

Nanomaterials: Nomenclature, Novelty, and Necessity

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Nanomaterials are an enabling component of the popularly labeled area of "nanotechnology," but are generally not well understood in the materials community at large. The purpose of this article is to narrow this gap by framing nanomaterials in the traditional materials science and engineering context as well as discussing some potential implications to the materials enterprise.

INTRODUCTION

To understand and discuss nanomaterials, it is perhaps best to start with the broad area that is known as nanotechnology. Identification of the concept of nanotechnology has been attributed to Richard Feynman, who presented a speech in 1959 titled "There's Plenty of Room at the Bottom." In his speech, Feynman described manipulating atoms to make materials many decades before it became possible to do so.¹ The term "nanotechnology" was not used until 1974 by Taniguchi at the University of Tokyo, Japan, to refer to the ability to engineer materials precisely at the nanometer level, driven by electronics industry needs.² In 1981, the advent of the scanning tunneling microscope enabled atom clusters to be seen, while in 1991 IBM demonstrated the ability to arrange individual xenon atoms using an atomic force instrument.

What is nanotechnology? A variety of definitions for nanotechnology have been presented. By the U.S. National Nanotechnology Initiative (NNI) standards, nanotechnology involves all of the following:

- Research and technology development at the atomic, molecular, or macromolecular levels, approximately 1–100 nanometers in length.

- Creation and use of structures, devices, and systems that have novel properties and functions because of their small and/or intermediate size.
- Ability to control or manipulate on the atomic scale.

The principles of physics, as far as I can see, do not speak against the possibility of moving things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it hasn't been done because we are too big.¹

Richard Feynman, 1960

The Royal Society and The Royal Academy of Engineering define nanotechnologies as the design, characterization, production, and application of structures, devices, and systems by controlling shape and size at the nanometer scale.³ Note the use of the plural due to the large number of tools, techniques, and potential applications involved. Others have more prosaic descriptions that perhaps lack definitional precision but provide insight. As Gary Stix described nanotechnology in *Scientific American*, "The field is a vast

grab bag of stuff that has to do with creating tiny things that sometimes just happen to be useful. It borrows liberally from condensed-matter physics, engineering, molecular biology and large swaths of chemistry."⁴

Within the nanotechnologies field are a wide variety of other terms used to describe its various facets, and the compilation of "Nanonomenclature" in the accompanying sidebar is an attempt to put many of these terms and descriptions of each in one place.

Included in this list is the term "nanomaterials," which are materials that have one or more dimensions in the range of 1 to 100 nanometers. The reason that size matters is that the properties of materials can have some unexpected differences from their behavior in larger bulk forms that makes for new application opportunities. The two reasons for this change in behavior are an increased relative surface area (producing increased chemical reactivity) and the increasing dominance of quantum effects (with effects on the material's optical, magnetic, or electrical properties).

NANOMATERIALS AND NANOTECHNOLOGY

Not unlike the situation in conventional technology, materials are a critical if sometimes underappreciated component in achieving the goals of nanotechnology. A central construct of materials science and engineering is that the structure and processing of a material give rise to its properties, which in turn determine its performance in use. This certainly applies to nanomaterials as well and provides a useful framework for understanding in a familiar context.

Nanomaterials have been important in the materials field for quite a long time. An early example was the incorpo-

ration of gold nanoparticles in stained glass in 10 A.D. At sizes in the nano-range, gold can exhibit a range of colors.³ Also, nano-sized carbon black particles have been used to reinforce tires for 100 years.⁴

Perhaps one manifestation of the concept of nanomaterials familiar to traditional metallurgists is precipitation hardening. As discussed by Hornbogen,⁵ the accidental discovery of precipitation hardening in 1906 by Wilm in Duralumin alloys opened the way to significant improvements in strength properties for aluminum. Although researchers were unable to image the precipitates with the instruments available at the time, it was

subsequently discovered that nanometer-sized precipitates were the source of hardening. Through the advent of electron microscopy came a better understanding of the structure of precipitates, including aspects such as size and coherency with the metal matrix. This allowed further improvement in nanoscale structures through composition selection and knowledgeable processing, resulting in further gains in a variety of materials systems. It is interesting to note that the ability to image precipitates was critical to optimizing processing and properties, much as the invention of scanning-probe instruments enabling the imaging of

nanostructures has accelerated progress in nanotechnology.

