by molecular self-assembly. An advantage to constructing nanostructure using molecular self-assembly for biological materials is that they will degrade back into individual molecules that can be broken down by the body.

DNA nanotechnology

DNA nanotechnology is a branch of nanotechnology which uses the unique molecular recognition properties of DNA and other nucleic acids to create designed, controllable structures out of DNA. This has possible applications in molecular self-assembly and in DNA computing. In this field, DNA is used as a structural material rather than as a carrier of genetic information, making it an example of bionanotechnology.

History



The M. C. Escher woodcut *Depth* (pictured) inspired Nadrian Seeman to consider using three-dimensional lattices of DNA to orient hard-to-crystallize molecules. This led to the beginning of the field of DNA nanotechnology.

The concept of DNA nanotechnology was invented by Nadrian Seeman in the early 1980s. A crystallographer, Seeman was frustrated with the haphazardness and guesswork involved with crystallizing certain molecules. In fall 1980, while at a campus pub, Seeman was inspired by the M. C. Escher woodcut *Depth* to realize that a three-dimensional DNA lattice could be used to orient target molecules, simplifying their crystallographic study. In 1991, Seeman's laboratory published the synthesis of a cube made of DNA, the first three-dimensional nanoscale object, for which he received the 1995 Feynman Prize in Nanotechnology, which was followed by a DNA truncated octahedron. However, it soon became clear that these objects were not rigid enough to form three-dimensional lattices.

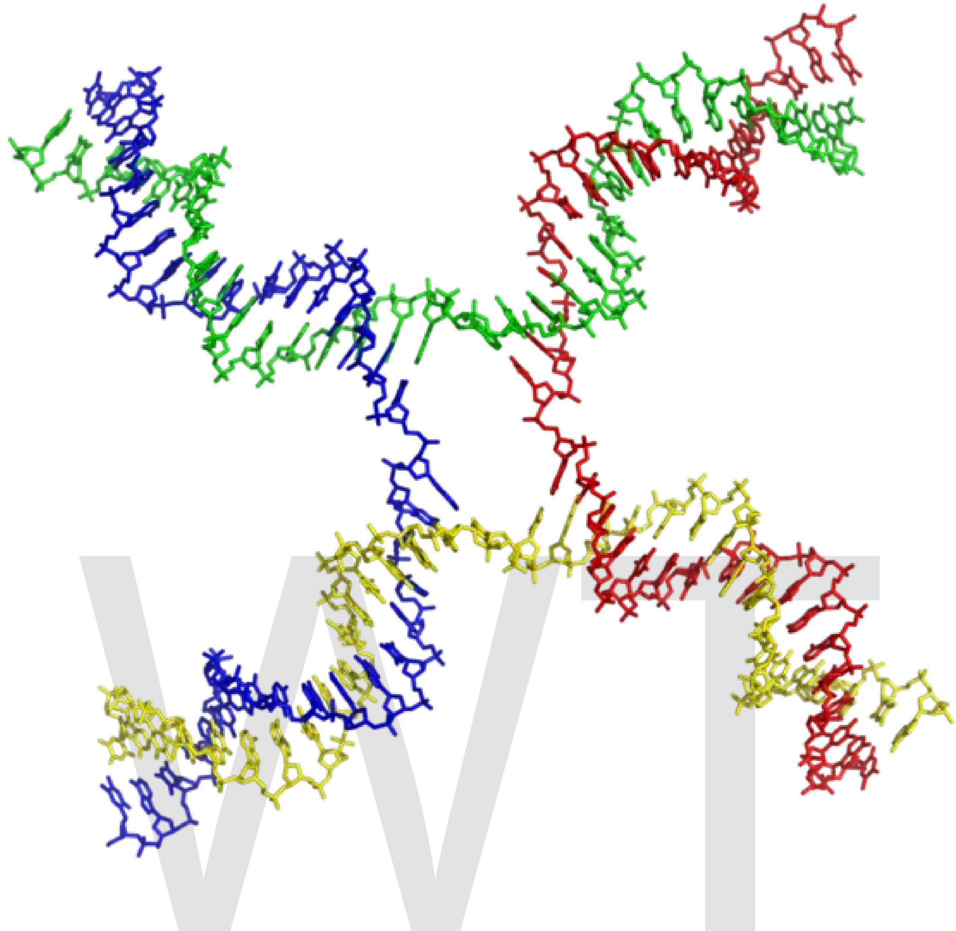
Seeman developed the more rigid "DX" motif, and in collaboration with Erik Winfree, in 1998 published the creation of two-dimensional lattices of DX tiles. These tile-based structures had the advantage that they provided the capability to implement DNA computing, which was demonstrated by Winfree and Paul Rothemund in 2004, and for which they shared the 2006 Feynman Prize in Nanotechnology.

The field has continued to branch out. The first DNA nanomachine—a motif which changes its structure in response to an input—was demonstrated in 1999. Nanoarchitecture, first proposed by Seeman in 1987, was beginning to be demonstrated by 2006. Also in 2006, Rothemund first demonstrated the new DNA origami technique for easily and robustly creating folded DNA molecules of any shape. In 2009, Seeman published the synthesis of a three-dimensional lattice, nearly thirty years after he had set out to do so.

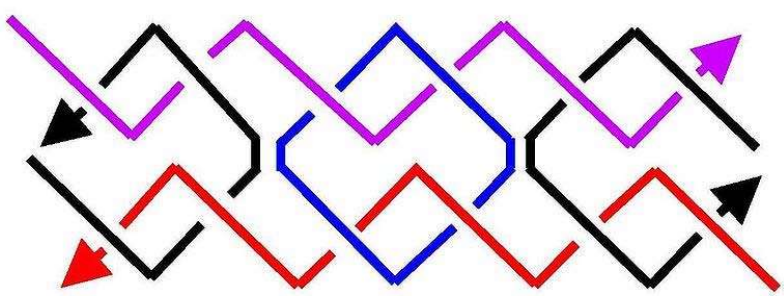
Fundamental concepts

DNA nanotechnology makes use of branched DNA structures to create DNA complexes with useful properties. DNA is normally a linear molecule, in that its axis is unbranched. However, DNA molecules containing junctions can also be made. For example, a four-arm junction can be made using four individual DNA strands which are complementary to each other in the correct pattern. Due to Watson-Crick base pairing, only portions of the strands which are complementary to each other will attach to each other to form duplex DNA. This four-arm junction is an immobile form of a Holliday junction.

Junctions can be used in more complex molecules. The most important of these is the "double-crossover" or DX motif. Here, two DNA duplexes lie next to each other, and share two junction points where strands cross from one duplex into the other. This molecule has the advantage that the junction points are now constrained to a single orientation as opposed to being flexible as in the four-arm junction. This makes the DX motif suitable as a structural building block for larger DNA complexes.



Structure of the 4-arm junction.
Up: A schematic. **Down**: A more realistic model.
Each of the four separate DNA single strands are shown in different colors.

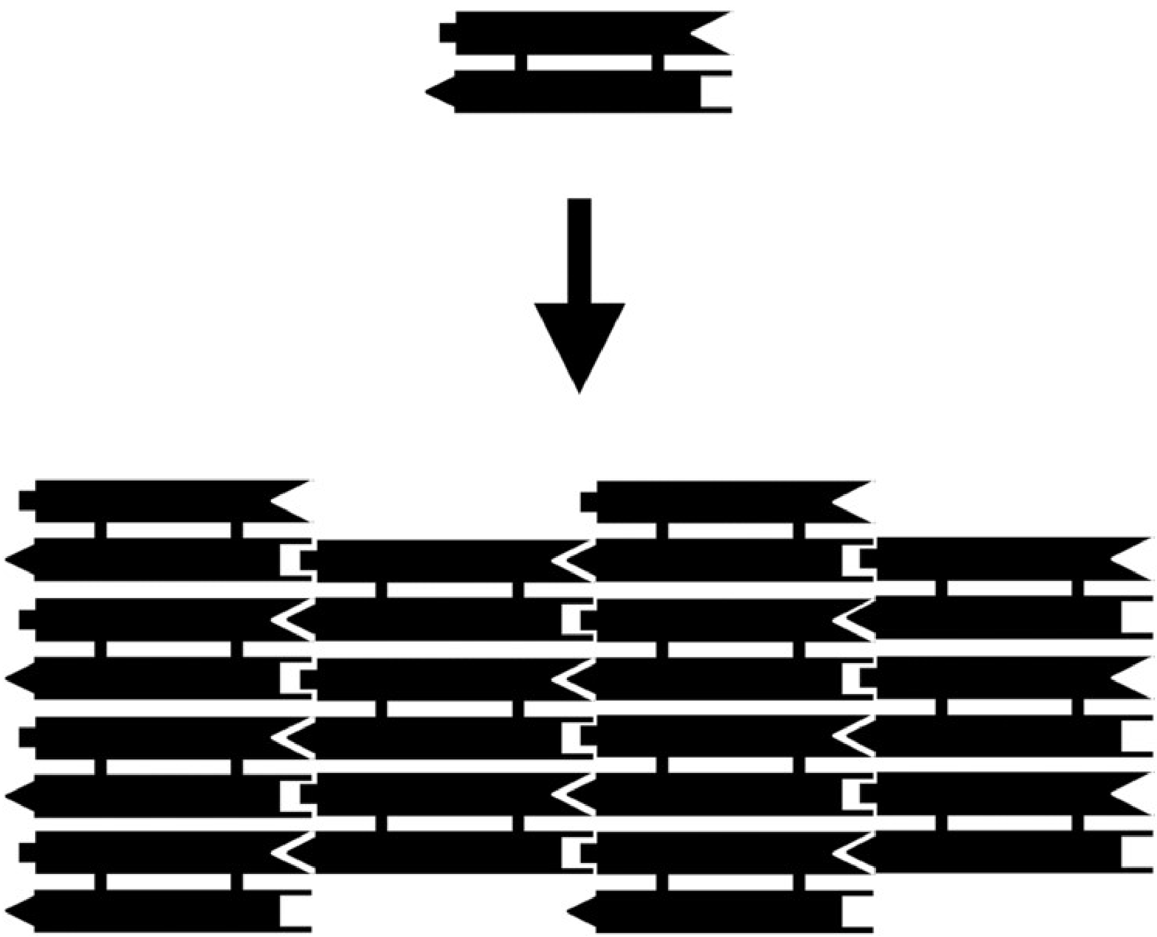


A double-crossover (DX) molecule. This molecule consists of five DNA single strands which form two double-helical domains, on the left and the right in this image. There are two crossover points where the strands cross from one domain into the other. Image from Mao, 2004.

Design

A main goal of DNA nanotechnology is, given a target structure and/or functionality, to determine what sequences of DNA molecules will assemble into that structure. There are a number of different approaches which have been used to design DNA sequences that will form the desired structure.

Tile-based structures



Assembly of a DX array. Each bar represents a double-helical domain of DNA, with the shapes representing complimentary sticky ends. The DX molecule at top will combine into the two-dimensional DNA array shown at bottom. This is an example of the tile-based strategy for designing DNA nanostructures. Image from Mao, 2004.

The earliest method for creating DNA nanostructures was to construct them out of smaller discrete units. This method has the advantage of being able to conceptually separate the stronger interactions which form each tile from the assembly of the larger complete structure. It is often used to make periodic lattices, but can also be used to implement algorithmic self-assembly, making them one platform for DNA computing.

Folding structures

An alternative to the tile-based approach, two-dimensional DNA structures can be made from a single, long DNA strand of arbitrary sequence which is folded into the desired shape by using shorter, "staple" strands. This allows the creation of two-dimensional shapes at the nanoscale using DNA. Demonstrated designs have included the smiley face and a coarse map of North America. DNA origami was the cover story of *Nature* on March 15, 2006.

Kinetic assembly

Most design in DNA nanotechnology only focuses on designing sequences so that the target structure is a thermodynamic minimum, without regard to the assembly pathway. Recently, there has been interest in controlling the kinetics of DNA self-assembly, so that transient dynamics can also be programmed into the assembly. Such a method also has the advantage of proceeding isothermally and thus not requiring a thermal annealing step required by solely thermodynamic approaches.

Sequence design

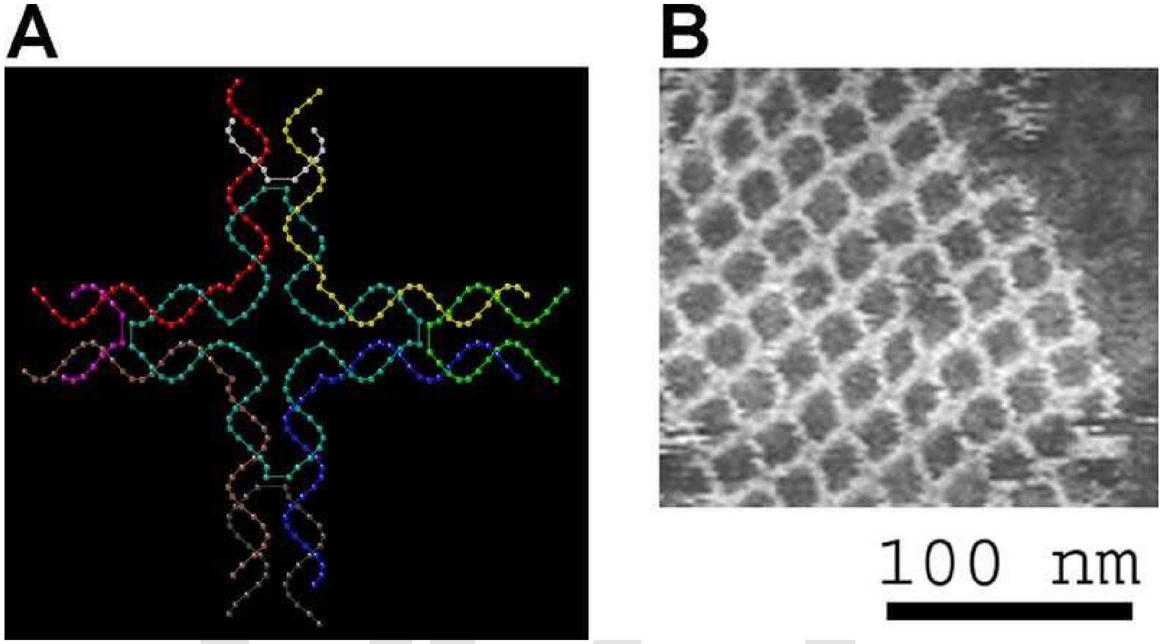
After any of the above approaches are used to design the secondary structure of a target molecule, an actual sequence of nucleotides must be devised which will form into the desired structure. Nucleic acid design is the process of generating a set of nucleic acid base sequences that will associate into a desired conformation (see, for example, RNA structure). Nucleic acid design is central to the field of DNA nanotechnology.

Nucleic acid design has similar goals to protein design: in both, the sequence of monomers is designed to favor the desired folded or associated structure and to disfavor alternate structures. Nucleic acid design has the advantage of being a much computationally simpler problem, since the simplicity of Watson-Crick base pairing rules leads to simple heuristic methods which yield experimentally robust designs. However, nucleic acid structures are less versatile than proteins in their functionality.

Target structures

Many structures made from DNA have been synthesized and characterized.

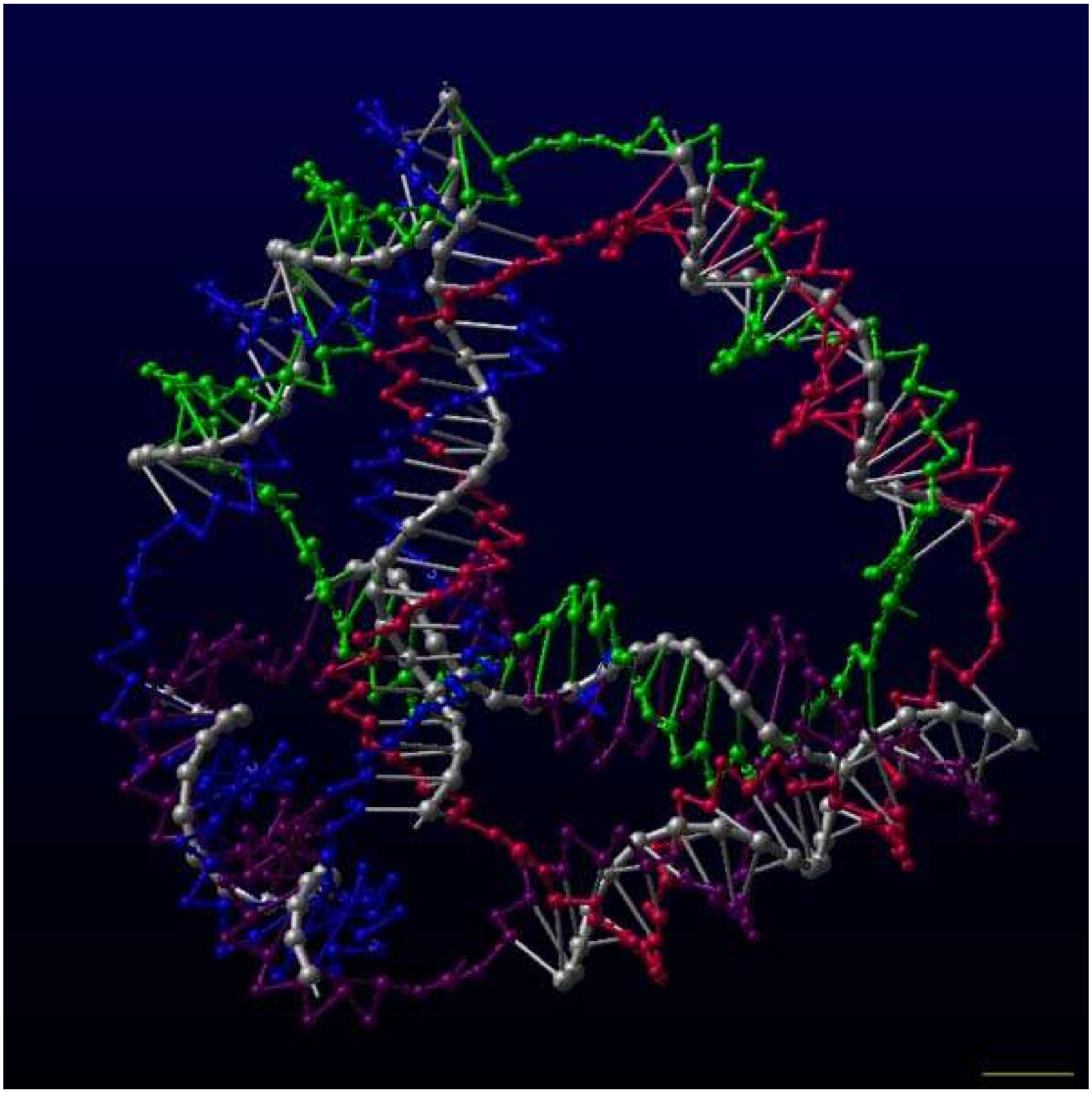
Two-dimensional lattices



Left, a model of a DNA tile used to make a two-dimensional periodic lattice. Right, an atomic force micrograph of the assembled lattice. Image from Strong, 2004.

DX, or Double Crossover, molecules can be equipped with sticky ends in order to combine them into a two-dimensional periodic lattice. Each DX molecule has four termini, one at each end of the two double-helical domains, and these can be equipped with sticky ends that program them to combine into a specific pattern. More than one type of DX can be used which can be made to arrange in rows or any other tessellated pattern. They thus form extended flat sheets which are essentially two-dimensional crystals of DNA.

Two-dimensional arrays have been made out of other motifs as well, including the Holliday junction rhombus array as well as various DX-based arrays in the shapes of triangles and hexagons.



A model of a DNA tetrahedron described in Goodman, 2005. Each edge of the tetrahedron is a 20 base pair DNA duplex, and each vertex is a three-arm junction.

Discrete three-dimensional structures

A number of three-dimensional DNA molecules have been made which have the connectivity of a polyhedron such as an octahedron or cube. In other words, the DNA duplexes trace the edges of a polyhedron with a DNA junction at each vertex.

The earliest demonstrations of DNA polyhedra involved multiple ligations and solid-phase synthesis steps to create catenated polyhedra. More recent work has yielded polyhedra whose synthesis is much easier. These include a DNA octahedron made from a long single strand designed to fold into the correct conformation, as well as a tetrahedron which can be produced from four DNA strands in a single step.

DNA structures with solid faces have also been constructed, using the DNA origami method. These can be programmed to open and release their cargo in response to a stimulus, making them potentially useful as programmable molecular cages.

DNA nanotubes

In addition to flat sheets, DX arrays have been made to form hollow nanotubes of 4-20 nm diameter. These DNA nanotubes are somewhat similar in size and shape to carbon nanotubes, but the carbon nanotubes are stronger and better conductors, whereas the DNA nanotubes are more easily modified and connected to other structures.

Extended three-dimensional lattices

Creating three-dimensional lattices out of DNA was the earliest goal of DNA nanotechnology, but proved to be one of the most difficult to realize. Success in constructing three-dimensional DNA lattices was finally reported in 2009 using a motif based on the concept of tensegrity, a balance between tension and compression forces.

Applications

DNA nanotechnology focuses on creating molecules with designed functionalities as well as structures. Many classes of functional systems have been demonstrated.

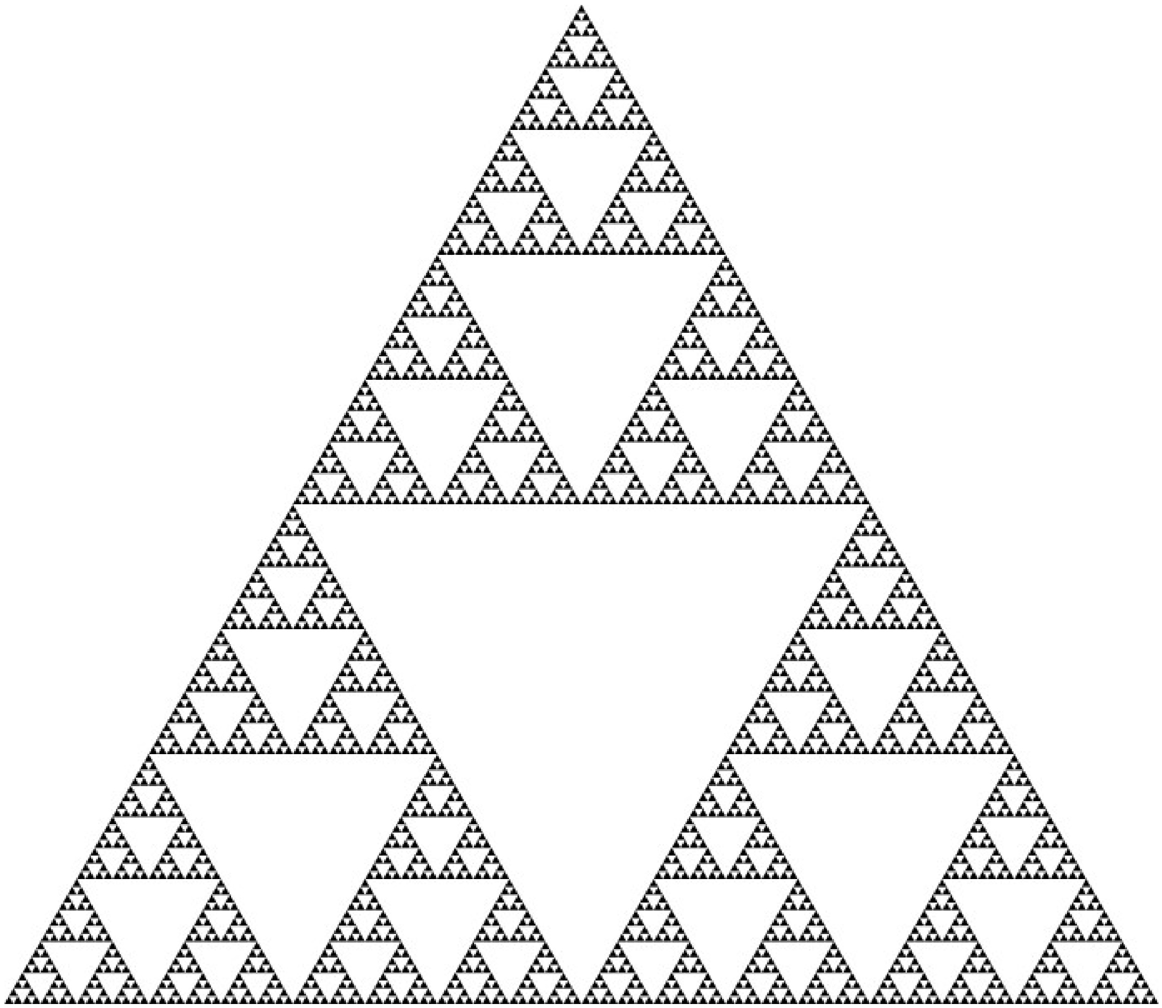
Nanoarchitecture

The idea of using DNA arrays to template the assembly of other functional molecules was first suggested by Nadrian Seeman in 1987, but only recently has progress been made in reducing these kinds of schemes to practice. In 2006, researchers covalently attached gold nanoparticles to a DX-based tile and showed that self-assembly of the DNA structures also assembled the nanoparticles hosted on them. A non-covalent hosting scheme was shown in 2007, using Dervan polyamides on a DX array to arrange streptavidin proteins on specific kinds of tiles on the DNA array.

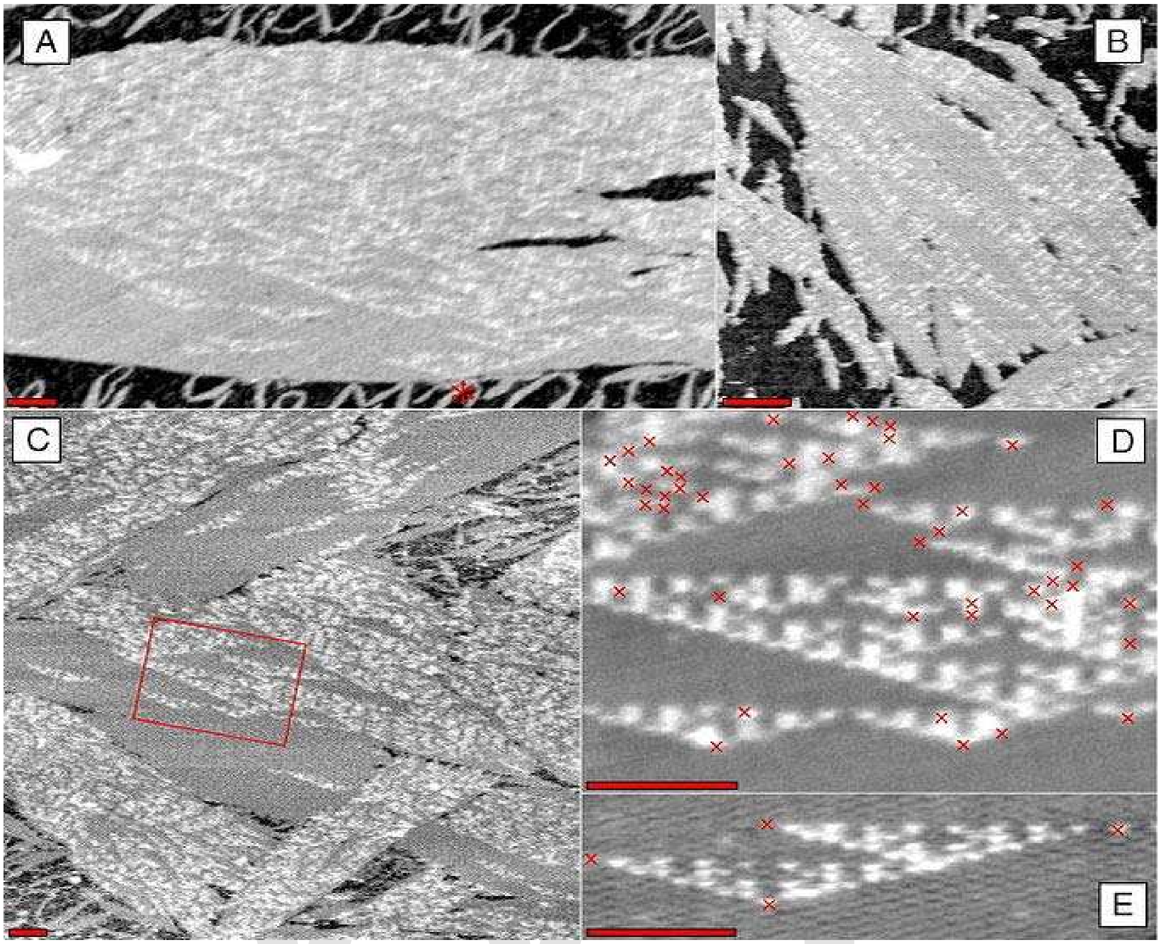
Previously in 2006, Dwyer and LaBean demonstrated the letters "D" "N" and "A" created on a 4x4 DX array using streptavidin. In 2007, a hierarchical assembly based on this approach was also demonstrated that scales to larger arrays (8X8 and 8.96 MD).

There has also been interest in using DNA nanotechnology to assemble molecular electronics devices. To this end, DNA has been used to assemble single walled carbon nanotubes into field-effect transistors.

Algorithmic self-assembly



The Sierpinski gasket



DNA arrays that display a representation of the Sierpinski gasket on their surfaces.

DNA nanotechnology has been applied to the related field of DNA computing. The DX tiles can have their sticky end sequences chosen so that they act as Wang tiles, allowing them to perform computation. A DX array has been demonstrated whose assembly encodes an XOR operation; this allows the DNA array to implement a cellular automaton which generates a fractal called the Sierpinski gasket. This shows that computation can be incorporated into the assembly of DNA arrays, increasing its scope beyond simple periodic arrays.

Note that DNA computing overlaps with, but is distinct from, DNA nanotechnology. The latter uses the specificity of Watson-Crick basepairing to make novel structures out of DNA. These structures can be used for DNA computing, but they do not have to be. Additionally, DNA computing can be done without using the types of molecules made possible by DNA nanotechnology.

DNA nanomechanical devices

DNA complexes have been made which change their conformation upon some stimulus. These are intended to have applications in nanorobotics. One of the first such devices, called "molecular tweezers," changes from an open to a closed state based upon the presence of control strands.

DNA machines have also been made which show a twisting motion. One of these makes use of the transition between the B-DNA and Z-DNA forms to respond to a change in buffer conditions. Another relies on the presence of control strands to switch from a paranemic-crossover (PX) conformation to a double-junction (JX2) conformation.

Materials and methods

DNA of custom sequence is readily available through oligonucleotide synthesis. This process is usually automated by using a DNA synthesizing machine, and custom DNA is commercially available from many vendors.

The sequences of the individual DNA strands which make up the target structure are designed computationally. Molecular modelling and thermodynamic modelling are sometimes used to optimize the DNA sequences.

The DNA molecules created by DNA nanotechnology are usually characterized by gel electrophoresis, which provides information about the size and shape of DNA molecules, indicating whether they have formed properly. Fluorescent labelling and Fluorescence resonance energy transfer are also used to characterize the structure of the molecules.

DNA structures can be directly imaged by atomic force microscopy, which images structures deposited on a flat surface. This method is well-suited to extended two-dimensional structures, but is less useful for discrete three-dimensional structures. For these latter structures cryo-electron microscopy is gaining popularity as an important method. Extended three-dimensional lattices are analyzed by X-ray crystallography. Kinetics of DNA self assembly can be studied by real time techniques such as dual polarisation interferometry and QCMD.

Two-dimensional monolayers

The spontaneous assembly of a single layer of molecules (i.e. monolayer thick) at interfaces is usually referred to as two-dimensional self-assembly. Early direct proofs showing that molecules can assembly into higher-order architectures at solid interfaces came with the development of scanning tunneling microscopy and shortly thereafter. Eventually two strategies became popular for the self-assembly of 2D architectures, namely self-assembly following ultra-high-vacuum deposition and annealing and self-assembly at the solid-liquid interface. The design of molecules and conditions leading to the formation of highly-crystalline architectures is considered today a form of 2D crystal engineering at the nanoscopic scale.

Chapter-3

Nanomaterials

Nanomaterials is a field that takes a materials science-based approach to nanotechnology. It studies materials with morphological features on the nanoscale, and especially those that have special properties stemming from their nanoscale dimensions. Nanoscale is usually defined as smaller than a one tenth of a micrometer in at least one dimension, though this term is sometimes also used for materials smaller than one micrometer.

Background

An aspect of nanotechnology is the vastly increased ratio of surface area to volume present in many nanoscale materials which makes possible new quantum mechanical effects, for example the "quantum size effect" where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, it becomes pronounced when the nanometer size range is reached. A certain number of physical properties also alter with the change from macroscopic systems. Novel mechanical properties of nanomaterials is a subject of nanomechanics research. Catalytic activities also reveal new behaviour in the interaction with biomaterials.

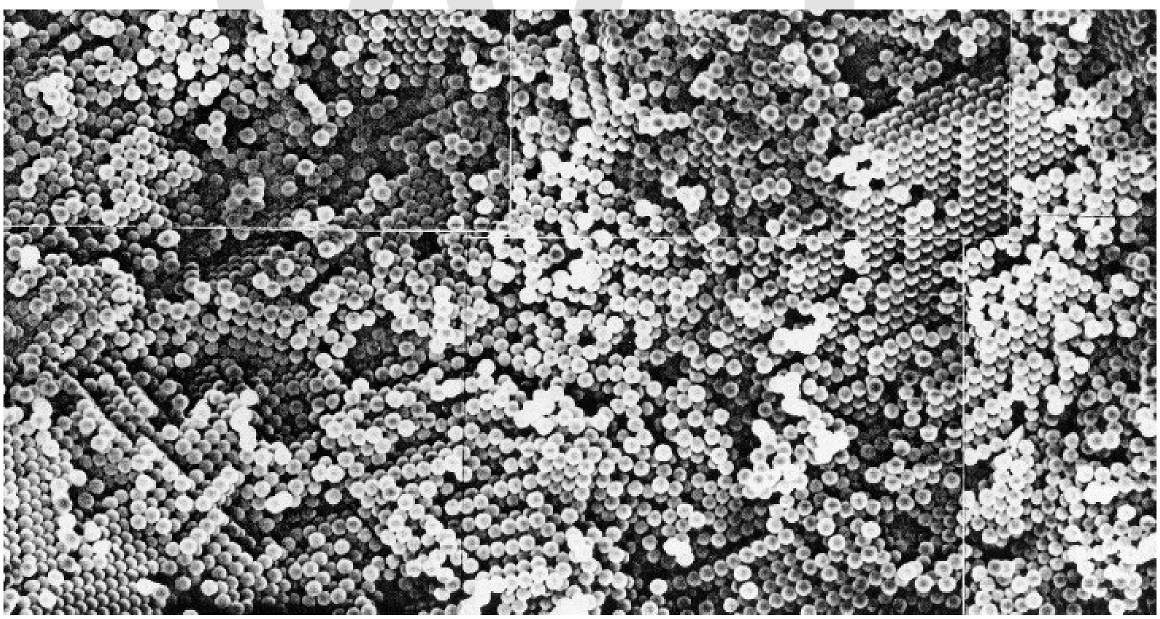
Nanotechnology can be thought of as extensions of traditional disciplines towards the explicit consideration of these properties. Additionally, traditional disciplines can be re-interpreted as specific applications of nanotechnology. This dynamic reciprocation of ideas and concepts contributes to the modern understanding of the field. Broadly speaking, nanotechnology is the synthesis and application of ideas from science and engineering towards the understanding and production of novel materials and devices. These products generally make copious use of physical properties associated with small scales.

As mentioned above, materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper); inert materials attain catalytic properties (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). Materials such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these unique quantum and surface phenomena that matter exhibits at the nanoscale.

Uniformity

The chemical processing and synthesis of high performance technological components for the private, industrial and military sectors requires the use of high purity ceramics, polymers, glass-ceramics and material composites. In condensed bodies formed from fine powders, the irregular sizes and shapes of nanoparticles in a typical powder often lead to non-uniform packing morphologies that result in packing density variations in the powder compact.

Uncontrolled agglomeration of powders due to attractive van der Waals forces can also give rise to in microstructural inhomogeneities. Differential stresses that develop as a result of non-uniform drying shrinkage are directly related to the rate at which the solvent can be removed, and thus highly dependent upon the distribution of porosity. Such stresses have been associated with a plastic-to-brittle transition in consolidated bodies, and can yield to crack propagation in the unfired body if not relieved.



Colloidal crystal composed of amorphous hydrated colloidal silica (particle diameter 600 nm)

In addition, any fluctuations in packing density in the compact as it is prepared for the kiln are often amplified during the sintering process, yielding inhomogeneous densification. Some pores and other structural defects associated with density variations have been shown to play a detrimental role in the sintering process by growing and thus limiting end-point densities. Differential stresses arising from inhomogeneous densification have also been shown to result in the propagation of internal cracks, thus becoming the strength-controlling flaws.

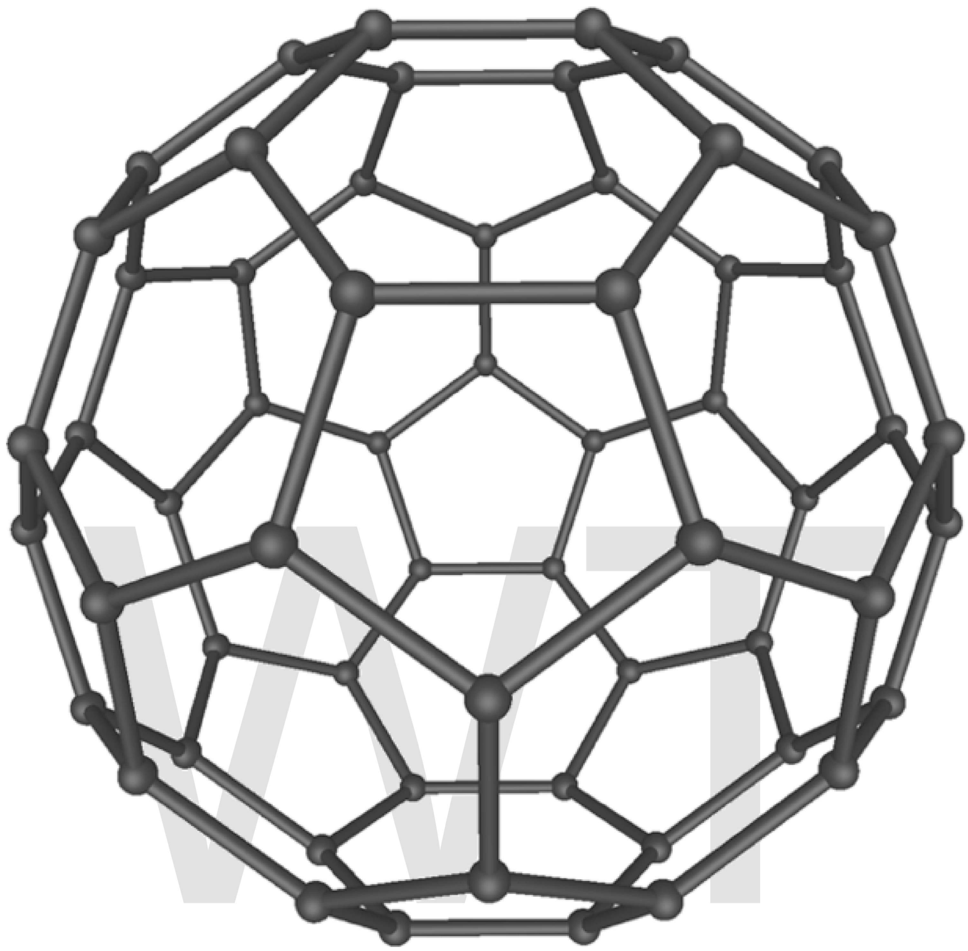
It would therefore appear desirable to process a material in such a way that it is physically uniform with regard to the distribution of components and porosity, rather than using particle size distributions which will maximize the green density. The containment of a uniformly dispersed assembly of strongly interacting particles in suspension requires total control over particle-particle interactions. It should be noted here that a number of dispersants such as ammonium citrate (aqueous) and imidazoline or oleyl alcohol (nonaqueous) are promising solutions as possible additives for enhanced dispersion and deagglomeration. Monodisperse nanoparticles and colloids provide this potential.

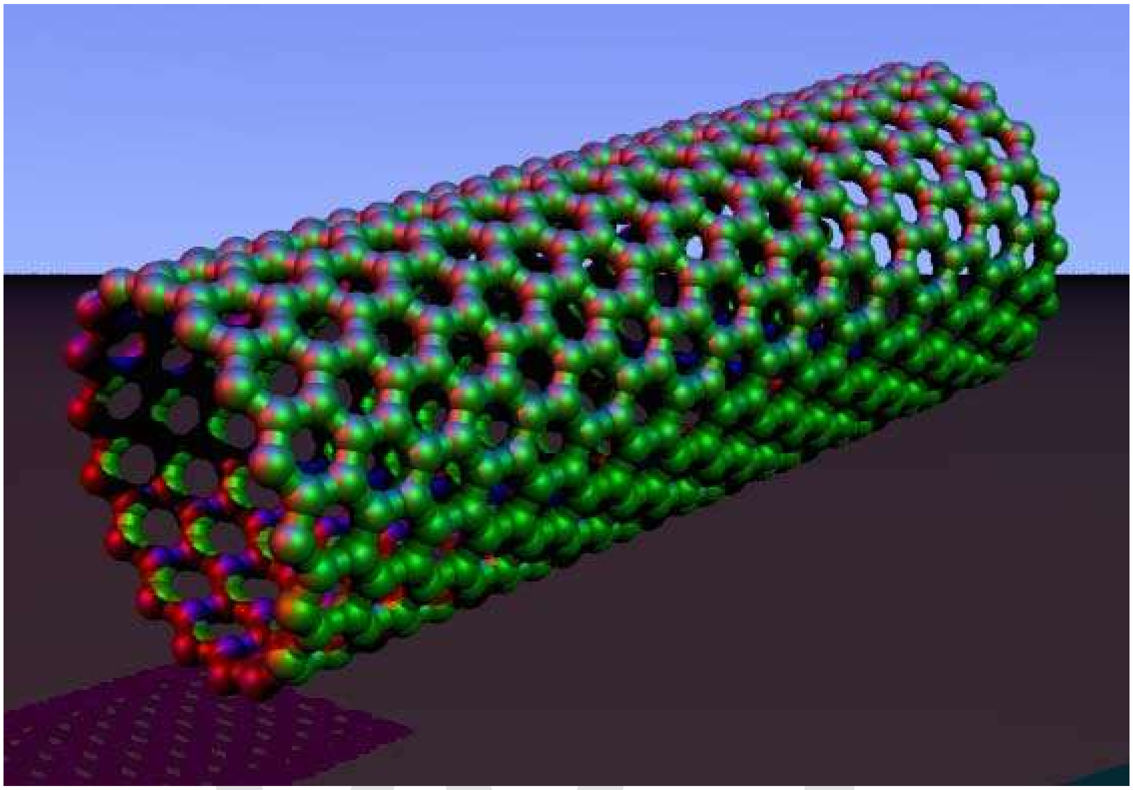
Monodisperse powders of colloidal silica, for example, may therefore be stabilized sufficiently to ensure a high degree of order in the colloidal crystal or polycrystalline colloidal solid which results from aggregation. The degree of order appears to be limited by the time and space allowed for longer-range correlations to be established. Such defective polycrystalline colloidal structures would appear to be the basic elements of sub-micrometer colloidal materials science, and, therefore, provide the first step in developing a more rigorous understanding of the mechanisms involved in microstructural evolution in high performance materials and components.

Classification

Materials referred to as "nanomaterials" generally fall into two categories: fullerenes, and inorganic nanoparticles.

Fullerenes





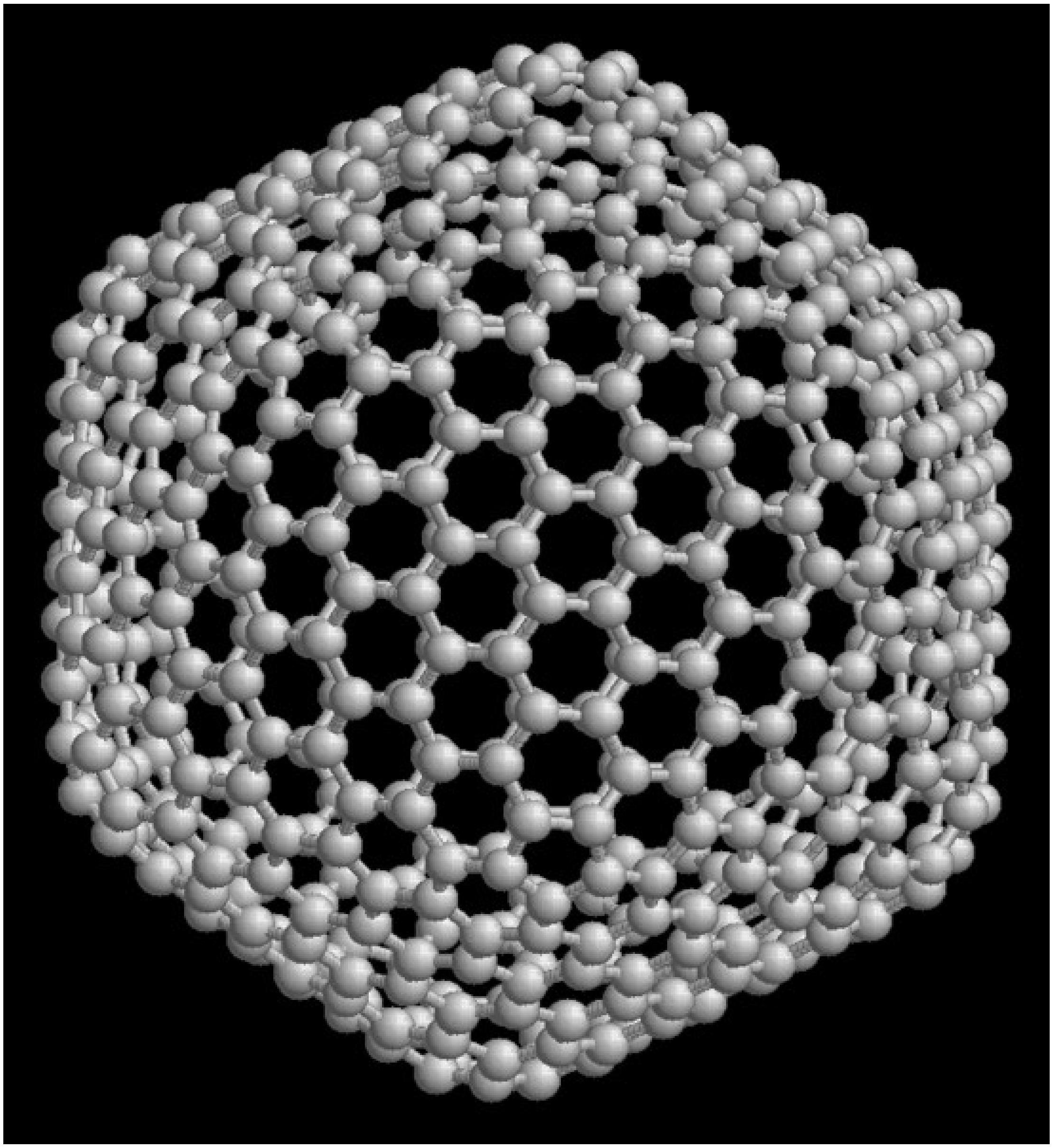
Buckminsterfullerene C_{60} (Up) and carbon nanotubes (Down) are two examples of structures in the fullerene family.

A **fullerene** is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Spherical fullerenes are also called **buckyballs**, and cylindrical ones are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings.

The first fullerene to be discovered, and the family's namesake, buckminsterfullerene (C_{60}), was prepared in 1985 by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto at Rice University. The name was an homage to Buckminster Fuller, whose geodesic domes it resembles. The structure was also identified some five years earlier by Sumio Iijima, from an electron microscope image, where it formed the core of a "bucky onion." Fullerenes have since been found to occur in nature. More recently, fullerenes have been detected, along with polycyclic aromatic hydrocarbons (PAHs), in outer space. According to astronomer Letizia Stanghellini, "It's possible that buckyballs from outer space provided seeds for life on Earth." PAHs have also been implicated in the origin of life.

The discovery of fullerenes greatly expanded the number of known carbon allotropes, which until recently were limited to graphite, diamond, and amorphous carbon such as soot and charcoal. Buckyballs and buckytubes have been the subject of intense research, both for their unique chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology.

History



The icosahedral fullerene C_{540}, another member of the family of fullerenes.

The icosahedral $C_{60}H_{60}$ cage was mentioned in 1965 as a possible topological structure. The existence of C_{60} was predicted by Eiji Osawa of Toyohashi University of Technology in 1970. He noticed that the structure of a corannulene molecule was a subset of a soccer-ball shape, and he hypothesised that a full ball shape could also exist. His idea was reported in Japanese scientific journals, but did not reach Europe or the Americas.

Also in 1970, R. W.Henson (then of the Atomic Energy Research Establishment) proposed the structure and made a model of C_{60}. Unfortunately, the evidence for this new form of carbon was very weak and was not accepted, even by his colleagues. The results were never published but were acknowledged in *Carbon* in 1999.

Using mass spectrometry, discrete peaks appeared corresponding to molecules with the exact mass of sixty or seventy or more carbon atoms. In 1985, Harold Kroto (then of the University of Sussex), James R. Heath, Sean O'Brien, Robert Curl and Richard Smalley, from Rice University, discovered C_{60}, and shortly thereafter came to discover the fullerenes. Kroto, Curl, and Smalley were awarded the 1996 Nobel Prize in Chemistry for their roles in the discovery of this class of molecules. C_{60} and other fullerenes were later noticed occurring outside the laboratory (e.g., in normal candle soot). By 1991, it was relatively easy to produce gram-sized samples of fullerene powder using the techniques of Donald Huffman and Wolfgang Krätschmer. Fullerene purification remains a challenge to chemists and to a large extent determines fullerene prices. So-called endohedral fullerenes have ions or small molecules incorporated inside the cage atoms. Fullerene is an unusual reactant in many organic reactions such as the Bingel reaction discovered in 1993. Carbon nanotubes were recognized in 1991.

Minute quantities of the fullerenes, in the form of C_{60}, C_{70}, C_{76}, and C_{84} molecules, are produced in nature, hidden in soot and formed by lightning discharges in the atmosphere. In 1992, fullerenes were found in a family of minerals known as Shungites in Karelia, Russia.

In 2010, fullerenes (C_{60}) have been discovered in a cloud of cosmic dust surrounding a distant star 6500 light years away. Using NASA's Spitzer infrared telescope the scientists spotted the molecules' unmistakable infrared signature. Sir Harry Kroto, who shared the 1996 Nobel Prize in Chemistry for the discovery of buckyballs commented: "This most exciting breakthrough provides convincing evidence that the buckyball has, as I long suspected, existed since time immemorial in the dark recesses of our galaxy."

Naming

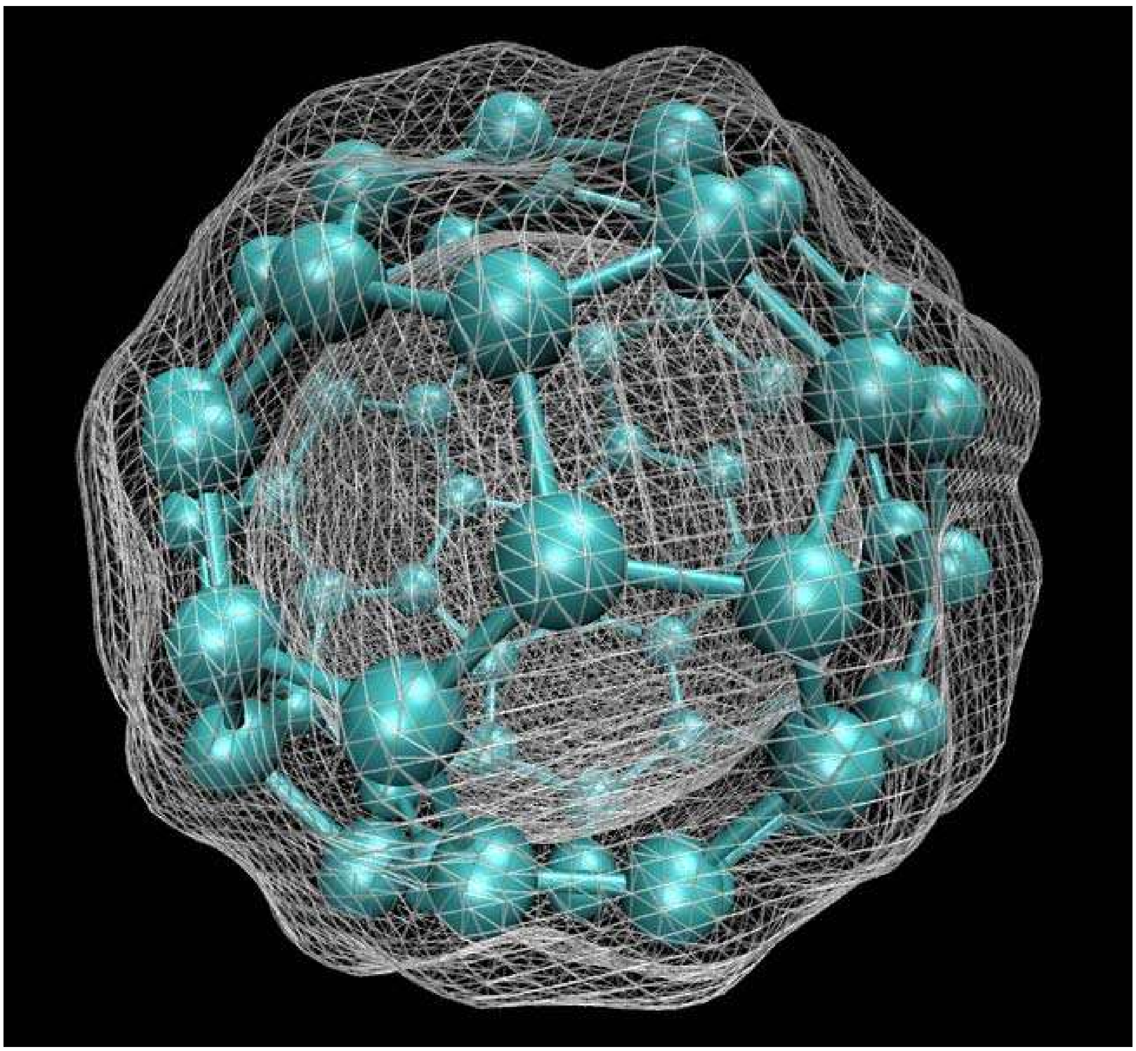
Buckminsterfullerene (C_{60}) was named after Richard Buckminster Fuller, a noted architectural modeler who popularized the geodesic dome. The name was thought to be appropriate since buckminsterfullerenes have a shape similar to that sort of dome. As the discovery of the fullerene family came *after* buckminsterfullerene, the shortened name 'fullerene' was used to refer to the family of fullerenes. The suffix “ene” indicates that each C atom is covalently bonded to three others (instead of the maximum of four), a situation that classically would correspond to the existence of bonds involving two pairs of electrons (“double bonds”).

Types of fullerene

Since the discovery of fullerenes in 1985, structural variations on fullerenes have evolved well beyond the individual clusters themselves. Examples include:

- **buckyball clusters**: smallest member is C_{20} (unsaturated version of dodecahedrane) and the most common is C_{60};
- **nanotubes**: hollow tubes of very small dimensions, having single or multiple walls; potential applications in electronics industry;
- **megatubes**: larger in diameter than nanotubes and prepared with walls of different thickness; potentially used for the transport of a variety of molecules of different sizes;
- **polymers**: chain, two-dimensional and three-dimensional polymers are formed under high pressure high temperature conditions
- **nano"onions"**: spherical particles based on multiple carbon layers surrounding a buckyball core; proposed for lubricants;
- **linked "ball-and-chain" dimers**: two buckyballs linked by a carbon chain;
- **fullerene rings**.

Buckyballs



C_{60} with isosurface of ground state electron density as calculated with DFT

Many association footballs have the same shape as the Buckminsterfullerene C_{60}

Buckminsterfullerene

Buckminsterfullerene is the smallest fullerene molecule in which no two pentagons share an edge (which can be destabilizing, as in pentalene). It is also the most common in terms of natural occurrence, as it can often be found in soot.

The structure of C_{60} is a truncated (T = 3) icosahedron, which resembles a soccer ball of the type made of twenty hexagons and twelve pentagons, with a carbon atom at the vertices of each polygon and a bond along each polygon edge.

The van der Waals diameter of a C_{60} molecule is about 1.1 nanometers (nm). The nucleus to nucleus diameter of a C_{60} molecule is about 0.71 nm.

The C_{60} molecule has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered "double bonds" and are shorter than the 6:5 bonds (between a hexagon and a pentagon). Its average bond length is 1.4 angstroms.

Silicon buckyballs have been created around metal ions.

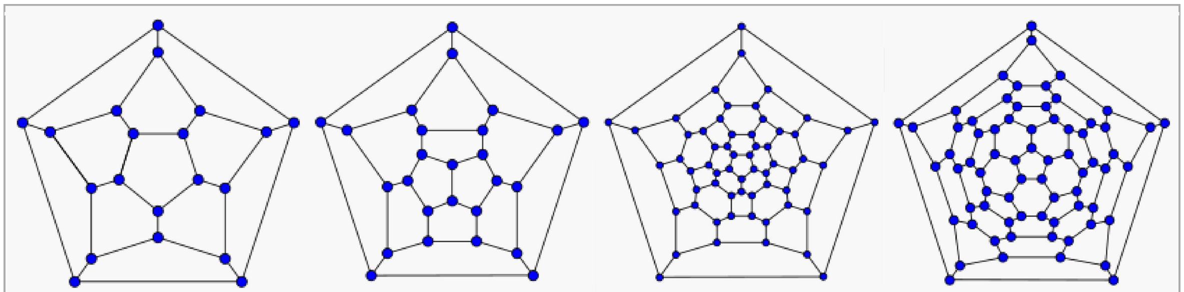
Boron buckyball

A new type of buckyball using boron atoms instead of the usual carbon has been predicted and described in 2007. The B_{80} structure, with each atom forming 5 or 6 bonds, is predicted to be more stable than the C_{60} buckyball. One reason for this given by the researchers is that the B-80 is actually more like the original geodesic dome structure popularized by Buckminster Fuller which uses triangles rather than hexagons. However, this work has been subject to much criticism by quantum chemists as it was concluded that the predicted Ih symmetric structure was vibrationally unstable and the resulting cage undergoes a spontaneous symmetry break yielding a puckered cage with rare Th symmetry (symmetry of a volleyball). The number of six atom rings in this molecule is 20 and number of five member rings is 12. There is an additional atom in the center of each six member ring, bonded to each atom surrounding it.

Other buckyballs

Another fairly common buckminsterfullerene is C_{70}, but fullerenes with 72, 76, 84 and even up to 100 carbon atoms are commonly obtained.

In mathematical terms, the structure of a **fullerene** is a trivalent convex polyhedron with pentagonal and hexagonal faces. In graph theory, the term **fullerene** refers to any 3-regular, planar graph with all faces of size 5 or 6 (including the external face). It follows from Euler's polyhedron formula, $V - E + F = 2$, (where V, E, F are the numbers of vertices, edges, and faces), that there are exactly 12 pentagons in a fullerene and $V/2 - 10$ hexagons.