What then are the nanomaterials of today and tomorrow? As a framework for this discussion, the approach of Jones⁶ for organizing nanotechnology into three categories can be applied to nanomaterials. The categories are:

- Incremental nanotechnology—improving the properties of materials by controlling their nanoscale structure.
- Evolutionary nanotechnology—taking a step beyond redesigning simple materials at the nanoscale and designing nanoscale devices that do something interesting
- Radical nanotechnology—developing nanoscale machines that would exist at the convergence of nanotechnology, biotechnology, information technology, and cognitive technology.

Incremental Nanotechnology

Incremental nanomaterials are materials that have improved properties at the nanoscale, typically as a result of their greatly increased surface area, but do not typically take advantage of the quantum effects.

Nanoparticles are already seeing application, taking advantage primarily of the high surface area of these fine powders. Nanoceramic powders, the most commercially important of which are simple metal oxides, constitute almost 90% of the total market.⁷ For example, nano-sized zinc oxide particles are in use in sunscreen. Nanostructured ceramic coatings are adding durability and toughness to hulls of U.S. Navy ships. Metal powders are important, as well. Iron nanoparticles have been used to treat groundwater contaminated with trichloroethylene while aluminum nanoparticles have been developed that, due to their increased surface area, have substantially greater “bang for the buck” as solid rocket propellant.

Incremental nanomaterials also include polymer nanocomposites in which clay nanoparticles are incorporated to increase the hardness and reduce the permeability of the polymer. These have seen application in automotive panels and step assists in vans. Other examples of these types of applications are nanoparticles in tennis balls and

NANONOMENCLATURE

Atomic-Force Microscope: A scanning-probe instrument that maps the surface topography by measuring the force acting on a tip as it slides along a surface or moves perpendicular to it.

Bottom-Up Nanofabrication: The building of nanostructures starting with small components such as atoms or molecules.

Buckminsterfullerene or Buckyball: A spheroidal fullerene; the first known example of a fullerene.

Fullerene: A form of carbon having a large molecule consisting of an empty cage of 60 or more carbon atoms

Nanocomposites: Composite structures whose characteristic dimensions are found at the nanoscale.

Nanocrystalline: Material with average grain size measured in billionths of a meter.

Nanodots: Nanoparticles that consist of homogeneous material, especially those that are almost spherical or cubical in shape.

Nanofabrication: The manufacture or preparation of nanostructures.

Nanoparticles: Aggregates of atoms bridging the continuum between small molecular clusters of a few atoms and dimensions of 0.2–1 nm and solids containing millions of atoms and having the properties of macroscopic bulk material

Nanorods: Nanostructures that are shaped like long sticks or dowels, with a diameter in the nanoscale and a length very much longer.

Nanoscale: Phenomena that occur on the length scale between 1 and 100 nanometers.

Nanoscience: The study of fundamental principles of molecules and structures with at least one dimension roughly between 1 and 100 nanometers.

Nanostructure/Nanostructured Materials: Structures whose characteristic variation in design length is at the nanoscale.

Nanotechnology: The application of nanoscience in technological devices.

Nanotubes: Almost always carbon nanotubes, referring to the wires of pure carbon that look like rolled sheets of graphite or like carbon soda straws

Nanowires: Another term for nanorods, especially nanorods that can conduct electricity.

Quantum Dots: Nanostructures of roughly spherical or cubic shape that are small enough to exhibit characteristically quantum behavior in optical or electrical processes.

Scanning-Probe Instruments: Tools for both measuring and preparing nanostructures on surfaces; they work using the interactions between a scanning-tip structure and the nanostructure on the surface, which can be either manipulated or measured.

Scanning-Tunneling Microscope: The first of the scanning probe instruments. It works at the scale of the nanostructure and measures electrons tunneling between a scanning tip and a conducting surface.

Top-Down Nanofabrication: The process of making nanostructures starting with larger structures and taking parts away.

carbon nanotubes in tennis racquets.