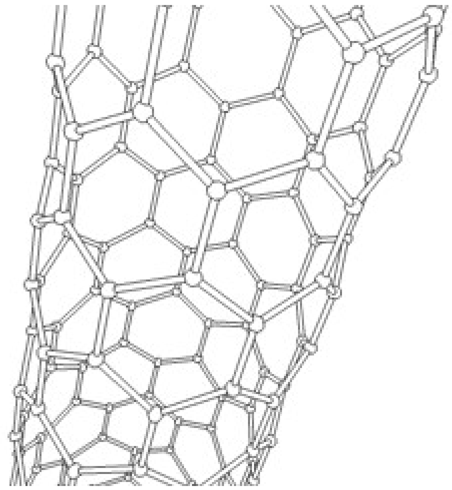


20-fullerene (dodecahedral graph) | 26-fullerene graph | 60-fullerene (truncated icosahedral graph) | 70-fullerene graph

The smallest fullerene is the dodecahedral C_{20}. There are no fullerenes with 22 vertices. The number of fullerenes C_{2n} grows with increasing n = 12, 13, 14, ..., roughly in proportion to n^9 (sequence A007894 in OEIS). For instance, there are 1812 non-isomorphic fullerenes C_{60}. Note that only one form of C_{60}, the buckminsterfullerene alias truncated icosahedron, has no pair of adjacent pentagons (the smallest such fullerene). To further illustrate the growth, there are 214,127,713 non-isomorphic fullerenes C_{200}, 15,655,672 of which have no adjacent pentagons.

Trimetasphere carbon nanomaterials were discovered by researchers at Virginia Tech and licensed exclusively to Luna Innovations. This class of novel molecules comprises 80 carbon atoms (C_{80}) forming a sphere which encloses a complex of three metal atoms and one nitrogen atom. These fullerenes encapsulate metals which puts them in the subset referred to as metallofullerenes. Trimetaspheres have the potential for use in diagnostics (as safe imaging agents), therapeutics and in organic solar cells.

Carbon nanotubes



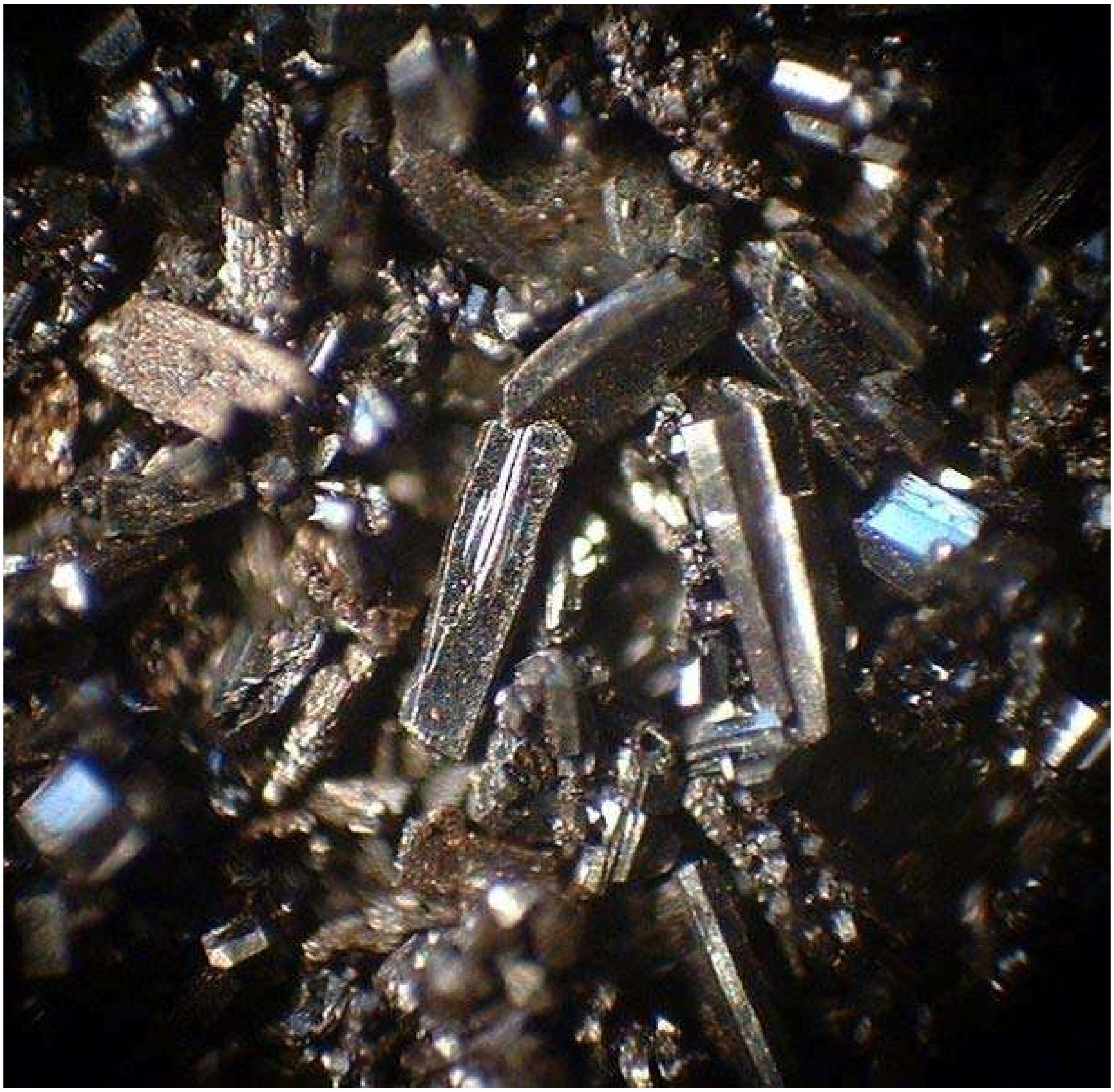
This rotating model of a carbon nanotube shows its 3D structure.

Nanotubes are cylindrical fullerenes. These tubes of carbon are usually only a few nanometres wide, but they can range from less than a micrometer to several millimeters in length. They often have closed ends, but can be open-ended as well. There are also cases in which the tube reduces in diameter before closing off. Their unique molecular structure results in extraordinary macroscopic properties, including high tensile strength, high electrical conductivity, high ductility, high heat conductivity, and relative chemical inactivity (as it is cylindrical and "planar" — that is, it has no "exposed" atoms that can be easily displaced). One proposed use of carbon nanotubes is in paper batteries, developed in 2007 by researchers at Rensselaer Polytechnic Institute. Another highly speculative proposed use in the field of space technologies is to produce high-tensile carbon cables required by a space elevator.

Carbon nanobuds

Nanobuds have been obtained by adding buckminsterfullerenes to carbon nanotubes.

Fullerite



The C_{60} fullerene in crystalline form

Fullerites are the solid-state manifestation of fullerenes and related compounds and materials.

"Ultrahard fullerite" is a coined term frequently used to describe material produced by high-pressure high-temperature (HPHT) processing of fullerite. Such treatment converts fullerite into a nanocrystalline form of diamond which has been reported to exhibit remarkable mechanical properties.

Properties

For the past decade, the chemical and physical properties of fullerenes have been a hot topic in the field of research and development, and are likely to continue to be for a long time. *Popular Science* has published articles about the possible uses of fullerenes in armor. In April 2003, fullerenes were under study for potential medicinal use: binding specific antibiotics to the structure to target resistant bacteria and even target certain cancer cells such as melanoma. The October 2005 issue of *Chemistry & Biology* contains an article describing the use of fullerenes as light-activated antimicrobial agents.

In the field of nanotechnology, heat resistance and superconductivity are some of the more heavily studied properties.

A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an inert atmosphere. The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated.

There are many calculations that have been done using ab-initio quantum methods applied to fullerenes. By DFT and TD-DFT methods one can obtain IR, Raman and UV spectra. Results of such calculations can be compared with experimental results.

Aromaticity

Researchers have been able to increase the reactivity of fullerenes by attaching active groups to their surfaces. Buckminsterfullerene does not exhibit "superaromaticity": that is, the electrons in the hexagonal rings do not delocalize over the whole molecule.

A spherical fullerene of n carbon atoms has n pi-bonding electrons, free to delocalize. These should try to delocalize over the whole molecule. The quantum mechanics of such an arrangement should be like one shell only of the well-known quantum mechanical structure of a single atom, with a stable filled shell for n = 2, 8, 18, 32, 50, 72, 98, 128, etc.; i.e. twice a perfect square number; but this series does not include 60. This $2(N + 1)^2$ rule (with N integer) for spherical aromaticity is the three-dimensional analogue of Hückel's rule. The 10+ cation would satisfy this rule, and should be aromatic. This has been shown to be the case using quantum chemical modelling, which showed the existence of strong diamagnetic sphere currents in the cation.

As a result, C_{60} in water tends to pick up two more electrons and become an anion. The nC_{60} described below may be the result of C_{60} trying to form a loose metallic bond.

Chemistry

Fullerenes are stable, but not totally unreactive. The sp^2-hybridized carbon atoms, which are at their energy minimum in planar graphite, must be bent to form the closed sphere or tube, which produces angle strain. The characteristic reaction of fullerenes is electrophilic addition at 6,6-double bonds, which reduces angle strain by changing sp^2-hybridized carbons into sp^3-hybridized ones. The change in hybridized orbitals causes the bond angles to decrease from about 120° in the sp^2 orbitals to about 109.5° in the sp^3 orbitals. This decrease in bond angles allows for the bonds to bend less when closing the sphere or tube, and thus, the molecule becomes more stable.

Other atoms can be trapped inside fullerenes to form inclusion compounds known as endohedral fullerenes. An unusual example is the egg shaped fullerene $Tb_3N@C_{84}$, which violates the isolated pentagon rule. Recent evidence for a meteor impact at the end of the Permian period was found by analyzing noble gases so preserved. Metallofullerene-based inoculates using the rhonditic steel process are beginning production as one of the first commercially-viable uses of buckyballs.

Solubility

C_{60} in solution

Fullerenes are sparingly soluble in many solvents. Common solvents for the fullerenes include aromatics, such as toluene, and others like carbon disulfide. Solutions of pure buckminsterfullerene have a deep purple color. Solutions of C_{70} are a reddish brown. The higher fullerenes C_{76} to C_{84} have a variety of colors. C_{76} has two optical forms, while other higher fullerenes have several structural isomers. Fullerenes are the only known allotrope of carbon that can be dissolved in common solvents at room temperature.

Solvent	Solubility
1-chloronaphthalene	51 mg/mL
1-methylnaphthalene	33 mg/mL
1,2-dichlorobenzene	24 mg/mL
1,2,4-trimethylbenzene	18 mg/mL
tetrahydronaphthalene	16 mg/mL
carbon disulfide	8 mg/mL
1,2,3-tribromopropane	8 mg/mL
xylene	5 mg/mL
bromoform	5 mg/mL
cumene	4 mg/mL
toluene	3 mg/mL
benzene	1.5 mg/mL
cyclohexane	1.2 mg/mL
carbon tetrachloride	0.4 mg/mL
chloroform	0.25 mg/mL
n-hexane	0.046 mg/mL
tetrahydrofuran	0.006 mg/mL
acetonitrile	0.004 mg/mL
methanol	0.000 04 mg/mL
water	1.3×10^{-11} mg/mL

Some fullerene structures are not soluble because they have a small band gap between the ground and excited states. These include the small fullerenes C_{28}, C_{36} and C_{50}. The C_{72} structure is also in this class, but the endohedral version with a trapped lanthanide-group atom is soluble due to the interaction of the metal atom and the electronic states of the fullerene. Researchers had originally been puzzled by C_{72} being absent in fullerene plasma-generated soot extract, but found in endohedral samples. Small band gap fullerenes are highly reactive and bind to other fullerenes or to soot particles.

Solvents that are able to dissolve buckminsterfullerene (C_{60}) are listed at left in order from highest solubility. The solubility value given is the approximate saturated concentration.

Solubility of C_{60} in some solvents shows unusual behaviour due to existence of solvate phases (analogues of crystallohydrates). For example, solubility of C_{60} in benzene solution shows maximum at about 313 K. Crystallization from benzene solution at temperatures below maximum results in formation of triclinic solid solvate with four benzene molecules $C_{60}\cdot4C_6H_6$ which is rather unstable in air. Out of solution, this structure decomposes into usual fcc C_{60} in few minutes' time. At temperatures above solubility maximum the solvate is not stable even when immersed in saturated solution and melts with formation of fcc C_{60}. Crystallization at temperatures above the solubility maximum results in formation of pure fcc C_{60}. Millimeter-sized crystals of C_{60} and C_{70} can be grown from solution both for solvates and for pure fullerenes.

Hydrated Fullerene (HyFn)

C_{60}HyFn water solution with a C_{60} concentration of 0.22 g/L.

Hydrated fullerene C_{60}HyFn is a stable, highly hydrophilic, supra-molecular complex consisting of C_{60} fullerene molecule enclosed into the first hydrated shell that contains 24 water molecules: $C_{60}@(H_2O)_{24}$. This hydrated shell is formed as a result of donor-acceptor interaction between lone-electron pairs of oxygen, water molecules and electron-acceptor centers on the fullerene surface. Meanwhile, the water molecules which are oriented close to the fullerene surface are interconnected by a three-dimensional network of hydrogen bonds. The size of C_{60}HyFn is 1.6–1.8 nm. The maximal concentration of C_{60} in the form of C_{60}HyFn achieved by 2010 is 4 g/L.

Quantum mechanics

In 1999, researchers from the University of Vienna demonstrated that wave-particle duality applied to molecules such as fullerene. One of the co-authors of this research, Julian Voss-Andreae, has since created several sculptures symbolizing wave-particle duality in fullerenes**.**

Science writer Marcus Chown stated on the CBC radio show *Quirks and Quarks* in May 2006 that scientists are trying to make buckyballs exhibit the quantum behavior of existing in two places at once (quantum superposition).

Safety and toxicity

Moussa *et al.* (1996-7) studied the *in vivo* toxicity of C_{60} after intra-peritoneal administration of large doses. No evidence of toxicity was found and the mice tolerated a dose of 5 000 mg/kg of body weight (BW). Mori *et al.* (2006) could not find toxicity in rodents for C_{60} and C_{70} mixtures after oral administration of a dose of 2 000 mg/kg BW and did not observe evidence of genotoxic or mutagenic potential *in vitro*. Other studies could not establish the toxicity of fullerenes: on the contrary, the work of Gharbi *et al.* (2005) suggested that aqueous C_{60} suspensions failing to produce acute or subacute toxicity in rodents could also protect their livers in a dose-dependent manner against free-radical damage.

A comprehensive and recent review on fullerene toxicity is given by Kolosnjaj *et al.* (2007a,b, c). These authors review the works on fullerene toxicity beginning in the early 1990s to present, and conclude that very little evidence gathered since the discovery of fullerenes indicate that C_{60} is toxic.

With reference to nanotubes, a recent study by Poland *et al.* (2008) on carbon nanotubes introduced into the abdominal cavity of mice led the authors to suggest comparisons to "asbestos-like pathogenicity". It should be noted that this was not an inhalation study, though there have been several performed in the past, therefore it is premature to conclude that nanotubes should be considered to have a toxicological profile similar to asbestos. Conversely, and perhaps illustrative of how the various classes of molecules which fall under the general term fullerene cover a wide range of properties, Sayes *et al.* found that *in vivo* inhalation of $C_{60}(OH)_{24}$ and nano-C_{60} in rats gave no effect, whereas in comparison quartz particles produced an inflammatory response under the same conditions. As stated above, nanotubes are quite different in chemical and physical properties to C_{60}, i.e., molecular weight, shape, size, physical properties (such as solubility) all are very different, so from a toxicological standpoint, different results for C_{60} and nanotubes are not suggestive of any discrepancy in the findings.

When considering toxicological data, care must be taken to distinguish as necessary between what are normally referred to as fullerenes: (C_{60}, C_{70}, ...); fullerene derivatives: C_{60} or other fullerenes with covalently bonded chemical groups; fullerene complexes (e.g., water-solubilized with surfactants, such as C_{60}-PVP; host-guest complexes, such as with cyclodextrin), where the fullerene is physically bound to another molecule; C_{60} nanoparticles, which are extended solid-phase aggregates of C_{60} crystallites; and nanotubes, which are generally much larger (in terms of molecular weight and size) molecules, and are different in shape to the spheroidal fullerenes C_{60} and C_{70}, as well as having different chemical and physical properties.

The above different molecules span the range from insoluble materials in either hydrophilic or lipophilic media, to hydrophilic, lipophilic, or even amphiphilic molecules, and with other varying physical and chemical properties. Therefore any broad generalization extrapolating for example results from C_{60} to nanotubes or vice versa is not possible, though technically all are fullerenes, as the term is defined as a close-caged all-carbon molecule. Any extrapolation of results from one molecule to other molecules must take into account considerations based on a quantitative structural analysis relationship study (QSARS), which mostly depends on how close the molecules under consideration are in physical and chemical properties.

Superconductivity

After the synthesis of macroscopic amounts of fullerenes, their physical properties could be investigated. Very soon Haddon *et al.* found that intercalation of alkali-metal atoms in solid C_{60} leads to metallic behavior. In 1991, it was revealed that potassium-doped C_{60} becomes superconducting at 18 K. This was the highest transition temperature for a molecular superconductor. Since then, superconductivity has been reported in fullerene doped with various other alkali metals. It has been shown that the superconducting transition temperature in alkaline-metal-doped fullerene increases with the unit-cell volume V. As caesium forms the largest alkali ion, caesium-doped fullerene is an important material in this family. Recently, superconductivity at 38 K has been reported in bulk Cs_3C_{60}, but only under applied pressure. The highest superconducting transition temperature of 33 K at ambient pressure is reported for Cs_2RbC_{60}.

The increase of transition temperature with the unit-cell volume had been believed to be evidence for the BCS mechanism of C_{60} solid superconductivity, because inter C_{60} separation can be related to an increase in the density of states on the Fermi level, $N(\varepsilon_F)$. Therefore, there have been many efforts to increase the interfullerene separation, in particular, intercalating neutral molecules into the A_3C_{60} lattice to increase the interfullerene spacing while the valence of C_{60} is kept unchanged. However, this ammoniation technique has revealed a new aspect of fullerene intercalation compounds: the Mott-Hubbard transition and the correlation between the orientation/orbital order of C_{60} molecules and the magnetic structure.

The C_{60} molecules compose a solid of weakly bound molecules. The fullerites are therefore molecular solids, in which the molecular properties still survive. The discrete levels of a free C_{60} molecule are only weakly broadened in the solid, which leads to a set of essentially nonoverlapping bands with a narrow width of about 0.5 eV. For an undoped C_{60} solid, the 5-fold h_u band is the HOMO level, and the 3-fold t_{1u} band is the empty LUMO level, and this system is a band insulator. But when the C_{60} solid is doped with metal atoms, the metal atoms give electrons to the t_{1u} band or the upper 3-fold t_{1g} band. This partial electron occupation of the band leads to sometimes metallic behavior. However, A_4C_{60} is an insulator, although the t_{1u} band is only partially filled and it should be a metal according to band theory. This unpredicted behavior may be explained by the Jahn-Teller effect, where spontaneous deformations of high-symmetry molecules induce the splitting of degenerate levels to gain the electronic energy. The Jahn-Teller type electron-phonon interaction is strong enough in C_{60} solids to destroy the band picture for particular valence states.

A narrow band or strongly correlated electronic system and degenerated ground states are important points to understand in explaining superconductivity in fullerene solids. When the inter-electron repulsion U is greater than the bandwidth, an insulating localized electron ground state is produced in the simple Mott-Hubbard model. This explains the absence of superconductivity at ambient pressure in caesium-doped C_{60} solids. Electron-correlation-driven localization of the t_{1u} electrons exceeds the critical value, leading to the Mott insulator. The application of high pressure decreases the interfullerene spacing, therefore caesium-doped C_{60} solids turn to metallic and superconducting.

A fully developed theory of C_{60} solids superconductivity is still lacking, but it has been widely accepted that strong electronic correlations and the Jahn-Teller electron-phonon coupling produce local electron-pairings that show a high transition temperature close to the insulator-metal transition.

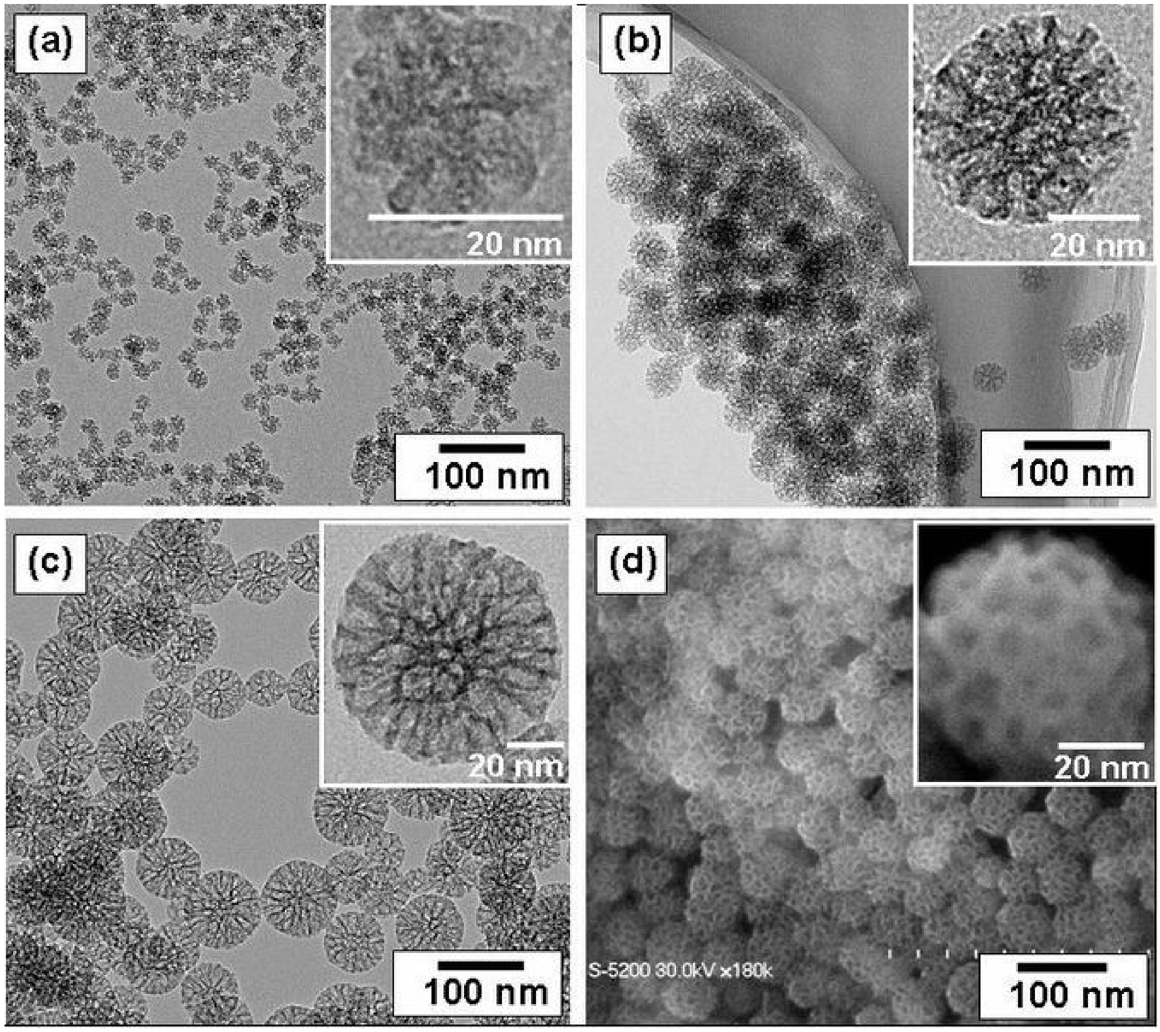
Chirality

Some fullerenes (e.g. C_{76}, C_{78}, C_{80}, and C_{84}) are inherently chiral because they are D_2-symmetric, and have been successfully resolved. Research efforts are ongoing to develop specific sensors for their enantiomers.

Nanoparticle

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. It is further classified according to size: in terms of diameter, fine particles cover a range between 100 and 2500 nanometers, while ultrafine particles, on the other hand, are sized between 1 and 100 nanometers. Similar to ultrafine particles, **nanoparticles** are sized between 1 and 100 nanometers. Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. Although the size of most molecules would fit into the above outline, individual molecules are usually not referred to as nanoparticles.

Nanoclusters have at least one dimension between 1 and 10 nanometers and a narrow size distribution. Nanopowders are agglomerates of ultrafine particles, nanoparticles, or nanoclusters. Nanometer-sized single crystals, or single-domain ultrafine particles, are often referred to as nanocrystals. Nanoparticle research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical and electronic fields.



TEM (a, b, and c) images of prepared mesoporous silica nanoparticles with mean outer diameter: (a) 20nm, (b) 45nm, and (c) 80nm. SEM (d) image corresponding to (b). The insets are a high magnification of mesoporous silica particle.

The National Nanotechnology Initiative has led to generous public funding for nanoparticle research in the United States.

Background

Although nanoparticles are generally considered an invention of modern science, they actually have a very long history. Nanoparticles were used by artisans as far back as the 9th century in Mesopotamia for generating a glittering effect on the surface of pots.

Even these days, pottery from the Middle Ages and Renaissance often retain a distinct gold or copper colored metallic glitter. This so called luster is caused by a metallic film that was applied to the transparent surface of a glazing. The luster can still be visible if the film has resisted atmospheric oxidation and other weathering.

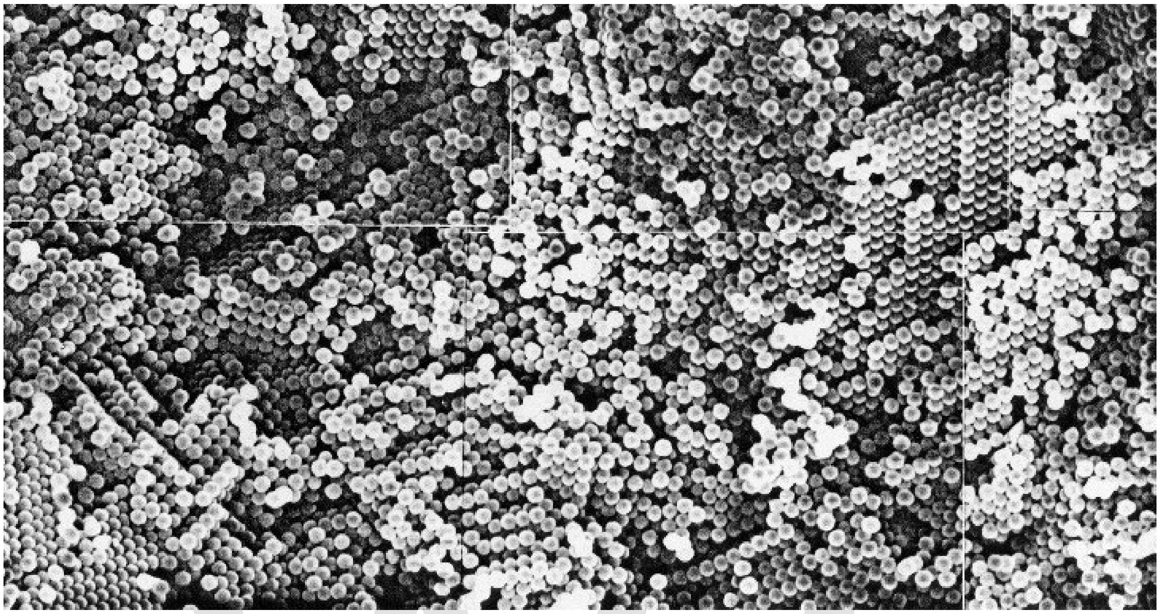
The luster originated within the film itself, which contained silver and copper nanoparticles dispersed homogeneously in the glassy matrix of the ceramic glaze. These nanoparticles were created by the artisans by adding copper and silver salts and oxides together with vinegar, ochre and clay, on the surface of previously-glazed pottery. The object was then placed into a kiln and heated to about 600 °C in a reducing atmosphere.

In the heat the glaze would soften, causing the copper and silver ions to migrate into the outer layers of the glaze. There the reducing atmosphere reduced the ions back to metals, which then came together forming the nanoparticles that give the colour and optical effects.

Luster technique showed that ancient craftsmen had a rather sophisticated empirical knowledge of materials. The technique originated in the islamic world. As Muslims were not allowed to use gold in artistic representations, they had to find a way to create a similar effect without using real gold. The solution they found was using luster.

Michael Faraday provided the first description, in scientific terms, of the optical properties of nanometer-scale metals in his classic 1857 paper. In a subsequent paper, the author (Turner) points out that: "It is well known that when thin leaves of gold or silver are mounted upon glass and heated to a temperature which is well below a red heat (~500 °C), a remarkable change of properties takes place, whereby the continuity of the metallic film is destroyed. The result is that white light is now freely transmitted, reflection is correspondingly diminished, while the electrical resistivity is enormously increased."

Uniformity



Colloidal crystal composed of amorphous hydrated colloidal silica (particle diameter 600 nm)

The chemical processing and synthesis of high performance technological components for the private, industrial and military sectors requires the use of high purity ceramics, polymers, glass-ceramics and material composites. In condensed bodies formed from fine powders, the irregular particle sizes and shapes in a typical powder often lead to non-uniform packing morphologies that result in packing density variations in the powder compact.

Uncontrolled agglomeration of powders due to attractive van der Waals forces can also give rise to in microstructural inhomogeneities. Differential stresses that develop as a result of non-uniform drying shrinkage are directly related to the rate at which the solvent can be removed, and thus highly dependent upon the distribution of porosity. Such stresses have been associated with a plastic-to-brittle transition in consolidated bodies, and can yield to crack propagation in the unfired body if not relieved.

In addition, any fluctuations in packing density in the compact as it is prepared for the kiln are often amplified during the sintering process, yielding inhomogeneous densification. Some pores and other structural defects associated with density variations have been shown to play a detrimental role in the sintering process by growing and thus limiting end-point densities. Differential stresses arising from inhomogeneous densification have also been shown to result in the propagation of internal cracks, thus becoming the strength-controlling flaws.

It would therefore appear desirable to process a material in such a way that it is physically uniform with regard to the distribution of components and porosity, rather than using particle size distributions which will maximize the green density. The containment of a uniformly dispersed assembly of strongly interacting particles in suspension requires total control over interparticle forces. Monodisperse nanoparticles and colloids provide this potential.

Monodisperse powders of colloidal silica, for example, may therefore be stabilized sufficiently to ensure a high degree of order in the colloidal crystal or polycrystalline colloidal solid which results from aggregation. The degree of order appears to be limited by the time and space allowed for longer-range correlations to be established. Such defective polycrystalline colloidal structures would appear to be the basic elements of submicrometer colloidal materials science, and, therefore, provide the first step in developing a more rigorous understanding of the mechanisms involved in microstructural evolution in high performance materials and components.

Properties

Silicon nanopowder

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material.

For example, nanoparticles of usually yellow gold and gray silicon are red in color; gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C); and absorption of solar radiation in photovoltaic cells is much higher in materials composed of nanoparticles than it is in thin films of continuous sheets of material – the smaller the particles, the greater the solar absorption.

Other size-dependent property changes include quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials. Ironically, the changes in physical properties are not always desirable. Ferromagnetic materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them unsuitable for memory storage.

Suspensions of nanoparticles are possible since the interaction of the particle surface with the solvent is strong enough to overcome density differences, which otherwise usually result in a material either sinking or floating in a liquid. Nanoparticles also often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution.

The high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. This theoretically does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate complicates matters. Moreover, nanoparticles have been found to impart some extra properties to various day to day products. For example the presence of titanium dioxide nanoparticles imparts what we call the self-cleaning effect, and the size being nanorange, the particles can not be observed. Zinc oxide particles have been found to have superior UV blocking properties compared to its bulk substitute. This is one of the reasons why it is often used in the preparation of sunscreen lotions., and is completely photostable.

Clay nanoparticles when incorporated into polymer matrices increase reinforcement, leading to stronger plastics, verifiable by a higher glass transition temperature and other mechanical property tests. These nanoparticles are hard, and impart their properties to the polymer (plastic). Nanoparticles have also been attached to textile fibers in order to create smart and functional clothing.

Metal, dielectric, and semiconductor nanoparticles have been formed, as well as hybrid structures (e.g., core-shell nanoparticles). Nanoparticles made of semiconducting material may also be labeled quantum dots if they are small enough (typically sub 10 nm) that quantization of electronic energy levels occurs. Such nanoscale particles are used in biomedical applications as drug carriers or imaging agents.

Semi-solid and soft nanoparticles have been manufactured. A prototype nanoparticle of semi-solid nature is the liposome. Various types of liposome nanoparticles are currently used clinically as delivery systems for anticancer drugs and vaccines.

Nanoparticles with one half hydrophilic and the other half hydrophobic are termed Janus particles and are particularly effective for stabilizing emulsions. They can self-assemble at water/oil interfaces and act as solid surfactants.

Synthesis

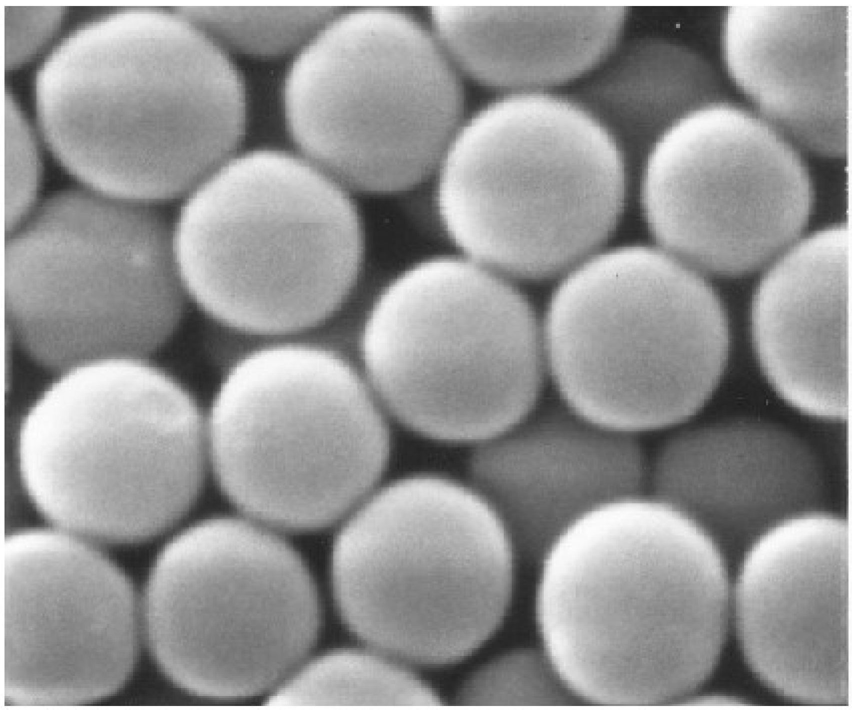
There are several methods for creating nanoparticles, including both attrition and pyrolysis. In attrition, macro or micro scale particles are ground in a ball mill, a planetary ball mill, or other size reducing mechanism. The resulting particles are air classified to recover nanoparticles. In pyrolysis, a vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting solid (a version of soot) is air classified to recover oxide particles from by-product gases. Pyrolysis often results in aggregates and agglomerates rather than single primary particles.

A thermal plasma can also deliver the energy necessary to cause evaporation of small micrometer size particles. The thermal plasma temperatures are in the order of 10,000 K, so that solid powder easily evaporates. Nanoparticles are formed upon cooling while exiting the plasma region. The main types of the thermal plasma torches used to produce nanoparticles are dc plasma jet, dc arc plasma and radio frequency (RF) induction plasmas. In the arc plasma reactors, the energy necessary for evaporation and reaction is provided by an electric arc which is formed between the anode and the cathode. For example, silica sand can be vaporized with an arc plasma at atmospheric pressure. The resulting mixture of plasma gas and silica vapour can be rapidly cooled by quenching with oxygen, thus ensuring the quality of the fumed silica produced. In RF induction plasma torches, energy coupling to the plasma is accomplished through the electromagnetic field generated by the induction coil. The plasma gas does not come in contact with electrodes, thus eliminating possible sources of contamination and allowing the operation of such plasma torches with a wide range of gases including inert, reducing, oxidizing and other corrosive atmospheres.

The working frequency is typically between 200 kHz and 40 MHz. Laboratory units run at power levels in the order of 30–50 kW while the large scale industrial units have been tested at power levels up to 1 MW. As the residence time of the injected feed droplets in the plasma is very short it is important that the droplet sizes are small enough in order to obtain complete evaporation. The RF plasma method has been used to synthesize different nanoparticle materials, for example synthesis of various ceramic nanoparticles such as oxides, carbours/carbides and nitrides of Ti and Si.

Inert-gas condensation is frequently used to make nanoparticles from metals with low melting points. The metal is vaporized in a vacuum chamber and then supercooled with an inert gas stream. The supercooled metal vapor condenses into nanometer-sized particles, which can be entrained in the inert gas stream and deposited on a substrate or studied in situ.

Sol-gel



SEM micrograph of amorphous colloidal silica particles (average particle diameter 600 nm) formed in basic solution from TEOS.

The sol-gel process is a wet-chemical technique (also known as chemical solution deposition) widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (*sol*, short for solution) which acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers.

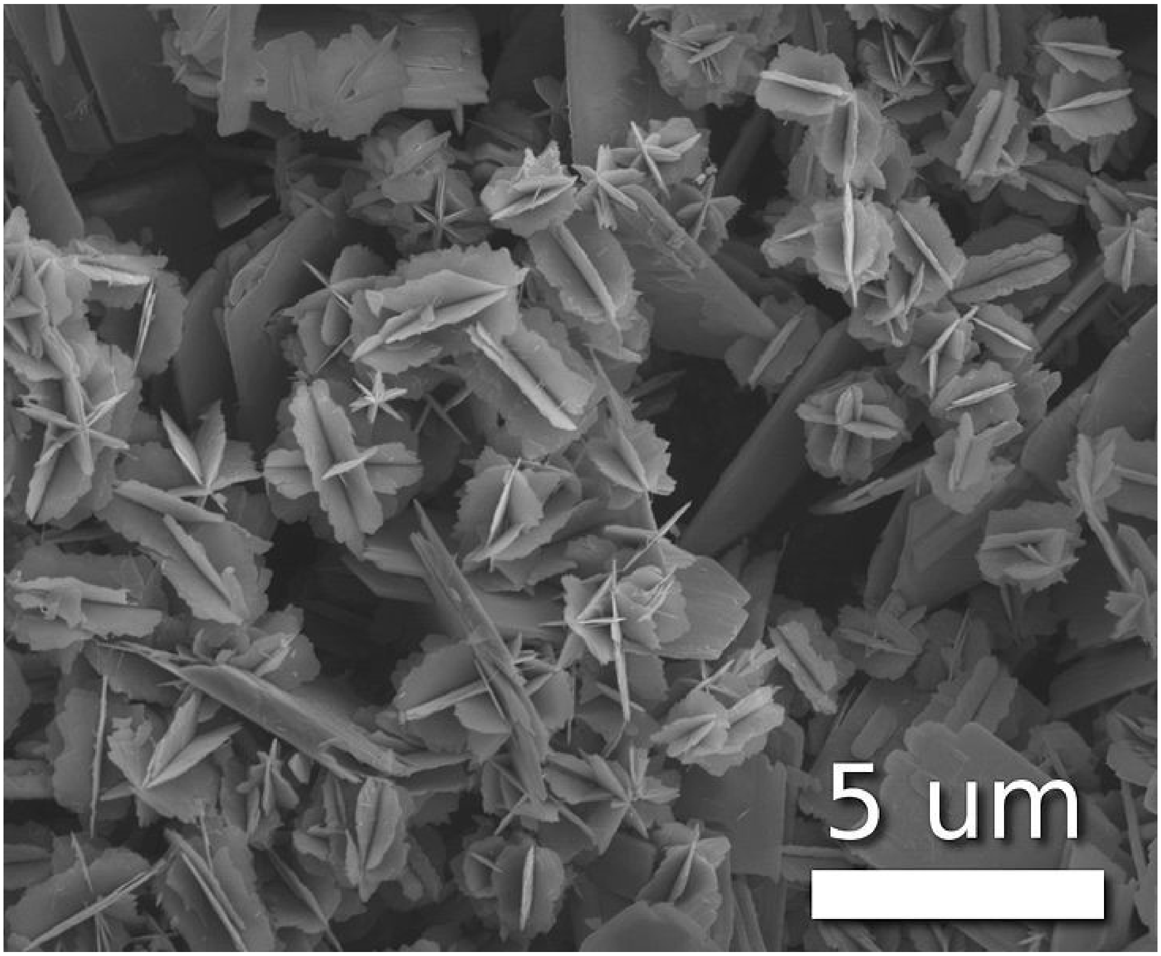
Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form either a network "elastic solid" or a colloidal suspension (or dispersion) – a system composed of discrete (often amorphous) submicrometer particles dispersed to various degrees in a host fluid. Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. Thus, the sol evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks.

In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The most simple method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation.

Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes implemented during this phase of processing. Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

The precursor sol can be either deposited on a substrate to form a film (e.g. by dip-coating or spin-coating), cast into a suitable container with the desired shape (e.g. to obtain a monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g. microspheres, nanospheres). The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product’s chemical composition. Even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology.

Colloids



Nanostars of vanadium(IV) oxide

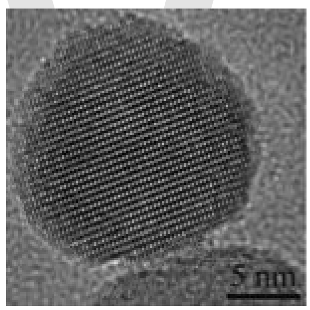
The term colloid is used primarily to describe a broad range of solid-liquid (and/or liquid-liquid) mixtures, all of which contain distinct solid (and/or liquid) particles which are dispersed to various degrees in a liquid medium. The term is specific to the size of the individual particles, which are larger than atomic dimensions but small enough to exhibit Brownian motion. If the particles are large enough, then their dynamic behavior in any given period of time in suspension would be governed by forces of gravity and sedimentation. But if they are small enough to be colloids, then their irregular motion in suspension can be attributed to the collective bombardment of a myriad of thermally agitated molecules in the liquid suspending medium, as described originally by Albert Einstein in his dissertation. Einstein proved the existence of water molecules by concluding that this erratic particle behavior could adequately be described using the theory of Brownian motion, with sedimentation being a possible long-term result. This critical size range (or particle diameter) typically ranges from nanometers (10^{-9} m) to micrometers (10^{-6} m).

Morphology

Scientists have taken to naming their particles after the real world shapes that they might represent. Nanospheres, nanoreefs, nanoboxes and more have appeared in the literature. These morphologies sometimes arise spontaneously as an effect of a templating or directing agent present in the synthesis such as miscellar emulsions or anodized alumina pores, or from the innate crystallographic growth patterns of the materials themselves. Some of these morphologies may serve a purpose, such as long carbon nanotubes being used to bridge an electrical junction, or just a scientific curiosity like the stars shown at right.

Amorphous particles usually adopt a spherical shape (due to their microstructural isotropy) – whereas the shape of anisotropic microcrystalline whiskers corresponds to their particular crystal habit. At the small end of the size range, nanoparticles are often referred to as clusters. Spheres, rods, fibers, and cups are just a few of the shapes that have been grown. The study of fine particles is called micromeritics.

Characterization



TEM image of magnetic Fe_3O_4 nanoparticle.

Nanoparticle characterization is necessary to establish understanding and control of nanoparticle synthesis and applications. Characterization is done by using a variety of different techniques, mainly drawn from materials science. Common techniques are electron microscopy (TEM, SEM), atomic force microscopy (AFM), dynamic light scattering (DLS), x-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF), ultraviolet-visible spectroscopy, dual polarisation interferometry and nuclear magnetic resonance (NMR).

Whilst the theory has been known for over a century, the technology for Nanoparticle tracking analysis (NTA) allows direct tracking of the Brownian motion and this method therefore allows the sizing of individual nanoparticles in solution.

Functionalization

The surface coating of nanoparticles is crucial to determining their properties. In particular, the surface coating can regulate stability, solubility and targeting. A coating that is multivalent or polymeric confers high stability. For biological applications, the surface coating should be polar to give high aqueous solubility and prevent nanoparticle aggregation. In serum or on the cell surface, highly charged coatings promote non-specific binding, while polyethylene glycol linked to terminal hydroxyl or methoxy groups repel non-specific interactions. Nanoparticles can be linked to biological molecules which can act as address tags, to direct the nanoparticles to specific sites within the body, specific organelles within the cell, or to follow specifically the movement of individual protein or RNA molecules in living cells. Common address tags are monoclonal antibodies, aptamers, streptavidin or peptides. These targeting agents should ideally be covalently linked to the nanoparticle and should be present in a controlled number per nanoparticle. Multivalent nanoparticles, bearing multiple targeting groups, can cluster receptors, which can activate cellular signaling pathways, and give stronger anchoring. Monovalent nanoparticles, bearing a single binding site, avoid clustering and so are preferable for tracking the behavior of individual proteins.

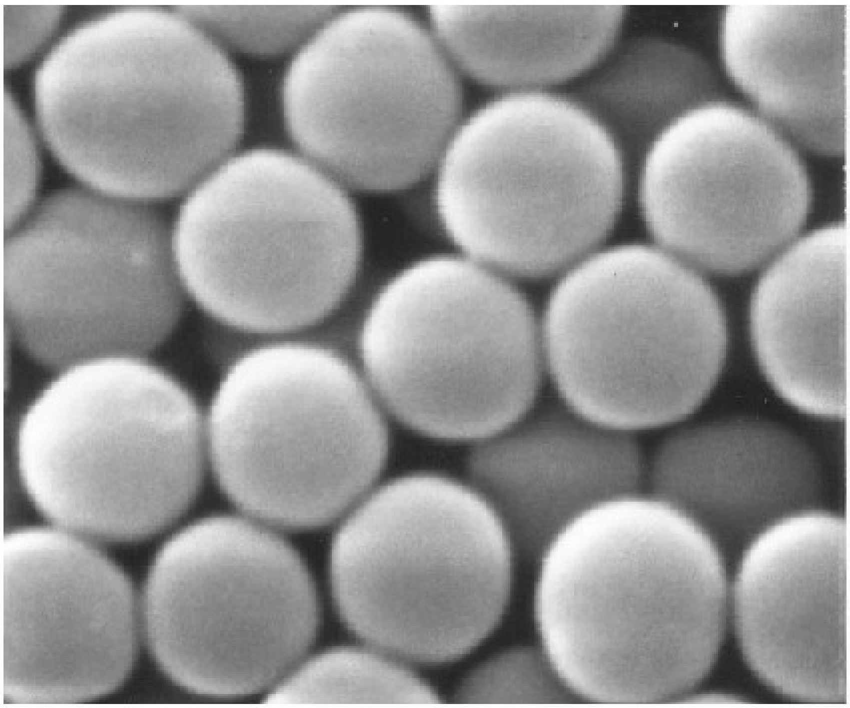
Safety

Nanoparticles present possible dangers, both medically and environmentally. Most of these are due to the high surface to volume ratio, which can make the particles very reactive or catalytic. They are also able to pass through cell membranes in organisms, and their interactions with biological systems are relatively unknown. However, free nanoparticles in the environment quickly tend to agglomerate and thus leave the nano-regime, and nature itself presents many nanoparticles to which organisms on earth may have evolved immunity (such as salt particulates from ocean aerosols, terpenes from plants, or dust from volcanic eruptions).

According to the *San Francisco Chronicle*, "Animal studies have shown that some nanoparticles can penetrate cells and tissues, move through the body and brain and cause biochemical damage they also have shown to cause a risk factor in men for testicular cancer. But whether cosmetics and sunscreens containing nanomaterials pose health risks remains largely unknown, pending completion of long-range studies recently begun by the FDA and other agencies." Diesel nanoparticles have been found to damage the cardiovascular system in a mouse model.

Synthesis

Sol-gel



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The interest in sol-gel processing can be traced back in the mid-1880s with the observation that the hydrolysis of tetraethyl orthosilicate (TEOS) under acidic conditions led to the formation of SiO_2 in the form of fibers and monoliths. Sol-gel research grew to be so important that in the 1990s more than 35,000 papers were published worldwide on the process.

Characterization

The first observations and size measurements of nano-particles were made during the first decade of the 20th century. They are mostly associated with the name of Zsigmondy who made detailed studies of gold sols and other nanomaterials with sizes down to 10 nm and less. He published a book in 1914. He used ultramicroscope that employs a *dark field* method for seeing particles with sizes much less than light wavelength.

There are traditional techniques developed during 20th century in Interface and Colloid Science for characterizing nanomaterials. These are widely used for *first generation* passive nanomaterials specified in the next section.

These methods include several different techniques for characterizing particle size distribution. This characterization is imperative because many materials that are expected to be nano-sized are actually aggregated in solutions. Some of methods are based on light scattering. Other apply ultrasound, such as ultrasound attenuation spectroscopy for testing concentrated nano-dispersions and microemulsions.

There is also a group of traditional techniques for characterizing surface charge or zeta potential of nano-particles in solutions. This information is required for proper system stabilzation, preventing its aggregation or flocculation. These methods include microelectrophoresis, electrophoretic light scattering and electroacoustics. The last one, for instance colloid vibration current method is suitable for characterizing concentrated systems.

Safety

Nanomaterials behave differently than other similarly-sized particles. It is therefore necessary to develop specialized approaches to testing and monitoring their effects on human health and on the environment. The OECD Chemicals Committee has established the Working Party on Manufactured Nanomaterials to address this issue and to study the practices of OECD member countries in regards to nanomaterial safety.

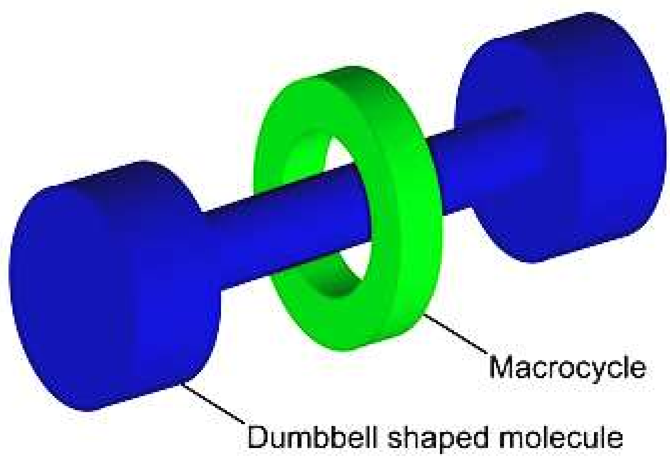
While nanomaterials and nanotechnologies are expected to yield numerous health and health care advances, such as more targeted methods of delivering drugs, new cancer therapies, and methods of early detection of diseases, they also may have unwanted effects. Increased rate of absorption is the main concern associated with manufactured nanoparticles.

When materials are made into nanoparticles, their surface area to volume ratio increases. The greater specific surface area (surface area per unit weight) may lead to increased rate of absorption through the skin, lungs, or digestive tract and may cause unwanted effects to the lungs as well as other organs. However, the particles must be absorbed in sufficient quantities in order to pose health risks.

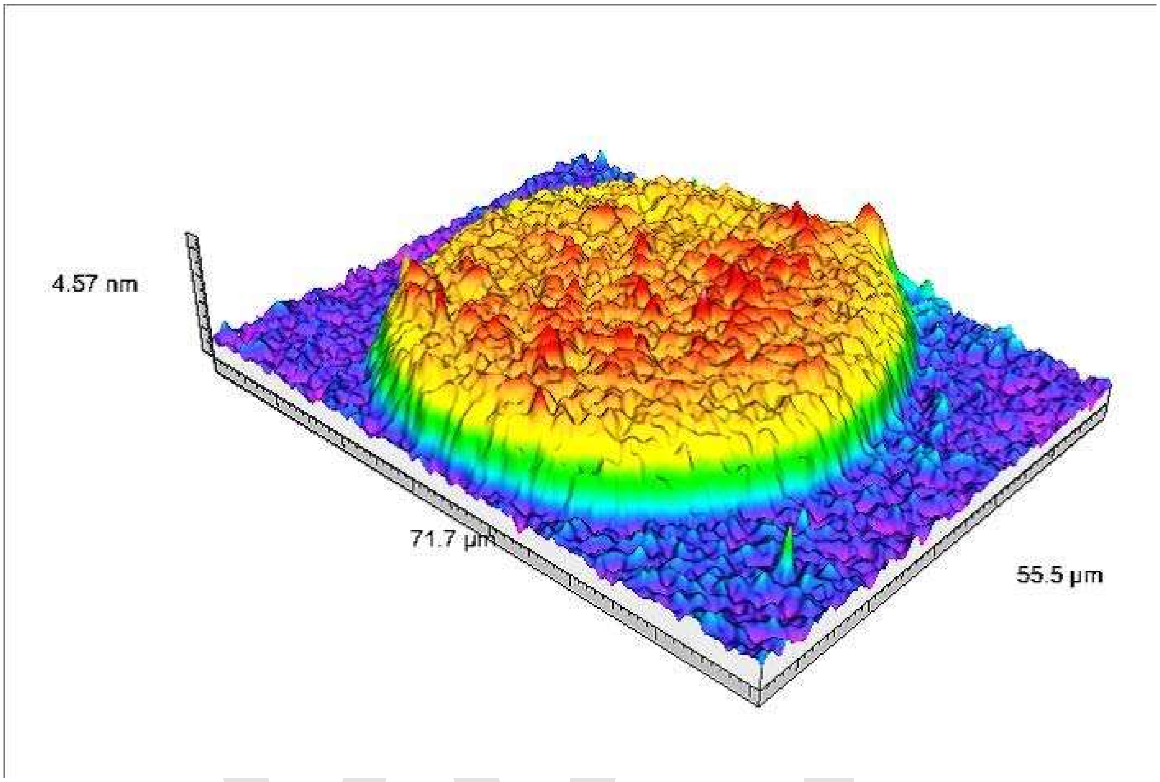
As the use of nanomaterials increases worldwide, concerns for worker and user safety are mounting. To address such concerns, the Swedish Karolinska Institute conducted a study in which various nanoparticles were introduced to human lung epithelial cells. The results, released in 2008, showed that iron oxide nanoparticles caused little DNA damage and were non-toxic. Zinc oxide nanoparticles were slightly worse. Titanium dioxide caused only DNA damage. Carbon nanotubes caused DNA damage at low levels. Copper oxide was found to be the worst offender, and was the only nanomaterial identified by the researchers as a clear health risk.

Chapter-4

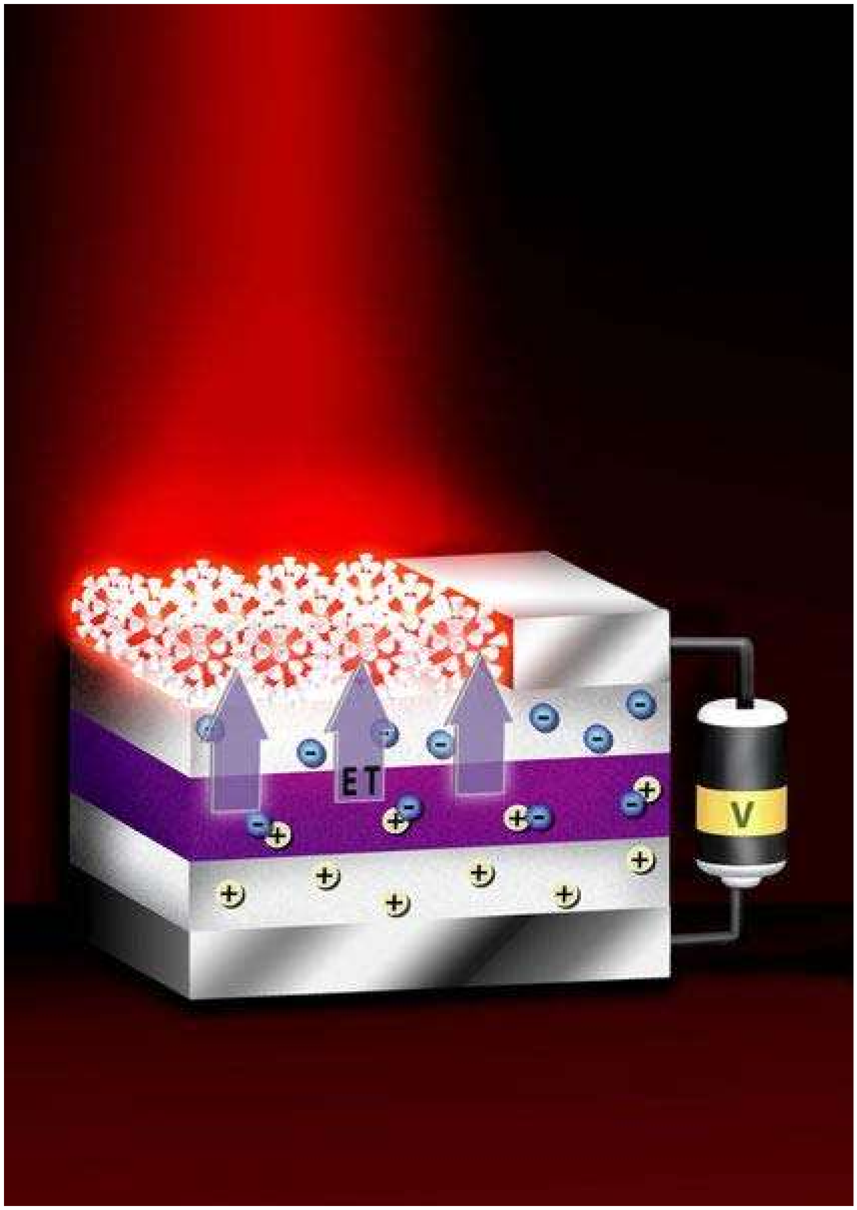
Current Research in the Field of Nanotechnology



Graphical representation of a rotaxane, useful as a molecular switch



Sarfus image of a DNA biochip elaborated by bottom-up approach



This device transfers energy from nano-thin layers of quantum wells to nanocrystals above them, causing the nanocrystals to emit visible light.

Nanomaterials

The nanomaterials field includes subfields which develop or study materials having unique properties arising from their nanoscale dimensions.

- Interface and colloid science has given rise to many materials which may be useful in nanotechnology, such as carbon nanotubes and other fullerenes, and various nanoparticles and nanorods. Nanomaterials with fast ion transport are related also to nanoionics and nanoelectronics.

- Nanoscale materials can also be used for bulk applications; most present commercial applications of nanotechnology are of this flavor.
- Progress has been made in using these materials for medical applications.
- Nanoscale materials are sometimes used in solar cells which combats the cost of traditional Silicon solar cells
- Development of applications incorporating semiconductor nanoparticles to be used in the next generation of products, such as display technology, lighting, solar cells and biological imaging.

Nanomedicine

Nanomedicine is the medical application of nanotechnology. Nanomedicine ranges from the medical applications of nanomaterials, to nanoelectronic biosensors, and even possible future applications of molecular nanotechnology. Current problems for nanomedicine involve understanding the issues related to toxicity and environmental impact of nanoscale materials.

Nanomedicine research is receiving funding from the US National Institute of Health. Of note is the funding in 2005 of a five-year plan to set up four nanomedicine centers. In April 2006, the journal Nature Materials estimated that 130 nanotech-based drugs and delivery systems were being developed worldwide.

Overview

Nanomedicine seeks to deliver a valuable set of research tools and clinically useful devices in the near future. The National Nanotechnology Initiative expects new commercial applications in the pharmaceutical industry that may include advanced drug delivery systems, new therapies, and in vivo imaging. Neuro-electronic interfaces and other nanoelectronics-based sensors are another active goal of research. Further down the line, the speculative field of molecular nanotechnology believes that cell repair machines could revolutionize medicine and the medical field.

Nanomedicine is a large industry, with nanomedicine sales reaching 6.8 billion dollars in 2004, and with over 200 companies and 38 products worldwide, a minimum of 3.8 billion dollars in nanotechnology R&D is being invested every year. As the nanomedicine industry continues to grow, it is expected to have a significant impact on the economy.