Incremental nanotechnology can also be found in the development of nanostructured materials by techniques such as equal channel angular extrusion and accumulative roll bonding, which fall in the category of severe plastic deformation processes. Articles by Semiatin et al.⁸ and Zhu⁹ elsewhere in this issue discuss these concepts in more depth. The primary benefit of these processes is to produce ultrafine-grained structures with dimensions in the submicrometer range, resulting in increased strengthening along with other enhanced properties. Note again that the benefits obtained in these nanostructured materials come primarily from the increase in surface area (in this case the surface area of grain boundaries) and the impact of the small scale of the structure on dislocation motion rather than quantum effects. Also note that the inherent coupling of the ability to image these structures and their behavior is inextricably linked to their optimization. For example, recent work has described changes in deformation mode from dislocation-slip to grain boundary sliding as a function of grain size for nanocrystalline nickel using the in-situ microscope at the National Center for Electron Microscopy at the Lawrence Berkeley Laboratory.¹⁰

Evolutionary Nanotechnology

Evolutionary nanotechnology takes advantage of the changes that can occur in materials at the nanoscale related both to increased chemical reactivity and the increasing importance of quantum effects. Examples include nanoscale sensors that exploit the large surface area of nanotubes and semiconductor nanostructures such as quantum dots and quantum wells. For example, silica-based nanomaterials, molecular imprinted polymers, and silicon platforms are envisioned for collection, concentration, and detection of chemical weapons and other related compounds in security and defense applications.¹¹ The biggest steps are being made in evolutionary nanotechnology, with more and more products expected to appear in the market in the next five years.

A material that has generated substantial interest is the class of molecularly perfect carbon structures called fullerenes. The creation of a 60 carbon atom

molecule in the form of a geodesic sphere, termed the buckyball by Smalley in 1985, has led to other fullerenes containing many more atoms of carbon and taking different shapes. One such shape is the carbon nanotube (CNT), which has a range of unique properties. These materials can act as either highly conductive nanowires or as semiconductors, depending on the specific arrangement of the carbon atoms. The perfection of the CNT creates a material with a strength reported to be 30 times that of steel at 1/6 the density. The thermal conductivity of CNTs is 50% higher than that of diamond. These unique properties have already led to the use of

CNTs in specialty applications such as high-performance tennis racquets and selected electronics. Longer term, CNTs are seen as key components in fuel cells, electrical transmission lines, and thermoelectric conversion devices. (The area will be the subject of its own short course at the upcoming 2005 TMS Annual Meeting. See details in News and Update in this issue.)

Carbon nanotubes are by no means the sole materials focus of evolutionary nanotechnology. Other materials are in development that will generate immediate interest and impact on the electronic materials field. As described in an earlier *JOM* paper by Rittner, these include

THE DOUBLE-EDGED SWORD OF NANOMATERIALS

Many of the greatly enhanced properties of nanomaterials, and in particular nanoparticles, are derived from their very small size and very large surface area. These properties can also present challenges in the environmental, health, and safety (EHS) realm.

Two issues identified in a recent report by insurance company Swiss Re²⁶ are the mobility of nanoparticles in the environment and their unrestricted access to the human body. Coated nanoparticles, once airborne, will not settle on surfaces as larger particles would, and may be difficult or impossible to filter. Entry of nanoparticles into the body through inhalation, possibly through the skin, and via the digestive tract are all considered options. Once in the body, nanoparticles may be able to migrate freely, even scaling the blood-brain barrier. Whether nanoparticles, with their changed chemical properties, are a threat has not been determined and toxicological studies are recommended. Such studies are under way in the United States as part of the National Nanotechnology Initiative²⁰ as well as in Europe.

Some initial viewpoints have been expressed in reviews such as that carried out by The Royal Society and The Royal Academy of Engineering.³ While only scant evidence is currently available, it suggests that at least some manufactured nanoparticles will be more toxic per unit of mass than larger particles of the same chemical. Also, there is concern about the potential effects of the physical characteristics of nanomaterials. For example, carbon and other nanotubes may have toxic properties similar to asbestos fibers, although preliminary studies suggest that they may not escape into the air as individual fibers. Recent research has been published in which carbon nanotubes and related carbon nanocrystal aggregates present in the atmosphere were analyzed via transmission electron microscopy.²⁷ These nanoparticles occur naturally and have been created for many millennia as a result of combustion and food cooking. While qualitative in nature, this type of work indicates increasing attention to environmental and health considerations.