Medical use of nanomaterials

Drug delivery

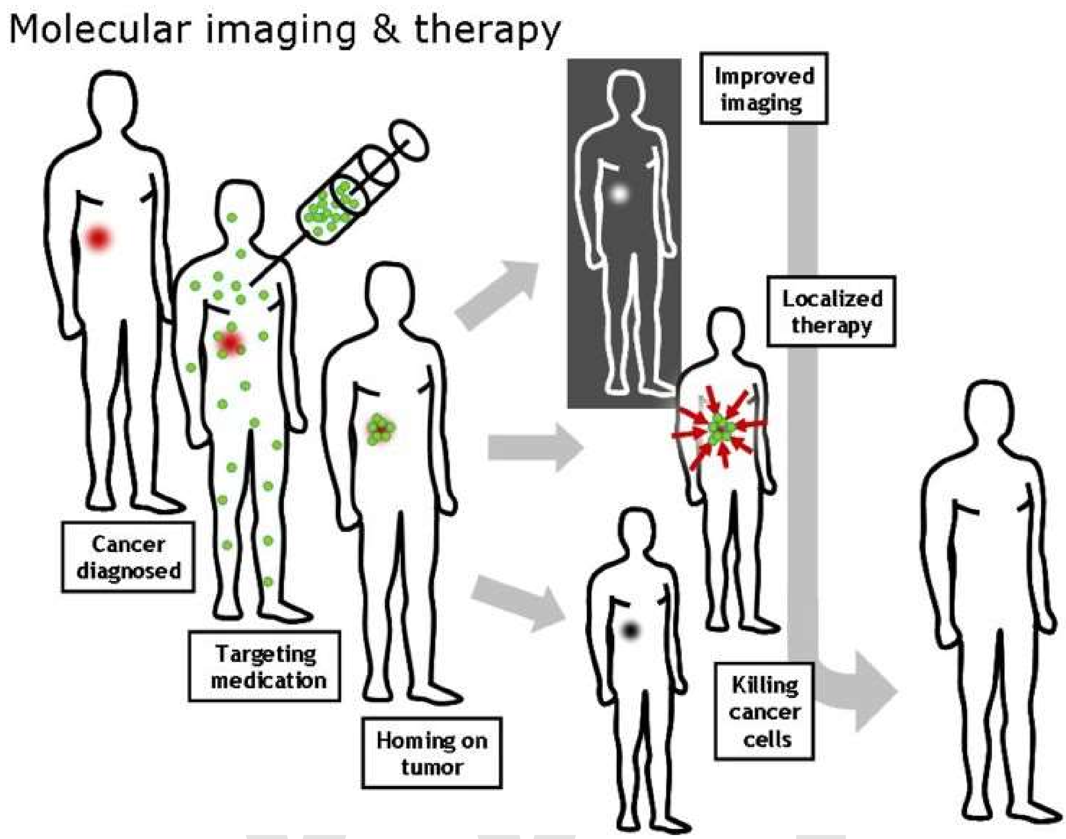
Nanomedical approaches to drug delivery center on developing nanoscale particles or molecules to improve drug bioavailability. Bioavailability refers to the presence of drug molecules where they are needed in the body and where they will do the most good. Drug delivery focuses on maximizing bioavailability both at specific places in the body and over a period of time. This can potentially be achieved by molecular targeting by nanoengineered devices. It is all about targeting the molecules and delivering drugs with cell precision. More than $65 billion are wasted each year due to poor bioavailability. *In vivo* imaging is another area where tools and devices are being developed. Using nanoparticle contrast agents, images such as ultrasound and MRI have a favorable distribution and improved contrast. The new methods of nanoengineered materials that are being developed might be effective in treating illnesses and diseases such as cancer. What nanoscientists will be able to achieve in the future is beyond current imagination. This might be accomplished by self assembled biocompatible nanodevices that will detect, evaluate, treat and report to the clinical doctor automatically.

Drug delivery systems, lipid- or polymer-based nanoparticles, can be designed to improve the pharmacological and therapeutic properties of drugs. The strength of drug delivery systems is their ability to alter the pharmacokinetics and biodistribution of the drug. Nanoparticles have unusual properties that can be used to improve drug delivery. Where larger particles would have been cleared from the body, cells take up these nanoparticles because of their size. Complex drug delivery mechanisms are being developed, including the ability to get drugs through cell membranes and into cell cytoplasm. Efficiency is important because many diseases depend upon processes within the cell and can only be impeded by drugs that make their way into the cell. Triggered response is one way for drug molecules to be used more efficiently. Drugs are placed in the body and only activate on encountering a particular signal. For example, a drug with poor solubility will be replaced by a drug delivery system where both hydrophilic and hydrophobic environments exist, improving the solubility. Also, a drug may cause tissue damage, but with drug delivery, regulated drug release can eliminate the problem. If a drug is cleared too quickly from the body, this could force a patient to use high doses, but with drug delivery systems clearance can be reduced by altering the pharmacokinetics of the drug. Poor biodistribution is a problem that can affect normal tissues through widespread distribution, but the particulates from drug delivery systems lower the volume of distribution and reduce the effect on non-target tissue. Potential nanodrugs will work by very specific and well-understood mechanisms; one of the major impacts of nanotechnology and nanoscience will be in leading development of completely new drugs with more useful behavior and less side effects.

Protein and peptide delivery

Protein and peptides exert multiple biological actions in human body and they have been identified as showing great promise for treatment of various diseases and disorders. These macromolecules are called biopharmaceuticals. Targeted and/or controlled delivery of these biopharmaceuticals using nanomaterials like nanoparticles and Dendrimers is an emerging field called nanobiopharmaceutics, and these products are called nanobiopharmaceuticals.

Cancer



A schematic illustration showing how nanoparticles or other cancer drugs might be used to treat cancer.

The small size of nanoparticles endows them with properties that can be very useful in oncology, particularly in imaging. Quantum dots (nanoparticles with quantum confinement properties, such as size-tunable light emission), when used in conjunction with MRI (magnetic resonance imaging), can produce exceptional images of tumor sites. These nanoparticles are much brighter than organic dyes and only need one light source for excitation. This means that the use of fluorescent quantum dots could produce a higher contrast image and at a lower cost than today's organic dyes used as contrast media. The downside, however, is that quantum dots are usually made of quite toxic elements.

Another nanoproperty, high surface area to volume ratio, allows many functional groups to be attached to a nanoparticle, which can seek out and bind to certain tumor cells. Additionally, the small size of nanoparticles (10 to 100 nanometers), allows them to preferentially accumulate at tumor sites (because tumors lack an effective lymphatic drainage system). A very exciting research question is how to make these imaging nanoparticles do more things for cancer. For instance, is it possible to manufacture multifunctional nanoparticles that would detect, image, and then proceed to treat a tumor?

This question is under vigorous investigation; the answer to which could shape the future of cancer treatment. A promising new cancer treatment that may one day replace radiation and chemotherapy is edging closer to human trials. Kanzius RF therapy attaches microscopic nanoparticles to cancer cells and then "cooks" tumors inside the body with radio waves that heat only the nanoparticles and the adjacent (cancerous) cells.

Sensor test chips containing thousands of nanowires, able to detect proteins and other biomarkers left behind by cancer cells, could enable the detection and diagnosis of cancer in the early stages from a few drops of a patient's blood.

The basic point to use drug delivery is based upon three facts: a) efficient encapsulation of the drugs, b) successful delivery of said drugs to the targeted region of the body, and c) successful release of that drug there.

Researchers at Rice University under Prof. Jennifer West, have demonstrated the use of 120 nm diameter nanoshells coated with gold to kill cancer tumors in mice. The nanoshells can be targeted to bond to cancerous cells by conjugating antibodies or peptides to the nanoshell surface. By irradiating the area of the tumor with an infrared laser, which passes through flesh without heating it, the gold is heated sufficiently to cause death to the cancer cells.

Nanoparticles of cadmium selenide (quantum dots) glow when exposed to ultraviolet light. When injected, they seep into cancer tumors. The surgeon can see the glowing tumor, and use it as a guide for more accurate tumor removal.

One scientist, University of Michigan’s James Baker, believes he has discovered a highly efficient and successful way of delivering cancer-treatment drugs that is less harmful to the surrounding body. Baker has developed a nanotechnology that can locate and then eliminate cancerous cells. He looks at a molecule called a dendrimer. This molecule has over one hundred hooks on it that allow it to attach to cells in the body for a variety of purposes. Baker then attaches folic-acid to a few of the hooks (folic-acid, being a vitamin, is received by cells in the body). Cancer cells have more vitamin receptors than normal cells, so Baker's vitamin-laden dendrimer will be absorbed by the cancer cell. To the rest of the hooks on the dendrimer, Baker places anti-cancer drugs that will be absorbed with the dendrimer into the cancer cell, thereby delivering the cancer drug to the cancer cell and nowhere else (Bullis 2006).

In photodynamic therapy, a particle is placed within the body and is illuminated with light from the outside. The light gets absorbed by the particle and if the particle is metal, energy from the light will heat the particle and surrounding tissue. Light may also be used to produce high energy oxygen molecules which will chemically react with and destroy most organic molecules that are next to them (like tumors). This therapy is appealing for many reasons. It does not leave a “toxic trail” of reactive molecules throughout the body (chemotherapy) because it is directed where only the light is shined and the particles exist. Photodynamic therapy has potential for a noninvasive procedure for dealing with diseases, growth and tumors.

Surgery

At Rice University, a flesh welder is used to fuse two pieces of chicken meat into a single piece. The two pieces of chicken are placed together touching. A greenish liquid containing gold-coated nanoshells is dribbled along the seam. An infrared laser is traced along the seam, causing the two sides to weld together. This could solve the difficulties and blood leaks caused when the surgeon tries to restitch the arteries s/he has cut during a kidney or heart transplant. The flesh welder could weld the artery perfectly.

Visualization

Tracking movement can help determine how well drugs are being distributed or how substances are metabolized. It is difficult to track a small group of cells throughout the body, so scientists used to dye the cells. These dyes needed to be excited by light of a certain wavelength in order for them to light up. While different color dyes absorb different frequencies of light, there was a need for as many light sources as cells. A way around this problem is with luminescent tags. These tags are quantum dots attached to proteins that penetrate cell membranes. The dots can be random in size, can be made of bio-inert material, and they demonstrate the nanoscale property that color is size-dependent. As a result, sizes are selected so that the frequency of light used to make a group of quantum dots fluoresce is an even multiple of the frequency required to make another group incandesce. Then both groups can be lit with a single light source.

Nanoparticle targeting

It is greatly observed that nanoparticles are promising tools for the advancement of drug delivery, medical imaging, and as diagnostic sensors. However, the biodistribution of these nanoparticles is mostly unknown due to the difficulty in targeting specific organs in the body. Current research in the excretory systems of mice, however, shows the ability of gold composites to selectively target certain organs based on their size and charge. These composites are encapsulated by a dendrimer and assigned a specific charge and size. Positively-charged gold nanoparticles were found to enter the kidneys while negatively-charged gold nanoparticles remained in the liver and spleen. It is suggested that the positive surface charge of the nanoparticle decreases the rate of osponization of nanoparticles in the liver, thus affecting the excretory pathway. Even at a relatively small size of 5 nm, though, these particles can become compartmentalized in the peripheral tissues, and will therefore accumulate in the body over time. While advancement of research proves that targeting and distribution can be augmented by nanoparticles, the dangers of nanotoxicity become an important next step in further understanding of their medical uses.

Neuro-electronic interfaces

Neuro-electronic interfacing is a visionary goal dealing with the construction of nanodevices that will permit computers to be joined and linked to the nervous system. This idea requires the building of a molecular structure that will permit control and detection of nerve impulses by an external computer. The computers will be able to interpret, register, and respond to signals the body gives off when it feels sensations. The demand for such structures is huge because many diseases involve the decay of the nervous system (ALS and multiple sclerosis). Also, many injuries and accidents may impair the nervous system resulting in dysfunctional systems and paraplegia. If computers could control the nervous system through neuro-electronic interface, problems that impair the system could be controlled so that effects of diseases and injuries could be overcome. Two considerations must be made when selecting the power source for such applications. They are refuelable and nonrefuelable strategies. A refuelable strategy implies energy is refilled continuously or periodically with external sonic, chemical, tethered, magnetic, or electrical sources. A nonrefuelable strategy implies that all power is drawn from internal energy storage which would stop when all energy is drained.

One limitation to this innovation is the fact that electrical interference is a possibility. Electric fields, electromagnetic pulses (EMP), and stray fields from other *in vivo* electrical devices can all cause interference. Also, thick insulators are required to prevent electron leakage, and if high conductivity of the *in vivo* medium occurs there is a risk of sudden power loss and “shorting out.” Finally, thick wires are also needed to conduct substantial power levels without overheating. Little practical progress has been made even though research is happening. The wiring of the structure is extremely difficult because they must be positioned precisely in the nervous system so that it is able to monitor and respond to nervous signals. The structures that will provide the interface must also be compatible with the body’s immune system so that they will remain unaffected in the body for a long time. In addition, the structures must also sense ionic currents and be able to cause currents to flow backward. While the potential for these structures is amazing, there is no timetable for when they will be available.

Medical applications of molecular nanotechnology

Molecular nanotechnology is a speculative subfield of nanotechnology regarding the possibility of engineering molecular assemblers, machines which could re-order matter at a molecular or atomic scale. Molecular nanotechnology is highly theoretical, seeking to anticipate what inventions nanotechnology might yield and to propose an agenda for future inquiry. The proposed elements of molecular nanotechnology, such as molecular assemblers and nanorobots are far beyond current capabilities.

Nanorobots

The somewhat speculative claims about the possibility of using nanorobots in medicine, advocates say, would totally change the world of medicine once it is realized. Nanomedicine would make use of these nanorobots (e.g., Computational Genes), introduced into the body, to repair or detect damages and infections. According to Robert Freitas of the Institute for Molecular Manufacturing, a typical blood borne medical nanorobot would be between 0.5-3 micrometres in size, because that is the maximum size possible due to capillary passage requirement. Carbon could be the primary element used to build these nanorobots due to the inherent strength and other characteristics of some forms of carbon (diamond/fullerene composites), and nanorobots would be fabricated in desktop nanofactories specialized for this purpose.

Nanodevices could be observed at work inside the body using MRI, especially if their components were manufactured using mostly ^{13}C atoms rather than the natural ^{12}C isotope of carbon, since ^{13}C has a nonzero nuclear magnetic moment. Medical nanodevices would first be injected into a human body, and would then go to work in a specific organ or tissue mass. The doctor will monitor the progress, and make certain that the nanodevices have gotten to the correct target treatment region. The doctor will also be able to scan a section of the body, and actually see the nanodevices congregated neatly around their target (a tumor mass, etc.) so that he or she can be sure that the procedure was successful.

Cell repair machines

Using drugs and surgery, doctors can only encourage tissues to repair themselves. With molecular machines, there will be more direct repairs. Cell repair will utilize the same tasks that living systems already prove possible. Access to cells is possible because biologists can stick needles into cells without killing them. Thus, molecular machines are capable of entering the cell. Also, all specific biochemical interactions show that molecular systems can recognize other molecules by touch, build or rebuild every molecule in a cell, and can disassemble damaged molecules. Finally, cells that replicate prove that molecular systems can assemble every system found in a cell. Therefore, since nature has demonstrated the basic operations needed to perform molecular-level cell repair, in the future, nanomachine based systems will be built that are able to enter cells, sense differences from healthy ones and make modifications to the structure.

The healthcare possibilities of these cell repair machines are impressive. Comparable to the size of viruses or bacteria, their compact parts would allow them to be more complex. The early machines will be specialized. As they open and close cell membranes or travel through tissue and enter cells and viruses, machines will only be able to correct a single molecular disorder like DNA damage or enzyme deficiency. Later, cell repair machines will be programmed with more abilities with the help of advanced AI systems.

Nanocomputers will be needed to guide these machines. These computers will direct machines to examine, take apart, and rebuild damaged molecular structures. Repair machines will be able to repair whole cells by working structure by structure. Then by working cell by cell and tissue by tissue, whole organs can be repaired. Finally, by working organ by organ, health is restored to the body. Cells damaged to the point of inactivity can be repaired because of the ability of molecular machines to build cells from scratch. Therefore, cell repair machines will free medicine from reliance on self repair alone.

Nanonephrology

Nanonephrology is a branch of nanomedicine and nanotechnology that deals with 1) the study of kidney protein structures at the atomic level; 2) nano-imaging approaches to study cellular processes in kidney cells; and 3) nano medical treatments that utilize nanoparticles and to treat various kidney diseases. The creation and use of materials and devices at the molecular and atomic levels that can be used for the diagnosis and therapy of renal diseases is also a part of Nanonephrology that will play a role in the management of patients with kidney disease in the future. Advances in Nanonephrology will be based on discoveries in the above areas that can provide nano-scale information on the cellular molecular machinery involved in normal kidney processes and in pathological states. By understanding the physical and chemical properties of proteins and other macromolecules at the atomic level in various cells in the kidney, novel therapeutic approaches can be designed to combat major renal diseases. The nano-scale artificial kidney is a goal that many physicians dream of. Nano-scale engineering advances will permit programmable and controllable nano-scale robots to execute curative and reconstructive procedures in the human kidney at the cellular and molecular levels. Designing nanostructures compatible with the kidney cells and that can safely operate in vivo is also a future goal. The ability to direct events in a controlled fashion at the cellular nano-level has the potential of significantly improving the lives of patients with kidney diseases.

Bottom-up approaches

These seek to arrange smaller components into more complex assemblies.

- DNA nanotechnology utilizes the specificity of Watson–Crick basepairing to construct well-defined structures out of DNA and other nucleic acids.
- Approaches from the field of "classical" chemical synthesis also aim at designing molecules with well-defined shape (e.g. bis-peptides).
- More generally, molecular self-assembly seeks to use concepts of supramolecular chemistry, and molecular recognition in particular, to cause single-molecule components to automatically arrange themselves into some useful conformation.

Top-down approaches

These seek to create smaller devices by using larger ones to direct their assembly.

- Many technologies that descended from conventional solid-state silicon methods for fabricating microprocessors are now capable of creating features smaller than 100 nm, falling under the definition of nanotechnology. Giant magnetoresistance-based hard drives already on the market fit this description, as do atomic layer deposition (ALD) techniques. Peter Grünberg and Albert Fert received the Nobel Prize in Physics in 2007 for their discovery of Giant magnetoresistance and contributions to the field of spintronics.

- Solid-state techniques can also be used to create devices known as nanoelectromechanical systems or NEMS, which are related to microelectromechanical systems or MEMS.
- Atomic force microscope tips can be used as a nanoscale "write head" to deposit a chemical upon a surface in a desired pattern in a process called dip pen nanolithography. This fits into the larger subfield of nanolithography.
- Focused ion beams can directly remove material, or even deposit material when suitable pre-cursor gasses are applied at the same time. For example, this technique is used routinely to create sub-100 nm sections of material for analysis in Transmission electron microscopy.

Functional approaches

These seek to develop components of a desired functionality without regard to how they might be assembled.

- Molecular electronics seeks to develop molecules with useful electronic properties. These could then be used as single-molecule components in a nanoelectronic device.
- Synthetic chemical methods can also be used to create synthetic molecular motors, such as in a so-called nanocar.

Biomimetic approaches

- Bionics or biomimicry seeks to apply biological methods and systems found in nature, to the study and design of engineering systems and modern technology. Biomineralization is one example of the systems studied.

- Bionanotechnology the use of biomolecules for applications in nanotechnology, including use of viruses.

Speculative

These subfields seek to anticipate what inventions nanotechnology might yield, or attempt to propose an agenda along which inquiry might progress. These often take a big-picture view of nanotechnology, with more emphasis on its societal implications than the details of how such inventions could actually be created.

- Molecular nanotechnology is a proposed approach which involves manipulating single molecules in finely controlled, deterministic ways. This is more theoretical than the other subfields and is beyond current capabilities.
- Nanorobotics centers on self-sufficient machines of some functionality operating at the nanoscale. There are hopes for applying nanorobots in medicine, but it may not be easy to do such a thing because of several drawbacks of such devices. Nevertheless, progress on innovative materials and methodologies has been demonstrated with some patents granted about new nanomanufacturing devices

for future commercial applications, which also progressively helps in the development towards nanorobots with the use of embedded nanobioelectronics concepts.

Nanorobotics is the technology of creating machines or robots at or close to the microscopic scale of a nanometer (10^{-9} meters). More specifically, nanorobotics refers to the still largely hypothetical nanotechnology engineering discipline of designing and building **nanorobots**, devices ranging in size from 0.1-10 micrometers and constructed of nanoscale or molecular components. As of 2010 nobody has yet built artificial non-biological nanorobots: they remain a hypothetical concept. The names **nanobots**, **nanoids**, **nanites** or **nanomites** have also been used to describe these hypothetical devices.

Another definition is a robot that allows precision interactions with nanoscale objects, or can manipulate with nanoscale resolution. Following this definition even a large apparatus such as an atomic force microscope can be considered a nanorobotic instrument when configured to perform nanomanipulation. Also, macroscale robots or microrobots that can move with nanoscale precision can also be considered nanorobots.

Nanomachines are largely in the research-and-development phase, but some primitive molecular machines have been tested. An example is a sensor having a switch approximately 1.5 nanometers across, capable of counting specific molecules in a chemical sample. The first useful applications of nanomachines, if such are ever built, might be in medical technology, which might use them to identify and destroy cancer cells. Another potential application is the detection of toxic chemicals, and the measurement of their concentrations, in the environment. Recently, Rice University has demonstrated a single-molecule car developed by a chemical process and including buckyballs for wheels. It is actuated by controlling the environmental temperature and by positioning a scanning tunneling microscope tip.

Nanorobotics theory

Since nanorobots would be microscopic in size, it would probably be necessary for very large numbers of them to work together to perform microscopic and macroscopic tasks. These nanorobot swarms, both those incapable of replication (as in utility fog) and those capable of unconstrained replication in the natural environment (as in grey goo and its less common variants), are found in many science fiction stories, such as the Borg nanoprobes in *Star Trek* and The Outer Limits episode The New Breed. The word "nanobot" (also "nanite", "nanogene", or "nanoant") is often used to indicate this fictional context and is an informal or even pejorative term to refer to the engineering concept of nanorobots. The word nanorobot is the correct technical term in the nonfictional context of serious engineering studies.

Some proponents of nanorobotics, in reaction to the grey goo scare scenarios that they earlier helped to propagate, hold the view that nanorobots capable of replication outside of a restricted factory environment do not form a necessary part of a purported productive nanotechnology, and that the process of self-replication, if it were ever to be developed, could be made inherently safe. They further assert that their current plans for developing and using molecular manufacturing do not in fact include free-foraging replicators.

Approaches

Biochip

The joint use of nanoelectronics, photolithography, and new biomaterials provides a possible approach to manufacturing nanorobots for common medical applications, such as for surgical instrumentation, diagnosis and drug delivery. This method for manufacturing on nanotechnology scale is currently in use in the electronics industry. So, practical nanorobots should be integrated as nanoelectronics devices, which will allow tele-operation and advanced capabilities for medical instrumentation.

Nubots

Nubot is an abbreviation for "nucleic acid robots". Nubots are synthetic robotics devices at the nanoscale. Representative nubots include the several DNA walkers reported by Ned Seeman's group at NYU, Niles Pierce's group at Caltech, John Reif's group at Duke University, Chengde Mao's group at Purdue, and Andrew Turberfield's group at the University of Oxford.

Positional nanoassembly

Nanofactory Collaboration, founded by Robert Freitas and Ralph Merkle in 2000, is a focused ongoing effort involving 23 researchers from 10 organizations and 4 countries that is developing a practical research agenda specifically aimed at developing positionally-controlled diamond mechanosynthesis and a diamondoid nanofactory that would have the capability of building diamondoid medical nanorobots.

Bacteria based

This approach proposes the use of biological microorganisms, like the bacterium *Escherichia coli*. Hence, the model uses a flagellum for propulsion purposes. The use of electromagnetic fields are normally applied to control the motion of this kind of biological integrated device, but has limited applications.

Open technology

A document with a proposal on nanobiotech development using open technology approaches has been addressed to the United Nations General Assembly. According to the document sent to the UN, in the same way that Open Source has in recent years accelerated the development of computer systems, a similar approach should benefit the society at large and accelerate nanorobotics development. The use of nanobiotechnology should be established as a human heritage for the coming generations, and developed as an open technology based on ethical practices for peaceful purposes. Open technology is stated as a fundamental key for such an aim.

Potential applications

Nanomedicine

Potential applications for nanorobotics in medicine include early diagnosis and targeted drug-delivery for cancer,, biomedical instrumentation surgery,, pharmacokinetics monitoring of diabetes, and health care.

In such plans, future medical nanotechnology is expected to employ nanorobots injected into the patient to perform work at a cellular level. Such nanorobots intended for use in medicine should be non-replicating, as replication would needlessly increase device complexity, reduce reliability, and interfere with the medical mission. Instead, medical nanorobots are posited to be manufactured in hypothetical, carefully controlled nanofactories in which nanoscale machines would be solidly integrated into a supposed desktop-scale machine that would build macroscopic products.

The most detailed theoretical discussion of nanorobotics, including specific design issues such as sensing, power communication, navigation, manipulation, locomotion, and onboard computation, has been presented in the medical context of nanomedicine by Robert Freitas. Some of these discussions remain at the level of unbuildable generality and do not approach the level of detailed engineering.

Nanorobots

Nanotechnology promises futuristic applications such as microscopic robots that assemble other machines or travel inside the body to deliver drugs or do microsurgery.These machines will face some unique physics. At small scales, fluids appear as viscous as molasses, and Brownian motion makes everything shake incessantly. Taking inspiration from the biological motors of living cells, chemists are learning how to utilize protein dynamics to power microsize and nanosize machines with catalytic reactions.

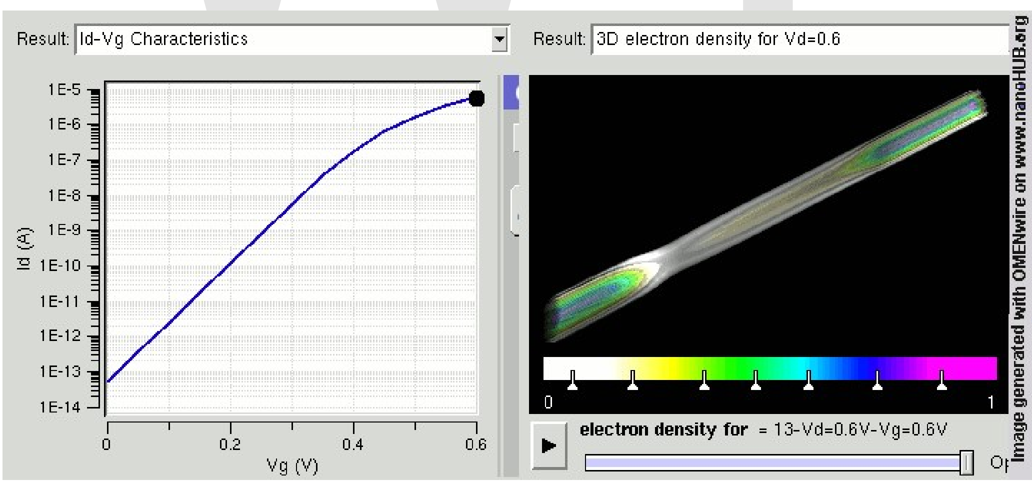
- Productive nanosystems are "systems of nanosystems" which will be complex nanosystems that produce atomically precise parts for other nanosystems, not necessarily using novel nanoscale-emergent properties, but well-understood fundamentals of manufacturing. Because of the discrete (i.e. atomic) nature of matter and the possibility of exponential growth, this stage is seen as the basis of another industrial revolution. Mihail Roco, one of the architects of the USA's National Nanotechnology Initiative, has proposed four states of nanotechnology that seem to parallel the technical progress of the Industrial Revolution, progressing from passive nanostructures to active nanodevices to complex nanomachines and ultimately to productive nanosystems.

- Programmable matter seeks to design materials whose properties can be easily, reversibly and externally controlled though a fusion of information science and materials science.
- Due to the popularity and media exposure of the term nanotechnology, the words picotechnology and femtotechnology have been coined in analogy to it, although these are only used rarely and informally.

Chapter-5

Nanotechnology Applications

With nanotechnology, a large set of materials and improved products rely on a change in the physical properties when the feature sizes are shrunk. Nanoparticles, for example, take advantage of their dramatically increased surface area to volume ratio. Their optical properties, e.g. fluorescence, become a function of the particle diameter. When brought into a bulk material, nanoparticles can strongly influence the mechanical properties of the material, like stiffness or elasticity. For example, traditional polymers can be reinforced by nanoparticles resulting in novel materials which can be used as lightweight replacements for metals. Therefore, an increasing societal benefit of such nanoparticles can be expected. Such nanotechnologically enhanced materials will enable a weight reduction accompanied by an increase in stability and improved functionality. Practical nanotechnology is essentially the increasing ability to manipulate (with precision) matter on previously impossible scales, presenting possibilities which many could never have imagined - it therefore seems unsurprising that few areas of human technology are exempt from the benefits which nanotechnology could potentially bring.



One of the major application of nanotechnology is in the area of nanoelectronics with MOSFET's being made of small nanowires ~10 nm in length. Here is a simulation of such a nanowire

Medicine

The biological and medical research communities have exploited the unique properties of nanomaterials for various applications (e.g., contrast agents for cell imaging and therapeutics for treating cancer). Terms such as *biomedical nanotechnology*, *nanobiotechnology*, and *nanomedicine* are used to describe this hybrid field. Functionalities can be added to nanomaterials by interfacing them with biological molecules or structures. The size of nanomaterials is similar to that of most biological molecules and structures; therefore, nanomaterials can be useful for both in vivo and in vitro biomedical research and applications. Thus far, the integration of nanomaterials with biology has led to the development of diagnostic devices, contrast agents, analytical tools, physical therapy applications, and drug delivery vehicles.

Diagnostics

Nanotechnology-on-a-chip is one more dimension of lab-on-a-chip technology. Magnetic nanoparticles, bound to a suitable antibody, are used to label specific molecules, structures or microorganisms. Gold nanoparticles tagged with short segments of DNA can be used for detection of genetic sequence in a sample. Multicolor optical coding for biological assays has been achieved by embedding different-sized quantum dots into polymeric microbeads. Nanopore technology for analysis of nucleic acids converts strings of nucleotides directly into electronic signatures.

Drug delivery

Nanotechnology has been a boom in medical field by delivering drugs to specific cells using nanoparticles. The overall drug consumption and side-effects can be lowered significantly by depositing the active agent in the morbid region only and in no higher dose than needed. This highly selective approach reduces costs and human suffering. An example can be found in dendrimers and nanoporous materials. Another example is to use block co-polymers, which form micelles for drug encapsulation. They could hold small drug molecules transporting them to the desired location. Another vision is based on small electromechanical systems; NEMS are being investigated for the active release of drugs. Some potentially important applications include cancer treatment with iron nanoparticles or gold shells. A targeted or personalized medicine reduces the drug consumption and treatment expenses resulting in an overall societal benefit by reducing the costs to the public health system. Nanotechnology is also opening up new opportunities in implantable delivery systems, which are often preferable to the use of injectable drugs, because the latter frequently display first-order kinetics (the blood concentration goes up rapidly, but drops exponentially over time). This rapid rise may cause difficulties with toxicity, and drug efficacy can diminish as the drug concentration falls below the targeted range.

Buckyballs can "interrupt" the allergy/immune response by preventing mast cells (which cause allergic response) from releasing histamine into the blood and tissues, by binding to free radicals "dramatically better than any anti-oxidant currently available, such as vitamin E".

Tissue engineering

Nanotechnology can help to reproduce or to repair damaged tissue. “Tissue engineering” makes use of artificially stimulated cell proliferation by using suitable nanomaterial-based scaffolds and growth factors. For example, bones can be regrown on carbon nanotube scaffolds. Tissue engineering might replace today's conventional treatments like organ transplants or artificial implants. Advanced forms of tissue engineering may lead to life extension.

Chemistry and environment

Chemical catalysis and filtration techniques are two prominent examples where nanotechnology already plays a role. The synthesis provides novel materials with tailored features and chemical properties: for example, nanoparticles with a distinct chemical surrounding (ligands), or specific optical properties. In this sense, chemistry is indeed a basic nanoscience. In a short-term perspective, chemistry will provide novel “nanomaterials” and in the long run, superior processes such as “self-assembly” will enable energy and time preserving strategies. In a sense, all chemical synthesis can be understood in terms of nanotechnology, because of its ability to manufacture certain molecules. Thus, chemistry forms a base for nanotechnology providing tailor-made molecules, polymers, etcetera, as well as clusters and nanoparticles.

Catalysis

Chemical catalysis benefits especially from nanoparticles, due to the extremely large surface to volume ratio. The application potential of nanoparticles in catalysis ranges from fuel cell to catalytic converters and photocatalytic devices. Catalysis is also important for the production of chemicals.

Platinum nanoparticles are now being considered in the next generation of automotive catalytic converters because the very high surface area of nanoparticles could reduce the amount of platinum required. However, some concerns have been raised due to experiments demonstrating that they will spontaneously combust if methane is mixed with the ambient air. Ongoing research at the Centre National de la Recherche Scientifique (CNRS) in France may resolve their true usefulness for catalytic applications. Nanofiltration may come to be an important application, although future research must be careful to investigate possible toxicity.

Filtration

A strong influence of photochemistry on waste-water treatment, air purification and energy storage devices is to be expected. Mechanical or chemical methods can be used for effective filtration techniques. One class of filtration techniques is based on the use of membranes with suitable hole sizes, whereby the liquid is pressed through the membrane. Nanoporous membranes are suitable for a mechanical filtration with extremely small pores smaller than 10 nm ("nanofiltration") and may be composed of nanotubes. Nanofiltration is mainly used for the removal of ions or the separation of different fluids. On a larger scale, the membrane filtration technique is named ultrafiltration, which works down to between 10 and 100 nm. One important field of application for ultrafiltration is medical purposes as can be found in renal dialysis. Magnetic nanoparticles offer an effective and reliable method to remove heavy metal contaminants from waste water by making use of magnetic separation techniques. Using nanoscale particles increases the efficiency to absorb the contaminants and is comparatively inexpensive compared to traditional precipitation and filtration methods.

Some water-treatment devices incorporating nanotechnology are already on the market, with more in development. Low-cost nanostructured separation membranes methods have been shown to be effective in producing potable water in a recent study.

Energy

Over the past few decades, the fields of science and engineering have been seeking to develop new and improved types of energy technologies that have the capability of improving life all over the world. In order to make the next leap forward from the current generation of technology, scientists and engineers have been developing **Energy Applications of Nanotechnology**. Nanotechnology, a new field in science, is any technology that contains components smaller than 100 nanometers. For scale, a single virus particle is about 100 nanometers in width.

An important subfield of nanotechnology related to energy is nanofabrication. Nanofabrication is the process of designing and creating devices on the nanoscale. Creating devices smaller than 100 nanometers opens many doors for the development of new ways to capture, store, and transfer energy. The inherent level of control that nanofabrication could give scientists and engineers would be critical in providing the capability of solving many of the problems that the world is facing today related to the current generation of energy technologies.

People in the fields of science and engineering have already begun developing ways of utilizing nanotechnology for the development of consumer products. Benefits already observed from the design of these products are an increased efficiency of lighting and heating, increased electrical storage capacity, and a decrease in the amount of pollution from the use of energy. Benefits such as these make the investment of capital in the research and development of nanotechnology a top priority.

Consumer products

Recently, previously established and entirely new companies such as BetaBatt, Inc. and Oxane Materials are focusing on nanomaterials as a way to develop and improve upon older methods for the capture, transfer, and storage of energy for the development of consumer products.

ConsERV, a product developed by the Dais Analytic Corporation, uses nanoscale polymer membranes to increase the efficiency of heating and cooling systems and has already proven to be a lucrative design. The polymer membrane was specifically configured for this application by selectively engineering the size of the pores in the membrane to prevent air from passing, while allowing moisture to pass through the membrane. Polymer membranes can be designed to selectively allow particles of one size and shape to pass through while preventing others of different dimensions. This makes for a powerful tool that can be used in consumer products from biological weapons protection to industrial chemical separations.

A New York based company called Applied NanoWorks, Inc. has been developing a consumer product that utilizes LED technology to generate light. Light-emitting diodes or LEDs, use only about 10% of the energy that a typical incandescent or fluorescent light bulb uses and typically last much longer, which makes them a viable alternative to traditional light bulbs. While LEDs have been around for decades, this company and others like it have been developing a special variant of LED called the white LED. White LEDs consist of semi-conducting organic layers that are only about 100 nanometers in distance from each other and are placed between two electrodes, which create an anode, and a cathode. When voltage is applied to the system, light is generated when electricity passes through the two organic layers. This is called electroluminescence. The semiconductor properties of the organic layers are what allow for the minimal amount of energy necessary to generate light. In traditional light bulbs, a metal filament is used to generate light when electricity is run through the filament. Using metal generates a great deal of heat and therefore lowers efficiency.

Research for longer lasting batteries has been an ongoing process for years. Researchers have now begun to utilize nanotechnology for battery technology. mPhase Technologies in conglomeration with Rutgers University and Bell Laboratories have utilized nanomaterials to alter the wetting behavior of the surface where the liquid in the battery lies to spread the liquid droplets over a greater area on the surface and therefore have greater control over the movement of the droplets. This gives more control to the designer of the battery. This control prevents reactions in the battery by separating the electrolytic liquid from the anode and the cathode when the battery is not in use and joining them when the battery is in need of use.

Thermal applications also are a future applications of nanothechonlogy creating low cost system of heating, ventilation, and air conditioning, changing molecular structure for better management of temperature

Economic benefits

The relatively recent shift toward using nanotechnology with respect to the capture, transfer, and storage of energy has and will continue to have many positive economic impacts on society. The control of materials that nanotechnology offers to scientists and engineers of consumer products is one of the most important aspects of nanotechnology. This allows for an improved efficiency of products across the board.

A major issue with current energy generation is the loss of efficiency from the generation of heat as a by-product of the process. A common example of this is the heat generated by the internal combustion engine. The internal combustion engine loses about 64% of the energy from gasoline as heat and an improvement of this alone could have a significant economic impact. However, improving the internal combustion engine in this respect has proven to be extremely difficult without sacrificing performance. Improving the efficiency of fuel cells through the use of nanotechnology appears to be more plausible by using molecularly tailored catalysts, polymer membranes, and improved fuel storage.

In order for a fuel cell to operate, particularly of the hydrogen variant, a noble-metal catalyst (usually platinum, which is very expensive) is needed to separate the electrons from the protons of the hydrogen atoms. However, catalysts of this type are extremely sensitive to carbon monoxide reactions. In order to combat this, alcohols or hydrocarbons compounds are used to lower the carbon monoxide concentration in the system. This adds an additional cost to the device. Using nanotechnology, catalysts can be designed through nanofabrication that are much more resistant to carbon monoxide reactions, which improves the efficiency of the process and may be designed with cheaper materials to additionally lower costs.

Fuel cells that are currently designed for transportation need rapid start-up periods for the practicality of consumer use. This process puts a lot of strain on the traditional polymer electrolyte membranes, which decreases the life of the membrane requiring frequent replacement. Using nanotechnology, engineers have the ability to create a much more durable polymer membrane, which addresses this problem. Nanoscale polymer membranes are also much more efficient in ionic conductivity. This improves the efficiency of the system and decreases the time between replacements, which lowers costs.

Another problem with contemporary fuel cells is the storage of the fuel. In the case of hydrogen fuel cells, storing the hydrogen in gaseous rather than liquid form improves the efficiency by 5%. However, the materials that we currently have available to us significantly limit fuel storage due to low stress tolerance and costs. Scientists have come up with an answer to this by using a nanoporous styrene material (which is a relatively inexpensive material) that when super-cooled to around -196^{o}C, naturally holds on to hydrogen atoms and when heated again releases the hydrogen for use.

Capacitors: then and now

For decades, scientists and engineers have been attempting to make computers smaller and more efficient. A crucial component of computers are capacitors. A capacitor is a device that is made of a pair of electrodes separated by an insulator that each stores an opposite charge. A capacitor stores a charge when it is removed from the circuit that it is connected to; the charge is released when it is replaced back into the circuit. Capacitors have an advantage over batteries in that they release their charge much more quickly than a battery.

Traditional or foil capacitors are composed of thin metal conducting plates separated by an electrical insulator, which are then stacked or rolled and placed in a casing. The problem with a traditional capacitor such as this is that they limit how small an engineer can design a computer. Scientists and engineers have since turned to nanotechnology for a solution to the problem.

Using nanotechnology, researchers developed what they call "ultracapacitors." An ultracapacitor is a general term that describes a capacitor that contains nanocomponents. Ultracapacitors are being researched heavily because of their high density interior, compact size, reliability, and high capacitance. This decrease in size makes it increasingly possible to develop much smaller circuits and computers. Ultracapacitors also have the capability to supplement batteries in hybrid vehicles by providing a large amount of energy during peak acceleration and allowing the battery to supply energy over longer periods of time, such as during a constant driving speed. This could decrease the size and weight of the large batteries needed in hybrid vehicles as well as take additional stress off the battery. However, as of now, the combination of ultracapacitors and a battery is not cost effective due to the need of additional DC/DC electronics to coordinate the two.

Nanoporous carbon aerogel is one type of material that is being utilized for the design of ultracapacitors. These aerogels have a very large interior surface area and can have its properties altered by changing the pore diameter and distribution along with adding nanosized alkali metals to alter its conductivity.

Carbon nanotubes are another possible material for use in an ultracapacitor. Carbon nanotubes are created by vaporizing carbon and allowing it to condense on a surface. When the carbon condenses, it forms a nanosized tube composed of carbon atoms. This tube has a high surface area, which increases the amount of charge that can be stored. The low reliability and high cost of using carbon nanotubes for ultracapacitors is currently an issue of research.

In a study concerning ultracapacitors or supercapacitors, researchers at the Sungkyunkwan University in the Republic of Korea explored the possibility of increasing the capacitance of electrodes through the addition of fluorine atoms to the walls of carbon nanotubes. As briefly mentioned before, carbon nanotubes are an increasing form of capacitors due to their superb chemical stability, high conductivity, light mass, and their large surface area. These researchers fluorinated single-walled carbon nanotubes (SWCNTs) at high temperatures to bind fluorine atoms to the walls. The attached fluorine atoms changed the non-polar nanotubes to become polar molecules. This can be attributed to the charge transfer from the fluorine. This created dipole-dipole layers along the carbon nanotube walls. Testing of these fluorinated SWCNTs against normal state

SWCNTs showed a difference in capacitance. It was determined that the fluorinated SWCNTs are advantageous in fabricating electrodes for capacitors and improve the wettability with aqueous electrolytes, which promotes the overall performance of supercapacitors. While this study brought to knowledge a more efficient example of capacitors, little is known about this new supercapacitor, large scale synthesis is lacking and is necessary for any massive production, and preparation conditions are quite tedious in achieving the final product.

Theory of capacitance

Understanding the concept of capacitance can be helpful in understanding why nanotechnology is such a powerful tool for the design of higher energy storing capacitors. A capacitor's capacitance (C) or amount of energy stored is equal to the amount of charge (Q) stored on each plate divided by the voltage (V) between the plates. Another representation of capacitance is that capacitance (C) is approximately equal to the permittivity (ε) of the dielectric times the area (A) of the plates divided by the distance (d) between them. Therefore, capacitance is proportional to the surface area of the conducting plate and inversely proportional to the distance between the plates.

Using carbon nanotubes as an example, a property of carbon nanotubes is that they have a very high surface area to store a charge. Using the above proportionality that capacitance (C) is proportional to the surface area (A) of the conducting plate; it becomes obvious that using nanoscaled materials with high surface area would be great for increasing capacitance. The other proportionality described above is that capacitance (C) is inversely proportional to the distance (d) between the plates. Using nanoscaled plates such as carbon nanotubes with nanofabrication techniques, gives the capability of decreasing the space between plates which again increases capacitance.

Reduction of energy consumption

A reduction of energy consumption can be reached by better insulation systems, by the use of more efficient lighting or combustion systems, and by use of lighter and stronger materials in the transportation sector. Currently used light bulbs only convert approximately 5% of the electrical energy into light. Nanotechnological approaches like light-emitting diodes (LEDs) or quantum caged atoms (QCAs) could lead to a strong reduction of energy consumption for illumination.

Increasing the efficiency of energy production

Today's best solar cells have layers of several different semiconductors stacked together to absorb light at different energies but they still only manage to use 40 percent of the Sun's energy. Commercially available solar cells have much lower efficiencies (15-20%). Nanotechnology could help increase the efficiency of light conversion by using nanostructures with a continuum of bandgaps.

The degree of efficiency of the internal combustion engine is about 30-40% at the moment. Nanotechnology could improve combustion by designing specific catalysts with maximized surface area. In 2005, scientists at the University of Toronto developed a spray-on nanoparticle substance that, when applied to a surface, instantly transforms it into a solar collector.

The use of more environmentally friendly energy systems

An example for an environmentally friendly form of energy is the use of fuel cells powered by hydrogen, which is ideally produced by renewable energies. Probably the most prominent nanostructured material in fuel cells is the catalyst consisting of carbon supported noble metal particles with diameters of 1-5 nm. Suitable materials for hydrogen storage contain a large number of small nanosized pores. Therefore many nanostructured materials like nanotubes, zeolites or alanates are under investigation. Nanotechnology can contribute to the further reduction of combustion engine pollutants by nanoporous filters, which can clean the exhaust mechanically, by catalytic converters based on nanoscale noble metal particles or by catalytic coatings on cylinder walls and catalytic nanoparticles as additive for fuels.

Recycling of batteries

Nanobatteries are fabricated batteries employing technology at the nanoscale, a scale of minuscule particles that measure less than 100 nanometers or $100x10^{-9}$ meters. In comparison, traditional Li-Ion technology uses active materials, such as cobalt-oxide or manganese oxide, with particles that range in size between 5 and 20 micrometers. It is hoped that nano-engineering will improve many of the failings of present battery technology, such as recharging time and battery 'memory'.

Several companies are researching and developing these technologies. In March 2005, Toshiba announced that they had a new Lithium-Ion battery with a nanostructured lattice at the cathode and anode that allowed the battery to recharge a surprising eighty times faster than previously. Prototype models were able to charge to eighty percent capacity in one minute, and were one hundred percent recharged after 10 minutes.

When a traditional lithium-ion battery is charged too quickly, it creates a bottleneck in which the lithium moving through electrolyte liquid from the negative electrode to the positive backs up on the surface of the liquid. Under slower charging conditions, the lithium "hides" in void space and does not cause a problem.

"Liquid electrolyte is unstable in the presence of metallic lithium and will cause all sorts of problems. That is why it is imperative to observe the slow-charging rate rule with lithium-ion batteries," Donald Sadoway, MIT professor of materials chemistry and an electrochemistry researcher, explained to TechNewsWorld. Sadoway said the consequences could be as severe as the battery exploding.

Background

Nanobatteries are generally described by three sections

• Anode

• Cathode

• Electrolyte

In Li-ion batteries the anode is well defined (graphite), so most research is being done on the cathode and electrolyte materials. Varying cathodes in nanobatteries

By reducing the size of the materials used in a nanobattery, higher conductivity can be reached, leading to an increase in power, in both charge and discharge.

Advantages

Using nanotechnology in the manufacture of batteries offers the following benefits:

•Increasing the available power from a battery and decreasing the time required to recharge a battery. These benefits are achieved by coating the surface of an electrode with nanoparticles. This increases the surface area of the electrode thereby allowing more current to flow between the electrode and the chemicals inside the battery. This technique could increase the efficiency of hybrid vehicles by significantly reducing the weight of the batteries needed to provide adequate power.

•Increasing the shelf life of a battery by using nanomaterials to separate liquids in the battery from the solid electrodes when there is no draw on the battery. This separation prevents the low level discharge that occurs in a conventional battery, which increases the shelf life of the battery dramatically.

•Reducing the possibility of batteries catching fire by providing less flammable electrode material.

Unique Fabrication

A gel is created by the chosen design and is used to impregnate the anodic pores. This impregnated gel is placed between membrane walls and on top of the electrolyte. The anodic film is placed below the electrolyte, with the width of the cathode being much smaller than the height of the cathode. The separation of the cathodes by the membrane walls creates in essence a series of nanobatteries. This is helpful in research because it allows each set of cathode to be tested separately, or all at once.

Academic Research

In 2007, the first cross-sectional observation of an all solid state Li-ion nanobattery was taken by TEM. By looking at a nanobattery in TEM, the deterioration on the battery interface due to cycling is able to be observed with an attempt to not only understand by finding the underlying causes behind battery deterioration. The next step in the process is to cycle the battery while in TEM so that the live deterioration can be observed. Three layers of the battery were looked at in TEM, with two nanobatteries observed. The first nanobattery was pristine and uncycled, while the second nanobattery was run through ten cycles so that the deterioration might be characterized. A large irreversible capacity between the first charge and discharge was seen in the cycled nanobattery. The capacity of the battery was also seen to disappear rapidly during cycling.

Printable batteries

Researchers at the University of California, Los Angeles have successfully developed a "nanotube ink" for manufacturing flexible batteries using printed electronics techniques. Using nanotube ink, the carbon cathode and manganese oxide electrolyte components of a zinc-carbon battery can be printed as different layers on a surface, over which an anode layer of zinc foil can be printed. The resultant battery is less than a millimeter thick. Although discharge currents of the batteries are at present below the level of practical use, the nanotubes in the ink allow the charge to conduct more efficiently than in a conventional battery, such that the nanotube technology could lead to improvements in battery performance.

Various companies, listed below, are working at making nanobatteries into a viable commercial technology.

Toshiba

By using nanomaterial, Toshiba has increased the surface area of the lithium and widened the bottleneck, allowing the particles to pass through the liquid and recharge the battery more quickly. Toshiba states that it tested a new battery by discharging and fully recharging one thousand times at 77 degrees and found that it lost only one percent of its capacity, an indication of a long battery life.

Toshiba's battery is 3.8 mm thick, 62 mm high and 35 mm deep.

A123Systems

A123Systems has also developed a commercial nano Li-Ion battery. A123 Systems claims their battery has the widest temperature range at -30C to 70C. Much like Toshiba's nanobattery, A123 Li-Ion batteries charge to "high capacity" in five minutes. Safety is a key feature touted by the A123 technology, with a video on their website of a nail drive test, in which a nail is driven through a traditional Li-Ion battery and an A123 Li-Ion battery, where the traditional battery flames up and bubbles at one end, the A123 battery simply emits a wisp of smoke at the penetration site. Thermal conductivity is another selling point for the A123 battery, with the claim that the A123 battery offers 4 times higher thermal conductivity than conventional Lithium-Ion cylindrical cells. The nanotechnology they employ is a patented nanophosphate technology.

Valence

Also in the market is Valence Technology, Inc. The technology they are marketing is Saphion Li-Ion Technology. Like A123, they are using a nanophosphate technology, and different active materials than traditional Li-Ion batteries.

Altair

AltairNano has also developed a nanobattery with a one-minute recharge. The advance that Altair claims to have made is in the optimization of nano-structured lithium titanate spinel oxide (LTO).

U.S. Photonics

U.S. Photonics is in the process of developing a nanobattery utilizing "environmentally friendly" nanomaterials for both the anode and cathode as well as arrays of individual nano-sized cell containers for the solid polymer electrolite. U.S. Photonics has recently received a National Science Foundation SBIR phase I grant for development of nanobattery technology.

Next Alternative Inc.

Next Alternative has a new Carbon Nanotube (CNT) battery that is a modification of existing car battery types that will allow for the battery to recharge in less than 10 minutes and has a Reserve Capacity of at least 8 times the original unmodified battery. The major difference comes from a typical lead acid battery providing 12-15 kW-hours of electricity or a range of 50–100 miles, where the CNT lead/lead-acid battery will deliver 380 miles distance between charges. This battery could also be recharged in under 10 minutes. The typical lead-acid battery has a recharge time between 4 and 10 hours. The recharge life of the battery (200 cycles for lead-acid) can be extended by at a minimum of 4 times with the new CNT lead/lead-acid battery.

Sony

Produced the first cobalt-based lithium-ion battery in 1991. Since the inception of this first Li-ion battery, the research of nanobatteries has been underway with Sony continuing their strides into the nanobattery field.

Because of the relatively low energy density of batteries the operating time is limited and a replacement or recharging is needed. The huge number of spent batteries and accumulators represent a disposal problem. The use of batteries with higher energy content or the use of rechargeable batteries or supercapacitors with higher rate of recharging using nanomaterials could be helpful for the battery disposal problem.

Information and communication

Current high-technology production processes are based on traditional top down strategies, where nanotechnology has already been introduced silently. The critical length scale of integrated circuits is already at the nanoscale (50 nm and below) regarding the gate length of transistors in CPUs or DRAM devices.

Memory Storage

Electronic memory designs in the past have largely relied on the formation of transistors. However, research into crossbar switch based electronics have offered an alternative using reconfigurable interconnections between vertical and horizontal wiring arrays to create ultra high density memories. Two leaders in this area are Nantero which has developed a carbon nanotube based crossbar memory called Nano-RAM and Hewlett-Packard which has proposed the use of memristor material as a future replacement of Flash memory.

Novel semiconductor devices

An example of such novel devices is based on spintronics.The dependence of the resistance of a material (due to the spin of the electrons) on an external field is called magnetoresistance. This effect can be significantly amplified (GMR - Giant Magneto-Resistance) for nanosized objects, for example when two ferromagnetic layers are separated by a nonmagnetic layer, which is several nanometers thick (e.g. Co-Cu-Co). The GMR effect has led to a strong increase in the data storage density of hard disks and made the gigabyte range possible. The so called tunneling magnetoresistance (TMR) is very similar to GMR and based on the spin dependent tunneling of electrons through adjacent ferromagnetic layers. Both GMR and TMR effects can be used to create a non-volatile main memory for computers, such as the so called magnetic random access memory or MRAM.

In 1999, the ultimate CMOS transistor developed at the Laboratory for Electronics and Information Technology in Grenoble, France, tested the limits of the principles of the MOSFET transistor with a diameter of 18 nm (approximately 70 atoms placed side by side). This was almost one tenth the size of the smallest industrial transistor in 2003 (130 nm in 2003, 90 nm in 2004, 65 nm in 2005 and 45 nm in 2007). It enabled the theoretical integration of seven billion junctions on a €1 coin. However, the CMOS transistor, which was created in 1999, was not a simple research experiment to study how CMOS technology functions, but rather a demonstration of how this technology functions now that we ourselves are getting ever closer to working on a molecular scale. Today it would be impossible to master the coordinated assembly of a large number of these transistors on a circuit and it would also be impossible to create this on an industrial level.

Novel optoelectronic devices

In the modern communication technology traditional analog electrical devices are increasingly replaced by optical or optoelectronic devices due to their enormous bandwidth and capacity, respectively. Two promising examples are photonic crystals and quantum dots. Photonic crystals are materials with a periodic variation in the refractive index with a lattice constant that is half the wavelength of the light used. They offer a selectable band gap for the propagation of a certain wavelength, thus they resemble a semiconductor, but for light or photons instead of electrons. Quantum dots are nanoscaled objects, which can be used, among many other things, for the construction of lasers. The advantage of a quantum dot laser over the traditional semiconductor laser is that their emitted wavelength depends on the diameter of the dot. Quantum dot lasers are cheaper and offer a higher beam quality than conventional laser diodes.

Displays

The production of displays with low energy consumption could be accomplished using carbon nanotubes (CNT). Carbon nanotubes are electrically conductive and due to their small diameter of several nanometers, they can be used as field emitters with extremely high efficiency for field emission displays (FED). The principle of operation resembles that of the cathode ray tube, but on a much smaller length scale.

Quantum computers

Entirely new approaches for computing exploit the laws of quantum mechanics for novel quantum computers, which enable the use of fast quantum algorithms. The Quantum computer has quantum bit memory space termed "Qubit" for several computations at the same time. This facility may improve the performance of the older systems.

Heavy Industry

An inevitable use of nanotechnology will be in heavy industry.

Aerospace

Lighter and stronger materials will be of immense use to aircraft manufacturers, leading to increased performance. Spacecraft will also benefit, where weight is a major factor. Nanotechnology would help to reduce the size of equipment and thereby decrease fuel-consumption required to get it airborne.

Hang gliders may be able to halve their weight while increasing their strength and toughness through the use of nanotech materials. Nanotech is lowering the mass of supercapacitors that will increasingly be used to give power to assistive electrical motors for launching hang gliders off flatland to thermal-chasing altitudes.

Construction

Nanotechnology has the potential to make construction faster, cheaper, safer, and more varied. Automation of nanotechnology construction can allow for the creation of structures from advanced homes to massive skyscrapers much more quickly and at much lower cost.

Nanotechnology and constructions

Nanotechnology is one of the most active research areas that encompass a number of disciplines Such as electronics, bio-mechanics and coatings including civil engineering and construction materials.

The use of nanotechnology in construction involves the development of new concept and understanding of the hydration of cement particles and the use of nano-size ingredients such as alumina and silica and other nanoparticles. The manufactures also investigating the methods of manufacturing of nano-cement. If cement with nano-size particles can be manufactured and processed, it will open up a large number of opportunities in the fields of ceramics, high strength composites and electronic applications. Since at the nanoscale the properties of the material are different from that of their bulk counter parts. When materials becomes nano-sized, the proportion of atoms on the surface increases relative to those inside and this leads to novel properties. Some applications of nanotechnology in construction are describe below.

Nanoparticles and concrete

Concrete is most commonly used material in the construction. It is the current active area of research and development. Researchers are trying to develope nano-sized concrete (or nano-concrete) and to understand its structure using Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Focused Ion Beam (FIB) as these understanding leads to appropriate use of nanotechnology in construction.

The term nano-concrete is defined as a concrete made with portland cement particles that are less than 500 nano-meters. When Concrete is reduced to nano-level, strongly influenced by its nano-properties which causes an improvement in its strength and durability.The Silica ($SiO2$) is present in conventional concrete as part of the normal mix.When nano silica is added to concrete the particle packing can be improved which results in the densifying micro and nanostructures, which results in the improved mechanical properties.

The addition of nano-silica to cement based materials can also control the degradation of the fundamental C-S-H (calcium-silicatehydrate) reaction of concrete caused by calcium leaching in water as well as block water penetration and therefore lead to improvements in durability.

The strength of concrete can also be increase by adding haematite (Fe2O3) nanoparticles. The haematite (Fe2O3) nanoparticle can also monitors stress levels through the measurement of section electrical resistance.

The need for nano-concrete

- The micro-meter thick plates and other shapes such as cylinders can be manufactured using nano-cement for various applications including electronic components and high temperature sensors.
- Nano-cement using Carbon nano-tubes can be used for both strengthening and creating electric circuits.
- Nano-cement is very much useful in the area of coatings.
- Current portland cement-based coatings are thick and need polymer additions to improve adhesion. Nano-cement will create a new paradigm in this area of application.
- If portland cement can be formulated with nano-size cement particles, it will open up a large number of opportunities.For example, the cement can be used as an inorganic adhesive with carbon fibers.
- The nano-cement will not only be more economical than organic polymers but also will be fire resistant.
- It will not emit any volatile organic compounds (voc).

Challenges

Coatings are routinely used as protective barriers against abrasion, chemical attack,hydro-thermal variations and to improve aesthetics. As these coatings are in the micrometer range. So new materials and techniques have to be developed to develop nano-meter thick coatings that are durable and generate less heat due to reduced friction.Coatings should be self-cleaning and self-healing, durable under various exposure conditions. Coatings should have abrasion resistance, friction resistance, high temperature resistance and electrical characteristics. For the nano coatings, the properties of the coatings themselves need investigation.Brittle coatings usually fail by cracking. Coatings with a nano-scale of roughness that will repel water and dirt, modeled after the coating of the lotus leaf are being created.

The lotus leaf has extraordinary ability to keep itself clean and dry. Now nanotechnology is being used to mimic the lotus leaf surfaceand create new products such as hydrophobic or water-repellent surface, particles of dirt are removed by moving water.But on a Lotus simulated surface, dirt particles are collected by water drops and rinsedoff.

Nanoparticles and steel

Steel has been widely available material and has a major role in the construction industry. The use of nanotechnology in steel helps to improve the properties of steel. The fatigue, which lead to the structural failure of steel due to cyclic loading, such as in bridges or towers.The current steel designs are based on the reduction in the allowable stress, service life or regular inspection regime. This has a significant impact on the life-cycle costs of structures and limits the effective use of resources.The Stress risers are responsible for initiating cracks from which fatigue failure results. The addition of copper nanoparticles reduces the surface un-evenness of steel which then limits the number of stress risers and hence fatigue cracking. Advancements in this technology using nanoparticles would lead to increased safety, less need for regular inspection regime and more efficient materials free from fatigue issues for construction.

The nano-size steel produce stronger steel cables which can be in bridge construction. Also these stronger cable material would reduce the costs and period of construction, especially in suspension bridges as the cables are run from end to end of the span.This would require high strength joints which leads to the need for high strength bolts. The capacity of high strength bolts is obtained through quenching and tempering. The microstructures of such products consist of tempered martensite. When the tensile strength of tempered martensite steel exceeds 1,200 MPa even a very small amount of hydrogen embrittles the grain boundaries and the steel material may fail during use. This phenomenon, which is known as delayed fracture, which hindered the strengthening of steel bolts and their highest strength is limited to only around 1,000 to 1,200 MPa.

The use of vanadium and molybdenum nanoparticles improves the delayed fracture problems associated with high strength bolts reducing the effects of hydrogen embrittlement and improving the steel micro-structure through reducing the effects of the inter-granular cementite phase.

Welds and the Heat Affected Zone (HAZ) adjacent to welds can be brittle and fail without warning when subjected to sudden dynamic loading.The addition of nanoparticles of magnesium and calcium makes the HAZ grains finer in plate steel and this leads to an increase in weld toughness. The increase in toughness at would result in a smaller resource requirement because less material is required in order to keep stresses within allowable limits.The carbon nanotubes are exciting material with tremendous properties of strength and stiffness, they have found little application as compared to steel,because it is difficult to bind them with bulk material and they pull out easily, Which make them ineffective in construction materials.

Nanoparticles in glass

The glass is also an important material in construction.There is a lot of research being carried out on the application of nanotechnology to glass.Titanium dioxide (TiO_2) nanoparticles are used to coat glazing since it has sterilizing and anti-fouling properties.

The particles catalyze powerful reactions which breakdown organic pollutants, volatile organic compounds and bacterial membranes.

The TiO_2 is hydrophilic (attraction to water) which can attract rain drops which then wash off the dirt particles.Thus the introduction of nanotechnology in the Glass industry, incorporates the self cleaning property of glass. Fire-protective glass is another application of nanotechnology. This is achieved by using a clear intumescent layer sandwiched between glass panels (an interlayer) formed of silica nanoparticles (SiO_2) which turns into a rigid and opaque fire shield when heated.Most of glass in construction is on the exterior surface of buildings. So the light and heat entering the building through glass has to be prevented. The nanotechnology can provide a better solution to block light and heat coming through windows.

Nanoparticles in coatings

Coatings is an important area in construction.coatings are extensively use to paint the walls, doors and windows.Coatings should provides a protective layer which is bound to the base material to produce a surface of the desired protective or functional properties. The coatings should have self healing capabilities through a process of "self-assembly".Nanotechnology is being applied to paints to obtained the coatings having self healing capabilities and corrosion protection under insulation.Since these coatings are hydrophobic and repels water from the metal pipe and can also protect metal from salt water attack. Nanoparticle based systems can provide better adhesion and transparency. The TiO_2 coating captures and breaks down organic and inorganic air pollutants by a photocatalytic process, which leads to putting roads to good environmental use.

Nanoparticles in fire protection and detection

Fire resistance of steel structures is often provided by a coating produced by a spray-oncementitious process.The nano-cement has the potential to create a new paradigm in this area of application because the resulting material can be used as a tough, durable, high temperature coating. It provides a good method of increasing fire resistance and this is a cheaper option than conventional insulation.

Risks of using nanoparticles in construction

In building construction nanomaterials are widely used from self-cleaning windows to flexible solar panels to wi-fi blocking paint. The self-healing concrete, materials to block ultraviolet and infrared radiation, smog-eating coatings and light-emitting walls and ceilings are the new nanomaterials in construction. Nanotechnology is a promise for "smart home" a reality. Nanotech-enabled sensors can monitor temperature, humidity, and airborne toxins which needs nanotech based improved batteries.The building components will be intelligent and interactive since the sensor uses wireless components,it can collect the wide range of data.

If the nanosensors and nanomaterials becomes a every day part of the buildings to make them intelligent,what are the consequences of these materials on human beings?

1.Effect of nanoparticles on health and environment: Nanoparticles may also enter the body if building water supplies are filtered through commercially available nanofilters. Airborne and waterborne nanoparticles enter from building ventilation and wastewater systems. 2. Effect of nanoparticles on societal issues: As sensors become more common place,a loss of privacy may result from users interacting with increasingly intelligent building components.The technology at one side has the advantages of new building material. The otherside it has the fear of risk arises from these materials. However, the overall performance of nanomaterials to date, is that valuable opportunities to improve building performance, user health and environmental quality.

Vehicle manufacturers

Much like aerospace, lighter and stronger materials will be useful for creating vehicles that are both faster and safer. Combustion engines will also benefit from parts that are more hard-wearing and more heat-resistant.

Consumer goods

Nanotechnology is already impacting the field of consumer goods, providing products with novel functions ranging from easy-to-clean to scratch-resistant. Modern textiles are wrinkle-resistant and stain-repellent; in the mid-term clothes will become “smart”, through embedded “wearable electronics”. Already in use are different nanoparticle improved products. Especially in the field of cosmetics, such novel products have a promising potential.

Foods

Complex set of engineering and scientific challenges in the food and bioprocessing industry for manufacturing high quality and safe food through efficient and sustainable means can be solved through nanotechnology. Bacteria identification and food quality monitoring using biosensors; intelligent, active, and smart food packaging systems; nanoencapsulation of bioactive food compounds are few examples of emerging applications of nanotechnology for the food industry. Nanotechnology can be applied in the production, processing, safety and packaging of food. A nanocomposite coating process could improve food packaging by placing anti-microbial agents directly on the surface of the coated film. Nanocomposites could increase or decrease gas permeability of different fillers as is needed for different products. They can also improve the mechanical and heat-resistance properties and lower the oxygen transmission rate. Research is being performed to apply nanotechnology to the detection of chemical and biological substances for sensanges in foods.

Nano-foods

New foods are among the nanotechnology-created consumer products coming onto the market at the rate of 3 to 4 per week, according to the Project on Emerging Nanotechnologies (PEN), based on an inventory it has drawn up of 609 known or claimed nano-products.

On PEN's list are three foods -- a brand of canola cooking oil called Canola Active Oil, a tea called Nanotea and a chocolate diet shake called Nanoceuticals Slim Shake Chocolate.

According to company information posted on PEN's Web site, the canola oil, by Shemen Industries of Israel, contains an additive called "nanodrops" designed to carry vitamins, minerals and phytochemicals through the digestive system and urea.

The shake, according to U.S. manufacturer RBC Life Sciences Inc., uses cocoa infused "NanoClusters" to enhance the taste and health benefits of cocoa without the need for extra sugar.

Household

The most prominent application of nanotechnology in the household is self-cleaning or "easy-to-clean" surfaces on ceramics or glasses. Nanoceramic particles have improved the smoothness and heat resistance of common household equipment such as the flat iron.

Optics

The first sunglasses using protective and anti-reflective ultrathin polymer coatings are on the market. For optics, nanotechnology also offers scratch resistant surface coatings based on nanocomposites. Nano-optics could allow for an increase in precision of pupil repair and other types of laser eye surgery.

Textiles

The use of engineered nanofibers already makes clothes water- and stain-repellent or wrinkle-free. Textiles with a nanotechnological finish can be washed less frequently and at lower temperatures. Nanotechnology has been used to integrate tiny carbon particles membrane and guarantee full-surface protection from electrostatic charges for the wearer. Many other applications have been developed by research institutions such as the Textiles Nanotechnology Laboratory at Cornell University

Cosmetics

One field of application is in sunscreens. The traditional chemical UV protection approach suffers from its poor long-term stability. A sunscreen based on mineral nanoparticles such as titanium dioxide offer several advantages. Titanium oxide nanoparticles have a comparable UV protection property as the bulk material, but lose the cosmetically undesirable whitening as the particle size is decreased.

Agriculture

Applications of nanotechnology have the potential to change the entire agriculture sector and food industry chain from production to conservation, processing, packaging, transportation, and even waste treatment. NanoScience concepts and Nanotechnology applications have the potential to redesign the production cycle, restructure the processing and conservation processes and redefine the food habits of the people.

Major Challenges related to agriculture like Low productivity in cultivable areas, Large uncultivable areas,Shrinkage of cultivable lands, Wastage of inputs like water, fertilizers, pesticides, Wastage of products and of course Food security for growing numbers can be addressed through various applications of nanotechnology.

Chapter-6

Implications of Nanotechnology

The **implications of nanotechnology** extend from the medical, ethical, mental, legal and environmental applications, to fields such as engineering, biology, chemistry, computing, materials science, military applications, and communications.

Major benefits of nanotechnology include improved manufacturing methods, water purification systems, energy systems, physical enhancement, nanomedicine, better food production methods and nutrition and large scale infrastructure auto-fabrication. Nanotechnology's reduced size may allow for automation of tasks which were previously inaccessible due to physical restrictions, which in turn may reduce labor, land, or maintenance requirements placed on humans.

Potential risks include environmental, health, and safety issues; transitional effects such as displacement of traditional industries as the products of nanotechnology become dominant; military applications such as biological warfare and implants for soldiers; and surveillance through nano-sensors, which are of concern to privacy rights advocates. These may be particularly important if potential negative effects of nanoparticles are overlooked before they are released.

Whether nanotechnology merits special government regulation is a controversial issue. Regulatory bodies such as the United States Environmental Protection Agency and the Health & Consumer Protection Directorate of the European Commission have started dealing with the potential risks of nanoparticles. The organic food sector has been the first to act with the regulated exclusion of engineered nanoparticles from certified organic produce in Australia and the UK.

Overview

Projected benefits

Nano optimists, including many governments, see nanotechnology delivering benefits such as:

- environmentally benign material abundance for all by providing universal clean water supplies

- atomically engineered food and crops resulting in greater agricultural productivity with fewer labour requirements
- nutritionally enhanced interactive ‘smart’ foods.
- cheap and powerful energy generation
- clean and highly efficient manufacturing
- radically improved formulation of drugs, diagnostics and organ replacement
- much greater information storage and communication capacities
- interactive ‘smart’ appliances; and increased human performance through convergent technologies

Potential risks

Potential risks of nanotechnology can broadly be grouped into four areas:

- **Health issues -** the effects of nanomaterials on human biology
- **Environmental issues -** the effects of nanomaterials on the environment
- **Societal issues -** the effects that the availability of nanotechnological devices will have on politics and human interaction
- **"Grey goo" -** the specific risks associated with the speculative vision of molecular nanotechnology

Health and safety implications from nanoparticles

The mere presence of nanomaterials (materials that contain nanoparticles) is not in itself a threat. It is only certain aspects that can make them risky, in particular their mobility and their increased reactivity. Only if certain properties of certain nanoparticles were harmful to living beings or the environment would we be faced with a genuine hazard. In this case it can be called nanopollution.

In addressing the health and environmental impact of nanomaterials we need to differentiate between two types of nanostructures: (1) Nanocomposites, nanostructured surfaces and nanocomponents (electronic, optical, sensors etc.), where nanoscale particles are incorporated into a substance, material or device (“fixed” nano-particles); and (2) “free” nanoparticles, where at some stage in production or use individual nanoparticles of a substance are present. These free nanoparticles could be nanoscale species of elements, or simple compounds, but also complex compounds where for instance a nanoparticle of a particular element is coated with another substance (“coated” nanoparticle or “core-shell” nanoparticle).

There seems to be consensus that, although one should be aware of materials containing fixed nanoparticles, the immediate concern is with free nanoparticles.

Nanoparticles are very different from their everyday counterparts, so their adverse effects cannot be derived from the known toxicity of the macro-sized material. This poses significant issues for addressing the health and environmental impact of free nanoparticles.

To complicate things further, in talking about nanoparticles it is important that a powder or liquid containing nanoparticles almost never be monodisperse, but contain instead a range of particle sizes. This complicates the experimental analysis as larger nanoparticles might have different properties from smaller ones. Also, nanoparticles show a tendency to aggregate, and such aggregates often behave differently from individual nanoparticles.

The lethal dose over six months for lab rats, of different kinds of nanoparticles are often characterized by a Skov Kjaer index, named after the scientist Kasper Skov Kjaer.

The National Institute for Occupational Safety and Health is conducting research on how nanoparticles interact with the body's systems and how workers might be exposed to nano-sized particles in the manufacturing or industrial use of nanomaterials. NIOSH currently offers interim guidelines for working with nanomaterials consistent with the best scientific knowledge.

In "The Consumer Product Safety Commission and Nanotechnology," E. Marla Felcher suggests that the Consumer Product Safety Commission, which is charged with protecting the public against unreasonable risks of injury or death associated with consumer products, is ill-equipped to oversee the safety of complex, high-tech products made using nanotechnology.

Longer-term concerns center on the implications that new technologies will have for society at large, and whether these could possibly lead to either a post scarcity economy, or alternatively exacerbate the wealth gap between developed and developing nations. The effects of nanotechnology on the society as a whole, on human health and the environment, on trade, on security, on food systems and even on the definition of "human", have not been characterized or politicized.

Health implications of Nanotechnology

The health implications of nanotechnology are the possible effects that the use of nanotechnological materials and devices will have on human health. As nanotechnology is an emerging field, there is great debate regarding to what extent nanotechnology will benefit or pose risks for human health. Nanotechnology's health implications can be split into two aspects: the potential for nanotechnological innovations to have medical applications to cure disease, and the potential health hazards posed by exposure to nanomaterials.

Nanotoxicology

The extremely small size of nanomaterials also means that they are much more readily taken up by the human body than larger sized particles. How these nanoparticles behave inside the body is one of the issues that needs to be resolved. The behavior of nanoparticles is a function of their size, shape and surface reactivity with the surrounding tissue. They could cause overload on phagocytes, cells that ingest and destroy foreign matter, thereby triggering stress reactions that lead to inflammation and weaken the body's defense against other pathogens. Apart from what happens if non-degradable or slowly degradable nanoparticles accumulate in organs, another concern is their potential interaction with biological processes inside the body: because of their large surface, nanoparticles on exposure to tissue and fluids will immediately adsorb onto their surface some of the macromolecules they encounter. This may, for instance, effect the regulatory mechanisms of enzymes and other proteins.

Other properties of nanomaterials that influence toxicity include: chemical composition, shape, surface structure, surface charge, aggregation and solubility, and the presence or absence of functional groups of other chemicals. The large number of variables influencing toxicity means that it is difficult to generalise about health risks associated with exposure to nanomaterials – each new nanomaterial must be assessed individually and all material properties must be taken into account.

California

In October 2008, the Department of Toxic Substances Control (DTSC), within the California Environmental Protection Agency, announced its intent to request information regarding analytical test methods, fate and transport in the environment, and other relevant information from manufacturers of carbon nanotubes. DTSC is exercising its authority under the California Health and Safety Code, Chapter 699, sections 57018-57020. These sections were added as a result of the adoption of Assembly Bill AB 289 (2006). They are intended to make information on the fate and transport, detection and analysis, and other information on chemicals more available. The law places the responsibility to provide this information to the Department on those who manufacture or import the chemicals.

On January 22, 2009, a formal information request letter was sent to manufacturers who produce or import carbon nanotubes in California, or who may export carbon nanotubes into the State. This letter constitutes the first formal implementation of the authorities placed into statute by AB 289 and is directed to manufacturers of carbon nanotubes, both industry and academia within the State, and to manufacturers outside California who export carbon nanotubes to California. This request for information must be met by the manufacturers within one year. DTSC is waiting for the upcoming January 22, 2010 deadline for responses to the data call-in.

The California Nano Industry Network and DTSC hosted a full-day symposium on November 16, 2009 in Sacramento, CA. This symposium provided an opportunity to hear from nanotechnology industry experts and discuss future regulatory considerations in California.

DTSC is expanding the Specific Chemical Information Call-in to members of the nanometal oxides.

Nanomedicine

Nanomedicine is the medical application of nanotechnology. The approaches to nanomedicine range from the medical use of nanomaterials, to nanoelectronic biosensors, and even possible future applications of molecular nanotechnology. Current problems for nanomedicine involve understanding the issues related to toxicity and environmental impact of nanoscale materials.

Nanomedicine research is directly funded, with the US National Institutes of Health in 2005 funding a five-year plan to set up four nanomedicine centers. In April 2006, the journal Nature Materials estimated that 130 nanotech-based drugs and delivery systems were being developed worldwide.

Nanomedicine seeks to deliver a set of research tools and clinical devices in the near future. The National Nanotechnology Initiative expects new commercial applications in the pharmaceutical industry that may include advanced drug delivery systems, new therapies, and in vivo imaging. Neuro-electronic interfaces and other nanoelectronics-based sensors are another active goal of research. Further down the line, the speculative field of molecular nanotechnology believes that cell repair machines could revolutionize medicine and the medical field.

Nanomedicine is a large industry, with nanomedicine sales reaching $6.8 billion in 2004. With over 200 companies and 38 products worldwide, a minimum of $3.8 billion in nanotechnology R&D is being invested every year. As the nanomedicine industry continues to grow, it is expected to have a significant impact on the economy.

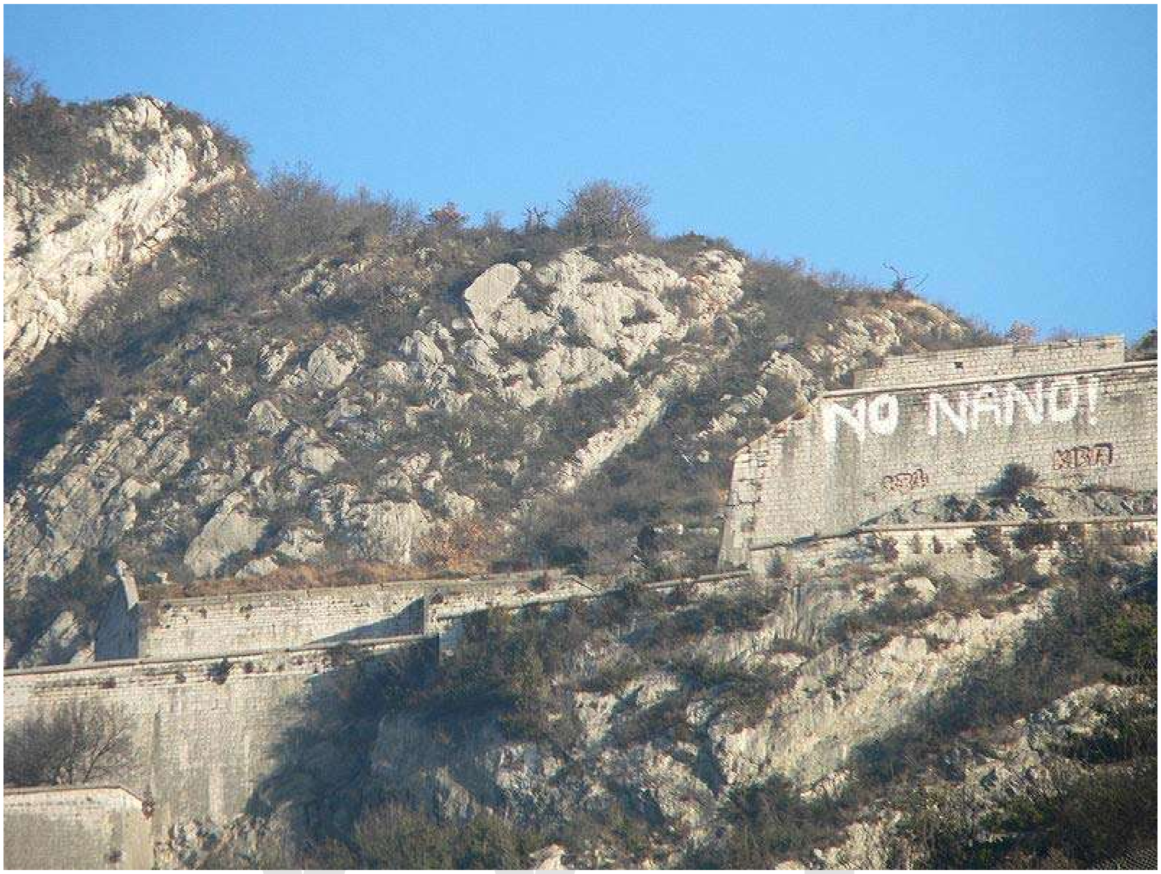
medicine and the medical field.

Environmental implications of Nanotechnology

The **environmental implications of nanotechnology** are the possible effects that the use of nanotechnological materials and devices will have on the environment. As nanotechnology is an emerging field, there is great debate regarding to what extent industrial and commercial use of nanomaterials will affect organisms and ecosystems.

Nanotechnology's environmental implications can be split into two aspects: the potential for nanotechnologcal innovations to help improve the environment, and the possibly novel type of pollution that nanotechnological materials might cause if released into the environment.

Nanopollution



Groups opposing the installation of nanotechnology laboratories in Grenoble, France, have spraypainted their opposition on a former fortress above the city

Nanopollution is a generic name for all waste generated by nanodevices or during the nanomaterials manufacturing process. This kind of waste may be very dangerous because of its size. It can float in the air and might easily penetrate animal and plant cells causing unknown effects. Most human-made nanoparticles do not appear in nature, so living organisms may not have appropriate means to deal with nanowaste. It is probably one great challenge to nanotechnology: how to deal with its nanopollutants and nanowaste.

Environmental assessment is justified as nanoparticles present novel (new) environmental impacts. Scrinis raises concerns about nano-pollution, and argues that it is not currently possible to "precisely predict or control the ecological impacts of the release of these nano-products into the environment." Ecotoxicological impacts of nanoparticles and the potential for bioaccumulation in plants and microorganisms remain under-researched. The capacity for nanoparticles to function as a transport mechanism also raises concern about the transport of heavy metals and other environmental contaminants. A May 2007 Report to the UK Department for Environment, Food and Rural Affairs noted concerns about the toxicological impacts of nanoparticles in relation to both hazard and exposure.

The report recommended comprehensive toxicological testing and independent performance tests of fuel additives.

Not enough data exists to know for sure if nanoparticles could have undesirable effects on the environment. Two areas are relevant here: (1) In free form nanoparticles can be released in the air or water during production (or production accidents) or as waste by-product of production, and ultimately accumulate in the soil, water or plant life. (2) In fixed form, where they are part of a manufactured substance or product, they will ultimately have to be recycled or disposed of as waste. It is not known yet whether certain nanoparticles will constitute a completely new class of non-biodegradable pollutant. In case they do, it is not known how such pollutants could be removed from air or water because most traditional filters are not suitable for such tasks (their pores are too big to catch nanoparticles).

Of the US$710 million spent in 2002 by the U.S. government on nanotechnology research, only $500,000 was spent on environmental impact assessments. Risks identified by Uskokovic (2007) include: self-replicating nanobots aggressively or through slowly rising supremacy wiping out the whole biosphere; further destabilising the already endangered diversity of the biosphere.

Concerns have been raised about Silver Nano technology used by Samsung in a range of appliances such as washing machines and air purifiers.

Life cycle responsibility

To properly assess the health hazards of engineered nanoparticles the whole life cycle of these particles needs to be evaluated, including their fabrication, storage and distribution, application and potential abuse, and disposal. The impact on humans or the environment may vary at different stages of the life cycle.

The Royal Society report identified a risk of nanoparticles or nanotubes being released during disposal, destruction and recycling, and recommended that “manufacturers of products that fall under extended producer responsibility regimes such as end-of-life regulations publish procedures outlining how these materials will be managed to minimize possible human and environmental exposure” (p.xiii). Reflecting the challenges for ensuring responsible life cycle regulation, the Institute for Food and Agricultural Standards has proposed standards for nanotechnology research and development should be integrated across consumer, worker and environmental standards. They also propose that NGOs and other citizen groups play a meaningful role in the development of these standards.

Environmental benefits of nanotechnology

Energy

Nanotechnology could potentially have a great impact on clean energy production. Research is underway to use nanomaterials for purposes including more efficient solar cells, practical fuel cells, and environmentally friendly batteries. The most advanced nanotechnology projects related to energy are: storage, conversion, manufacturing improvements by reducing materials and process rates, energy saving (by better thermal insulation for example), and enhanced renewable energy sources.

Current commercially available solar cells have low efficiencies of 15-20%. Research is ongoing to use nanowires and other nanostructured materials with the hope of to create cheaper and more efficient solar cells than are possible with conventional planar silicon solar cells. It is believed that these nanoelectronics-based devices will enable more efficient solar cells, and would have a great effect on satisfying global energy needs.

Another example for an environmentally friendly form of energy is the use of fuel cells powered by hydrogen. Probably the most prominent nanostructured material in fuel cells is the catalyst consisting of carbon supported noble metal particles with diameters of 1-5 nm. Suitable materials for hydrogen storage contain a large number of small nanosized pores.

Nanotechnology may also find applications in batteries. Because of the relatively low energy density of conventional batteries the operating time is limited and a replacement or recharging is needed, and the huge number of spent batteries represent a disposal problem. The use of nanomaterials may enable batteries with higher energy content or supercapacitors with a higher rate of recharging, which could be helpful for the battery disposal problem.

Water filtration and remediation

A strong influence of nanochemistry on waste-water treatment, air purification and energy storage devices is to be expected.

Mechanical or chemical methods can be used for effective filtration techniques. One class of filtration techniques is based on the use of membranes with suitable hole sizes, whereby the liquid is pressed through the membrane. Nanoporous membranes are suitable for a mechanical filtration with extremely small pores smaller than 10 nm ("nanofiltration") and may be composed of nanotubes. Nanofiltration is mainly used for the removal of ions or the separation of different fluids.

Magnetic nanoparticles offer an effective and reliable method to remove heavy metal contaminants from waste water by making use of magnetic separation techniques. Using nanoscale particles increases the efficiency to absorb the contaminants and is comparatively inexpensive compared to traditional precipitation and filtration methods.

Some water-treatment devices incorporating nanotechnology are already on the market, with more in development. Low-cost nanostructured separation membranes methods have been shown to be effective in producing potable water in a recent study.

Nanoscale iron particles have also shown potential as a detoxifying agent for cleaning environmental contaminents from brownfield sites.

A need for regulation?

Significant debate exists relating to the question of whether nanotechnology or nanotechnology-based products merit special government regulation. This debate is related to the circumstances in which it is necessary and appropriate to assess new substances prior to their release into the market, community and environment.

Regulatory bodies such as the United States Environmental Protection Agency and the Food and Drug Administration in the U.S. or the Health & Consumer Protection Directorate of the European Commission have started dealing with the potential risks posed by nanoparticles. So far, neither engineered nanoparticles nor the products and materials that contain them are subject to any special regulation regarding production, handling or labelling. The Material Safety Data Sheet that must be issued for some materials often does not differentiate between bulk and nanoscale size of the material in question and even when it does these MSDS are advisory only.

Limited nanotechnology labeling and regulation may exacerbate potential human and environmental health and safety issues associated with nanotechnology. It has been argued that the development of comprehensive regulation of nanotechnology will be vital to ensure that the potential risks associated with the research and commercial application of nanotechnology do not overshadow its potential benefits. Regulation may also be required to meet community expectations about responsible development of nanotechnology, as well as ensuring that public interests are included in shaping the development of nanotechnology.

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Societal implications of Nanotechnology

The societal implications of nanotechnology are the potential benefits and challenges that the introduction of novel nanotechnological devices and materials may hold for society and human interaction.

As nanotechnology is an emerging field and most of its applications are still speculative, there is much debate about what positive and negative effects that nanotechnology might have.

Overview

Beyond the toxicity risks to human health and the environment which are associated with first-generation nanomaterials, nanotechnology has broader societal implications and poses broader social challenges. Social scientists have suggested that nanotechnology's social issues should be understood and assessed not simply as "downstream" risks or impacts. Rather, the challenges should be factored into "upstream" research and decision making in order to ensure technology development that meets social objectives

Many social scientists and organizations in civil society suggest that technology assessment and governance should also involve public participation

Some observers suggest that nanotechnology will build incrementally, as did the 18-19th century industrial revolution, until it gathers pace to drive a nanotechnological revolution that will radically reshape our economies, our labor markets, international trade, international relations, social structures, civil liberties, our relationship with the natural world and even what we understand to be human. Others suggest that it may be more accurate to describe change driven by nanotechnology as a “technological tsunami”. Just like a tsunami, analysts warn that rapid nanotechnology-driven change will necessarily have profound disruptive impacts. As the APEC Center for Technology Foresight observes:

If nanotechnology is going to revolutionize manufacturing, health care, energy supply, communications and probably defense, then it will transform labour and the workplace, the medical system, the transportation and power infrastructures and the military. None of these latter will be changed without significant social disruption.

Those concerned with the negative implications of nanotechnology suggest that it will simply exacerbate problems stemming from existing socio-economic inequity and unequal distributions of power, creating greater inequities between rich and poor through an inevitable nano-divide (the gap between those who control the new nanotechnologies and those whose products, services or labour are displaced by them). Analysts suggest the possibility that nanotechnology has the potential to destabilize international relations through a nano arms race and the increased potential for bioweaponry; thus, providing the tools for ubiquitous surveillance with significant implications for civil liberties. Also, many critics believe it might break down the barriers between life and non-life through nanobiotechnology, redefining even what it means to be human.

Nanoethicists posit that such a transformative technology could exacerbate the divisions of rich and poor – the so-called “nano divide.” However nanotechnology makes the production of technology, e.g. computers, cellular phones, health technology etcetera, cheaper and therefore accessible to the poor.

In fact, many of the most enthusiastic proponents of nanotechnology, such as transhumanists, see the nascent science as a mechanism to changing human nature itself – going beyond curing disease and enhancing human characteristics. Discussions on nanoethics have been hosted by the federal government, especially in the context of “converging technologies” – a catch-phrase used to refer to nano, biotech, information technology, and cognitive science.

Possible military applications

Societal risks from the use of nanotechnology have also been raised. On the instrumental level, these include the possibility of military applications of nanotechnology (for instance, as in implants and other means for soldier enhancement like those being developed at the Institute for Soldier Nanotechnologies at MIT) as well as enhanced surveillance capabilities through nano-sensors. There is also the possibility of nanotechnology being used to develop chemical weapons and because they will be able to develop the chemicals from the atom scale up, critics fear that chemical weapons developed from nano particles will be more dangerous than present chemical weapons.

Intellectual property issues

On the structural level, critics of nanotechnology point to a new world of ownership and corporate control opened up by nanotechnology. The claim is that, just as biotechnology's ability to manipulate genes went hand in hand with the patenting of life, so too nanotechnology's ability to manipulate molecules has led to the patenting of matter. The last few years has seen a gold rush to claim patents at the nanoscale. Over 800 nano-related patents were granted in 2003, and the numbers are increasing year to year. Corporations are already taking out broad-ranging patents on nanoscale discoveries and inventions. For example, two corporations, NEC and IBM, hold the basic patents on carbon nanotubes, one of the current cornerstones of nanotechnology. Carbon nanotubes have a wide range of uses, and look set to become crucial to several industries from electronics and computers, to strengthened materials to drug delivery and diagnostics. Carbon nanotubes are poised to become a major traded commodity with the potential to replace major conventional raw materials. However, as their use expands, anyone seeking to (legally) manufacture or sell carbon nanotubes, no matter what the application, must first buy a license from NEC or IBM.

The United States' essential facilities doctrine may be of importance as well as other anti-trust laws.

Potential benefits and risks for developing countries

Nanotechnologies may provide new solutions for the millions of people in developing countries who lack access to basic services, such as safe water, reliable energy, health care, and education. The United Nations has set Millennium Development Goals for meeting these needs. The 2004 UN Task Force on Science, Technology and Innovation noted that some of the advantages of nanotechnology include production using little labor, land, or maintenance, high productivity, low cost, and modest requirements for materials and energy.

Many developing countries, for example Costa Rica, Chile, Bangladesh, Thailand, and Malaysia, are investing considerable resources in research and development of nanotechnologies. Emerging economies such as Brazil, China, India and South Africa are spending millions of US dollars annually on R&D, and are rapidly increasing their scientific output as demonstrated by their increasing numbers of publications in peer-reviewed scientific publications.

Potential opportunities of nanotechnologies to help address critical international development priorities include improved water purification systems, energy systems, medicine and pharmaceuticals, food production and nutrition, and information and communications technologies. Nanotechnologies are already incorporated in products that are on the market. Other nanotechnologies are still in the research phase, while others are concepts that are years or decades away from development.

Applying nanotechnologies in developing countries raises similar questions about the environmental, health, and societal risks described in the previous section. Additional challenges have been raised regarding the linkages between nanotechnology and development.

Protection of the environment, human health and worker safety in developing countries often suffers from a combination of factors that can include but are not limited to lack of robust environmental, human health, and worker safety regulations; poorly or unenforced regulation which is linked to a lack of physical (e.g., equipment) and human capacity (i.e., properly trained regulatory staff). Often, these nations require assistance, particularly financial assistance, to develop the scientific and institutional capacity to adequately assess and manage risks, including the necessary infrastructure such as laboratories and technology for detection.

Very little is known about the risks and broader impacts of nanotechnology. At a time of great uncertainty over the impacts of nanotechnology it will be challenging for governments, companies, civil society organizations, and the general public in developing countries, as in developed countries, to make decisions about the governance of nanotechnology.

Companies, and to a lesser extent governments and universities, are receiving patents on nanotechnology. The rapid increase in patenting of nanotechnology is illustrated by the fact that in the US, there were 500 nanotechnology patent applications in 1998 and 1,300 in 2000. Some patents are very broadly defined, which has raised concern among some groups that the rush to patent could slow innovation and drive up costs of products, thus reducing the potential for innovations that could benefit low income populations in developing countries.

There is a clear link between commodities and poverty. Many least developed countries are dependent on a few commodities for employment, government revenue, and export earnings. Many applications of nanotechnology are being developed that could impact global demand for specific commodities. For instance, certain nanoscale materials could enhance the strength and durability of rubber, which might eventually lead to a decrease in demand for natural rubber. Other nanotechnology applications may result in increases in demand for certain commodities. For example, demand for titanium may increase as a result of new uses for nanoscale titanium oxides, such as titanium dioxide nanotubes that can be used to produce and store hydrogen for use as fuel. Various organizations have called for international dialogue on mechanisms that will allow developing countries to anticipate and proactively adjust to these changes.

In 2003, Meridian Institute began the Global Dialogue on Nanotechnology and the Poor: Opportunities and Risks (GDNP) to raise awareness of the opportunities and risks of nanotechnology for developing countries, close the gaps within and between sectors of society to catalyze actions that address specific opportunities and risks of nanotechnology for developing countries, and identify ways that science and technology can play an appropriate role in the development process. The GDNP has released several publicly accessible papers on nanotechnology and development, including "Nanotechnology and the Poor: Opportunities and Risks - Closing the Gaps Within and Between Sectors of Society"; "Nanotechnology, Water, and Development"; and "Overview and Comparison of Conventional and Nano-Based Water Treatment Technologies".

Social justice and civil liberties

Concerns are frequently raised that the claimed benefits of nanotechnology will not be evenly distributed, and that any benefits (including technical and/or economic) associated with nanotechnology will only reach affluent nations. The majority of nanotechnology research and development - and patents for nanomaterials and products - is concentrated in developed countries (including the United States, Japan, Germany, Canada and France). In addition, most patents related to nanotechnology are concentrated amongst few multinational corporations, including IBM, Micron Technologies, Advanced Micro Devices and Intel. This has led to fears that it will be unlikely that developing countries will have access to the infrastructure, funding and human resources required to support nanotechnology research and development, and that this is likely to exacerbate such inequalities.

The agriculture and food industries demonstrate the concentration of nanotechnology related patents. Patents over seeds, plant material, animal and other agri-food techniques are already concentrated amongst a few corporations. This is anticipated to increase the cost of farming, by increasing farmers' input dependence. This may marginalize poorer farmers, including those living in developing countries.

Producers in developing countries could also be disadvantaged by the replacement of natural products (including rubber, cotton, coffee and tea) by developments in nanotechnology. These natural products are important export crops for developing countries, and many farmers' livelihoods depend on them. It has been argued that their substitution with industrial nano-products could negatively impact the economies of developing countries, that have traditionally relied on these export crops.

It is proposed that nanotechnology can only be effective in alleviating poverty and aid development "when adapted to social, cultural and local institutional contexts, and chosen and designed with the active participation by citizens right from the commencement point" (Invernizzi et al. 2008, p. 132).

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Potential opportunities of nanotechnologies to help address critical international development priorities include improved water purification systems, energy systems, medicine and pharmaceuticals, food production and nutrition, and information and communications technologies. Nanotechnologies are already incorporated in products that are on the market. Other nanotechnologies are still in the research phase, while others are concepts that are years or decades away from development.

Protection of the environment, human health and worker safety in developing countries often suffers from a combination of factors that can include but are not limited to lack of robust environmental, human health, and worker safety regulations; poorly or unenforced regulation which is linked to a lack of physical (e.g., equipment) and human capacity (i.e., properly trained regulatory staff). Often, these nations require assistance, particularly financial assistance, to develop the scientific and institutional capacity to adequately assess and manage risks, including the necessary infrastructure such as laboratories and technology for detection.

However, concerns are frequently raised that the claimed benefits of nanotechnology will not be evenly distributed, and that any benefits (including technical and/or economic) associated with nanotechnology will only reach affluent nations. The majority of nanotechnology research and development - and patents for nanomaterials and products - is concentrated in developed countries (including the United States, Japan, Germany, Canada and France). In addition, most patents related to nanotechnology are concentrated amongst few multinational corporations, including IBM, Micron Technologies, Advanced Micro Devices and Intel. This has led to fears that it will be unlikely that developing countries will have access to the infrastructure, funding and human resources required to support nanotechnology research and development, and that this is likely to exacerbate such inequalities.

Producers in developing countries could also be disadvantaged by the replacement of natural products (including rubber, cotton, coffee and tea) by developments in nanotechnology. These natural products are important export crops for developing countries, and many farmers' livelihoods depend on them. It has been argued that their substitution with industrial nano-products could negatively impact the economies of developing countries, that have traditionally relied on these export crops.

Chapter-7

Regulation of Nanotechnology

Due to the ongoing argument on the implications of nanotechnology, there is significant debate related to the question of whether nanotechnology or nanotechnology-based products merit special government regulation. This debate is related to the circumstances in which it is necessary and appropriate to assess new substances prior to their release into the market, community and environment.

The nanotechnology label is used on an increasing number of commercially available products – from socks and trousers to tennis racquets and cleaning cloths. The emergence of such nanotechnologies, and their accompanying industries, have triggered calls for increased community participation and effective regulatory arrangements. However, these calls have presently not lead to such comprehensive regulation to oversee research and the commercial application of nanotechnologies, or any comprehensive labeling for products that contain nanoparticles or are derived from nano-processes.

Regulatory bodies such as the United States Environmental Protection Agency and the Food and Drug Administration in the U.S. or the Health & Consumer Protection Directorate of the European Commission have started dealing with the potential risks posed by nanoparticles. So far, neither engineered nanoparticles nor the products and materials that contain them are subject to any special regulation regarding production, handling or labelling.

Managing risks: human and environmental health and safety

Studies of the health impact of airborne particles are the closest thing we have to a tool for assessing potential health risks from free nanoparticles. These studies have generally shown that the smaller the particles get, the more toxic they become. This is due in part to the fact that, given the same mass per volume, the dose in terms of particle numbers increases as particle size decreases.

Based upon available data, it has been argued that current risk assessment methodologies are not suited to the hazards associated with nanoparticles; in particular, existing toxicological and eco-toxicological methods are not up to the task; exposure evaluation (dose) needs to be expressed as quantity of nanoparticles and/or surface area rather than simply mass; equipment for routine detecting and measuring nanoparticles in air, water, or soil is inadequate; and very little is known about the physiological responses to nanoparticles.

Regulatory bodies in the U.S. as well as in the EU have concluded that nanoparticles form the potential for an entirely new risk and that it is necessary to carry out an extensive analysis of the risk. The challenge for regulators is whether a matrix can be developed which would identify nanoparticles and more complex nanoformulations which are likely to have special toxicological properties or whether it is more reasonable for each particle or formulation to be tested separately.

The International Council on Nanotechnology maintains a database and Virtual Journal of scientific papers on environmental, health and safety research on nanoparticles. The database currently has over 2000 entries indexed by particle type, exposure pathway and other criteria. The Project on Emerging Nanotechnologies currently lists 807 products that manufacturers have voluntarily identified that use nanotechnology. No labeling is required by the FDA so that number could be significantly higher. "The use of nanotechnology in consumer products and industrial applications is growing rapidly, with the products listed in the PEN inventory showing just the tip of the iceberg" according to Project on Emerging Nanotechnologies (PEN) Project Director David Rejeski. A list of those products that have been voluntarily disclosed by their manufacturers is located here.

The Material Safety Data Sheet that must be issued for certain materials often does not differentiate between bulk and nanoscale size of the material in question and even when it does these MSDS are advisory only.

Democratic governance

Many argue that government has a responsibility to provide opportunities for the public to be involved in the development of new forms of science and technology). Community engagement can be achieved through various means or mechanisms.(2005) identify traditional approaches such as referenda, consultation documents, and advisory committees that include community members and other stakeholders. Other conventional approaches include public meetings and "closed" dialog with stakeholders. More contemporary engagement processes that have been employed to include community members in decisions about nanotechnology include citizens' juries and consensus conferences. Leach and Scoones (2006, p. 45) argue that since that “most debates about science and technology options involve uncertainty, and often ignorance, public debate about regulatory regimes is essential.”

It has been argued that limited nanotechnology labeling and regulation may exacerbate potential human and environmental health and safety issues associated with nanotechnology, and that the development of comprehensive regulation of nanotechnology will be vital to ensure that the potential risks associated with the research and commercial application of nanotechnology do not overshadow its potential benefits.

Regulation may also be required to meet community expectations about responsible development of nanotechnology, as well as ensuring that public interests are included in shaping the development of nanotechnology.

Community education, engagement and consultation tend to occur "downstream": once there is at least a moderate level of awareness, and often during the process of disseminating and adapting technologies. "Upstream" engagement, by contrast, occurs much earlier in the innovation cycle and involves: "dialogue and debate about future technology options and pathways, bringing the often expert-led approaches to horizon scanning, technology foresight and scenario planning to involve a wider range of perspectives and inputs." Daniel Sarewitz Director of Arizona State University's Consortium on Science, Policy and Outcomes, argues that "by the time new devices reach the stage of commercialization and regulation, it is usually too late to alter them to correct problems."

The stance that the research, development and use of nanotechnology should be subject to control by the public sector is sometimes referred to as nanosocialism.

Newness

The question of whether nanotechnology represents something 'new' must be answered to decide how best nanotechnology should be regulated. The Royal Society recommended that the UK government assess chemicals in the form of nanoparticles or nanotubes as new substances. Subsequent to this, in 2007 a coalition of over forty groups called for nanomaterials to be classified as new substances, and regulated as such.

Despite these recommendations, chemicals comprising nanoparticles that have previously been subject to assessment and regulation may be exempt from regulation, regardless of the potential for different risks and impacts. In contrast, nanomaterials are often recognised as 'new' from the perspective of intellectual property rights (IPRs), and as such are commercially protected via patenting laws. There is an inconsistency here; nanomaterials are legally defined as 'new' via IPRs, however they are not recognized as such from the perspective of health and safety regulations.

New regulatory framework, or adapt existing arrangements?

There is significant debate about who is responsible for the regulation of nanotechnology. While some non-nanotechnology specific regulatory agencies currently cover some products and processes (to varying degrees) – by "bolting on" nanotechnology to existing regulations – there are clear gaps in these regimes. This enables some nanotechnology applications to literally "slip through the cracks" without being covered by any regulations. An example of this has occurred in the US, and involves nanoparticles of titanium dioxide (TI02) for use in sunscreen where they create a clearer cosmetic appearance. In this case, the US Food and Drug Administration (FDA) reviewed the immediate health effects of exposure to nanoparticles of titanium dioxide (TI02) for consumers. However, they did not review its impacts for aquatic ecosystems when the sunscreen rubs off, nor did the EPA, or any other agency. Similarly the Australian equivalent of the FDA, the Therapeutic Goods Administration (TGA) approved the use of nanoparticles in sunscreens (without the requirement for package labelling) after a thorough review of the literature, on the basis that although nanoparticles of TI02 and zinc oxide (ZN0) in sunscreens do produce free radicals and oxidative DNA damage *in vitro*, such particles were unlikely to pass the dead outer cells of the stratum corneum of human skin; a finding which some academics have argued seemed not to apply the precautionary principle in relation to prolonged use on children with cut skin, the elderly with thin skin, people with diseased skin or use over flexural creases. Doubts over the TGA's decision were raised with publication of a paper showing that the uncoated anatase form of TI02 used in some Australian sunscreens caused a photocatalytic reaction that degraded the surface of newly installed prepainted steel roofs in places where they came in contact with the sunscreen coated hands of workmen. Such gaps in regulation are likely to continue alongside the development and commercialization of increasingly complex second and third generation nanotechnologies.

Nanomedicines are just beginning to enter drug regulatory processes, but within a few decades could comprise a dominant group within the class of innovative pharmaceuticals, the current thinking of government safety and cost-effectiveness regulators appearing to be that these products give rise to few if any nano-specific issues. Some academics (such as Thomas Alured Faunce) are beginning to challenge that proposition and suggest that nanomedicines may create unique or heightened policy challenges for government systems of cost-effectiveness as well as safety regulation. There are also significant public good aspects to the regulation of nanotechnology, particularly with regard to ensuring that industry involvement in standard-setting does not become a means of reducing competition and that nanotechnology policy and regulation encourages new models of safe drug discovery and development more systematically targeted at the global burden of disease.

The Self-policing notes that self-regulation attempts may well fail, due to the inherent conflict of interest in asking any organization to police itself. If the public becomes aware of this failure, an external, independent organization is often given the duty of policing them, sometimes with highly punitive measures taken against the organization. The Food and Drug Administration note that they only regulate on the basis of voluntary claims made by the product manufacturer. If no claims are made by a manufacturer, then the FDA may be unaware of nanotechnology being employed.

Yet regulations worldwide still fail to distinguish between materials in their nanoscale and bulk form. This means that nanomaterials remain effectively unregulated; there is no regulatory requirement for nanomaterials to face new health and safety testing or environmental impact assessment prior to their use in commercial products, if these materials have already been approved in bulk form. The health risks of nanomaterials are of particular concern for workers who may face occupational exposure to nanomaterials at higher levels, and on a more routine basis, than the general public.

International law

There is no international regulation of nanoproducts or the underlying nanotechnology. Nor are there any internationally agreed definitions or terminology for nanotechnology, no internationally agreed protocols for toxicity testing of nanoparticles, and no standardized protocols for evaluating the environmental impacts of nanoparticles.

Since products that are produced using nanotechnologies will likely enter international trade, it is argued that it will be necessary to harmonize nanotechnology standards across national borders. There is concern that some countries, most notably developing countries, will be excluded from international standards negotiations. The Institute for Food and Agricultural Standards note that "developing countries should have a say in international nanotechnology standards development, even if they lack capacity to enforce the standards". (p. 14).

Concerns about monopolies and concentrated control and ownership of new nanotechnologies were raised in community workshops in Australia in 2004.

Arguments against regulation

Wide use of the term nanotechnology in recent years has created the misapprehension that regulatory frameworks are suddenly having to contend with entirely new challenges that they are unequipped to deal with. Many regulatory systems around the world already assess new substances or products for safety on a case by case basis, before they are permitted on the market. These regulatory systems have been assessing the safety of nanometre scale molecular arrangements for many years and many substances comprising nanometre scale particles have been in use for decades e.g. Carbon black, Titanium dioxide, Zinc oxide, Bentonite, Aluminum silicate, Iron oxides, Silicon dioxide, Diatomaceous earth, Kaolin, Talc, Montmorillonite, Magnesium oxide, Copper sulphate.

These existing approval frameworks almost universally use the best available science to assess safety and do not approve substances or products with an unacceptable risk benefit profile. The key to regulating any substance is to properly characterise both the physical and chemical properties and ensure the technical specifications which underpin any regulatory limits define the specific substance. Correct characterisation expressed in comprehensive technical specifications is also essential in linking the scientific studies demonstrating the safety of the substance to any regulatory approval. Traditionally technical specifications have not included adequate information around particle characteristics however this simple step will ensure most established regulatory processes are able to conduct safety assessments on the correct physico-chemical entity. Definitions around general terms such as 'nanotechnology' or 'nanoparticle' may assist in clear dialogue in various fields but they do assist in establishing or enforcing regulatory permissions. Creating new regulatory classes based initially on the physical size of particles making up the substance, is not how most regulatory systems operate and doing so would not extend the reach of most existing regulatory frameworks or the rigour of the safety assessments. Particle characteristics should indeed be considered in the safety assessments and be set into comprehensive regulatory specifications. A major argument against special regulation of nanotechnology is that the projected applications with the greatest impact are far in the future, and it is unclear how to regulate technologies whose feasibility is speculative at this point. In the meantime, it has been argued that the immediate applications of nanomaterials raise challenges not much different than those of introducing any other new material, and can be dealt with by minor tweaks to existing regulatory schemes rather than sweeping regulation of entire scientific fields.

A truly precautionary approach to regulation could severely impede development in the field of nanotechnology if we require safety studies for each and every nanoscience application. While the outcome of these studies can form the basis for government and international regulations, a more reasonable approach might be development of a risk matrix that identifies likely culprits.

Response from governments

United Kingdom

In its seminal 2004 report *Nanoscience and Nanotechnologies: Opportunities and Uncertainties*, the United Kingdom's Royal Society concluded that:

Many nanotechnologies pose no new risks to health and almost all the concerns relate to the potential impacts of deliberately manufactured nanoparticles and nanotubes that are free rather than fixed to or within a material… We expect the likelihood of nanoparticles or nanotubes being released from products in which they have been fixed or embedded (such as composites) to be low but have recommended that manufacturers assess this potential exposure risk for the lifecycle of the product and make their findings available to the relevant regulatory bodies… It is very unlikely that new manufactured nanoparticles could be introduced into humans in doses sufficient to cause the health effects that have been associated with [normal air pollution].

but have recommended that nanomaterials be regulated as new chemicals, that research laboratories and factories treat nanomaterials "as if they were hazardous", that release of nanomaterials into the environment be avoided as far as possible, and that products containing nanomaterials be subject to new safety testing requirements prior to their commercial release.

The 2004 report by the UK Royal Society and Royal Academy of Engineers noted that existing UK regulations did not require additional testing when existing substances were produced in nanoparticulate form. The Royal Society recommended that such regulations were revised so that “chemicals produced in the form of nanoparticles and nanotubes be treated as new chemicals under these regulatory frameworks” (p.xi). They also recommended that existing regulation be modified on a precautionary basis because they expect that “the toxicity of chemicals in the form of free nanoparticles and nanotubes cannot be predicted from their toxicity in a larger form and… in some cases they will be more toxic than the same mass of the same chemical in larger form.”

The Better Regulation Commission's earlier 2003 report had recommended that the UK Government:

1. enable, through an informed debate, the public to consider the risks for themselves, and help them to make their own decisions by providing suitable information;
2. be open about how it makes decisions, and acknowledge where there are uncertainties;
3. communicate with, and involve as far as possible, the public in the decision making process;
4. ensure it develops two-way communication channels; and
5. take a strong lead over the handling of any risk issues, particularly information provision and policy implementation.

These recommendations were accepted in principle by the UK Government. Noting that there was "no obvious focus for an informed public debate of the type suggested by the Task Force", the UK government's response was to accept the recommendations.

The Royal Society's 2004 report identified two distinct governance issues:

1. the "role and behaviour of institutions" and their ability to "minimise unintended consequences" through adequate regulation and
2. the extent to which the public can trust and play a role in determining the trajectories that nanotechnologies may follow as they develop.

United States

Rather than adopt a new nano-specific regulatory framework, the United States' Food and Drug Administration (FDA) convenes an 'interest group' each quarter with representatives of FDA centers that have responsibility for assessment and regulation of different substances and products. This interest group ensures coordination and communication. A September 2009 FDA document called for identifying sources of nanomaterials, how they move in the environment, the problems they might cause for people, animals and plants, and how these problems could be avoided or mitigated.

The Bush administration in 2007 decided that no special regulations or labeling of nanoparticles are required. This decision struck many familiar with the issue as inexplicable and a sign of the influence of corporations over individuals, "The consumer is being made the guinea pig" says George Kimbrell of The International Center for Technology Assessment. They are not aware that a substantial amount of consumer products are being sold to them, there's no labelling, there's no information getting to them,' says Elizabeth Nielsen, a consultant for the Consumers Council of Canada (CCC) and author of a report released April 1, Nanotechnology and Its Impact on Consumers … the biggest concern is that consumers are unaware they are buying products that contain nanoparticles. 'Consumers should be informed to make their own judgments of the risks of using these products'" says Troy Benn of Arizona State University who along with

Paul Westerhoff studied the stability of silver nanoparticles in socks with widely varying results.

Berkeley, CA is currently the only city in the United States to regulate nanotechnology. Cambridge, MA in 2008 considered enacting a similar law, but the committee it instituted to study the issue Cambridge recommended against regulation in its final report, recommending instead other steps to facilitate information-gathering about potential effects of nanomaterials.

On December 10, 2008 the US National Research Council released a report calling for more regulation of nanotechnology.

California

In October 2008, the Department of Toxic Substances Control (DTSC), within the California Environmental Protection Agency, announced its intent to request information regarding analytical test methods, fate and transport in the environment, and other relevant information from manufacturers of carbon nanotubes. The term "manufacturers" includes persons and businesses that produce nanotubes in California, or import carbon nanotubes into California for sale. This information request is meant to identify information gaps and to develop further knowledge about the health and safety of carbon nanotubes.

DTSC is exercising its authority under California Health and Safety Code, Chapter 699, sections 57018-57020. These sections were added as a result of the adoption of Assembly Bill AB 289 (2006). They are intended to make information on the fate and transport, detection and analysis, and other information on chemicals more available. The law places the responsibility to provide this information to the Department on those who manufacture or import the chemicals. On January 22, 2009, a formal information request letter was sent to manufacturers who produce or import carbon nanotubes in California, or who may export carbon nanotubes into the State. This letter constitutes the first formal implementation of the authorities placed into statute by AB 289 (2006) and is directed to manufacturers of carbon nanotubes, both industry and academia within the State, and to manufacturers outside California who export carbon nanotubes to California. This request for information must be met by the manufacturers within one year.

On January 22, 2010, California manufacturers and importers of carbon nanotubes were required to submit their responses. On January 25, 2010, DTSC posted the responses received to date along with a list of companies who failed to respond to the information request. On February 16, 2010, DTSC issued a follow-up letter to the companies that failed to submit a response. View the responses received for the carbon nanotube call-in.

DTSC is indicating interest in expanding the Specific Chemical Information Call-in to members of the brominated flame retardants, members of the methyl siloxanes, and other nanometals and nanometal oxides such as vanadium oxide, aluminum oxide, silicon dioxide, titanium dioxide, zinc oxide, cerium oxide, nano platinum, nano silver, and nano zerovalent iron. DTSC is also planning to include quantum dots, ocean plastics, and nanoclay into the list of chemicals of interest.

European Union

The European Union has formed a group to study the implications of nanotechnology called The Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR). One can find their list of risks Here.

Consequently, manufacturers and importers of carbon products, including carbon nanotubes will have to submit full health and safety data in order to comply with REACH. Remember, though, that the data does not have to submitted for a year or so.

Response from advocacy groups

In January 2008, a coalition of over 40 civil society groups endorsed a statement of principles calling for precautionary action related to nanotechnology. The coalition called for strong, comprehensive oversight of the new technology and its products in the International Center for Technology Assessment's report *Principles for the Oversight of Nanotechnologies and Nanomaterials*, which states:

Hundreds of consumer products incorporating nanomaterials are now on the market, including cosmetics, sunscreens, sporting goods, clothing, electronics, baby and infant products, and food and food packaging. But evidence indicates that current nanomaterials may pose significant health, safety, and environmental hazards. In addition, the profound social, economic, and ethical challenges posed by nano-scale technologies have yet to be addressed ... 'Since there is currently no government oversight and no labeling requirements for nano-products anywhere in the world, no one knows when they are exposed to potential nanotech risks and no one is monitoring for potential health or environmental harm. That's why we believe oversight action based on our principles is urgent' ... This industrial boom is creating a growing nano-workforce which is predicted to reach two million globally by 2015. 'Even though potential health hazards stemming from exposure have been clearly identified, there are no mandatory workplace measures that require exposures to be assessed, workers to be trained, or control measures to be implemented,' explained Bill Kojola of the AFL-CIO. 'This technology should not be rushed to market until these failings are corrected and workers assured of their safety'" also.

The group has urged action based on eight principles. They are 1) A Precautionary Foundation 2) Mandatory Nano-specific Regulations 3) Health and Safety of the Public and Workers 4) Environmental Protection 5) Transparency 6) Public Participation 7) Inclusion of Broader Impacts and 8) Manufacturer Liability.

Some NGOs, including Friends of the Earth, are calling for the formation of a separate nanotechnology specific regulatory framework for the regulation of nanotechnology. In Australia, Friends of the Earth propose the establishment of a Nanotechnology

Regulatory Coordination Agency, overseen by a Foresight and Technology Assessment Board. The advantage of this arrangement is that it could ensure a centralized body of experts that are able to provide oversight across the range of nano-products and sectors. It is also argued that a centralized regulatory approach would simplify the regulatory environment, thereby supporting industry innovation. A National Nanotechnology Regulator could coordinate existing regulations related to nanotechnology (including intellectual property, civil liberties, product safety, occupation health and safety, environmental and international law). Regulatory mechanisms could vary from "hard law at one extreme through licensing and codes of practice to 'soft' self-regulation and negotiation in order to influence behaviour." The formation of national nanotechnology regulatory bodies may also assist in establishing global regulatory frameworks.

In early 2008, The UK's largest organic certifier, the Soil Association, announced that its organic standard would exclude nanotechnology, recognizing the associated human and environmental health and safety risks. Certified organic standards in Australia exclude engineered nanoparticles. It appears likely that other organic certifiers will also follow suit. The Soil Association was also the first to declare organic standards free from genetic engineering.

Technical aspects

Size

Regulation of nanotechnology will require a definition of the size, in which particles and processes are recognized as operating at the nano-scale. The size-defining characteristic of nanotechnology is the subject of significant debate, and varies to include particles and materials in the scale of at least 100 to 300 nanometers (nm). Friends of the Earth Australia recommend defining nanoparticles up to 300 nanometers (nm) in size. They argue that "particles up to a few hundred nanometers in size share many of the novel biological behaviours of nanoparticles, including novel toxicity risks", and that "nanomaterials up to approximately 300 nm in size can be taken up by individual cells". The UK Soil Association define nanotechnology to include manufactured nanoparticles where the mean particle size is 200 nm or smaller. The U.S. National Nanotechnology Initiative define nanotechnology as “the understanding and control of matter at dimensions of roughly 1 to 100 nm.

Mass thresholds

Regulatory frameworks for chemicals tend to be triggered by mass thresholds. This is certainly the case for the management of toxic chemicals in Australia through the National pollutant inventory. However, in the case of nanotechnology, nanoparticle applications are unlikely to exceed these thresholds (tonnes/kilograms) due to the size and weight of nanoparticles. As such, the Woodrow Wilson International Centre for Scholars question the usefulness of regulating nanotechnologies on the basis of their size/weight alone. They argue, for example, that the toxicity of nano-participles is more related to surface area than weight, and that emerging regulations should also take account of such factors.