These sorts of concerns have resulted in recommendations that the release of nanoparticles and nanotubes into the environment be avoided as far as possible and treatment of these nanomaterials as though they were hazardous until proven otherwise. These concerns have even caused Prince Charles of Britain to weigh in. The Prince of Wales has called for greater consideration of the social, environmental, and ethical implications of nanotechnology, saying that at this early stage of research, risk assessment must keep pace with commercial development.²⁸

One of the challenges for the EHS area comes back to nomenclature. Regulators at agencies such as the United States Environmental Protection Agency and Occupational Safety and Health Administration need a systematic taxonomy so they can tell from a molecule's name what it looks like and how it behaves. The naming of nanoproducts poses novel challenges. Because they are so small they behave very differently than macrosized substances of similar chemical composition. Groups are beginning to address this issue, and Vicki Colvin, director of the Center for Biological and Environmental Nanotechnology at Rice University, is seeking funding for a series of nanomenclature meetings in the near future, with the expectation that it could take as long as two years to get a solid framework.

semiconductor nanowires, quantum dots, semiconductor nanocrystals, nanoscale thin films, and organic molecules.¹² It is anticipated that there will be significant impact in the energy area, including high-efficiency solar energy conversion as well as advanced fuel cells and batteries. Medical applications enabled by nanomaterials including diagnosis and treatment, along with

are concepts in which nanotechnology converges with biology, information technology, and cognition. Novelist Michael Crichton seized upon this convergence as the technological engine for his 2002 novel *Prey*. Based on a hypothetical future in which so-called nanobots develop evolutionary capability and self-replicate, becoming an out-of-control, dangerous force, the book paints a scary picture. Although the book is fiction, it does raise the question of responsibility—a question is being taken sufficiently seriously that there exists a Center for Responsible Nanotechnology Development (www.crnano.org). While interesting (for cocktail parties and novels), radical nanotechnology is viewed as being decades away if at all.

NANOFABRICATION

Since nanomaterials have little mass and are dominated by surface area and size effects, the processes and equipment for nanotechnology-based manufacturing are expected to differ significantly from those currently used. One of the key differences is the concept of manufacturing on an atom-by-atom basis, which has been labeled bottom-up processing. Conventional methods, called top-down techniques, start with a block of material, etching or milling it down to the desired shape. The main challenge for top-down manufacture is the creation of increasingly small structures with sufficient accuracy, whereas for bottom-up manufacture, the challenge is to make structures large enough, and of sufficient quality, for use as materials. These two methods have evolved separately and have now reached the point where the best achievable feature size for each technique is approximately the same.³

Most of the current nanomaterials with potential for structural use are powder based, produced from processes such as inert-gas condensation, electrodeposition, atomization, and mechanical alloying. They need to be consolidated into shapes with minimal porosity without creating significant structural coarsening and loss of the desirable nanostructural properties. This requires a balance of minimal high-temperature exposure and adequate pressure, and innovative methods of consolidation need to be developed to produce

Commercial nanotechnology is at a nascent stage. Large-scale production challenges, high production cost, the public's general reluctance to embrace innovative technology without real safety data or products, and a well-established micron-scale industry are just a few of the bottlenecks facing early-stage nanotechnology commercialization.¹⁴

Raj Bawa, 2004

markedly different approaches to pharmaceuticals, are also predicted to be on the horizon in the next decade.

Radical Nanotechnology

Radical nanotechnology is viewed as having an impact much farther into the future. Examples include next-generation military uniforms being developed by the Massachusetts Institute of Technology's Institute for Soldiering Nanotechnology. The uniforms are designed to defend against chemical and biological weapons, provide ballistic protection, monitor health, administer medical aid, and provide communication capabilities.¹³ Much farther in the future

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successful materials.¹⁵

While nanotubes have incredible strength, capturing this strength in a structural component is no small challenge. This challenge is analogous to the challenges faced by early metal-matrix composite materials engineers who sought to capture the ultrahigh strength of ceramic whiskers in structural materials. Incorporating these expensive reinforcement materials cost-effectively in large-volume operations was difficult, often resulting in damage to the whiskers and loss of much of their property advantage.

NANOTECHNOLOGY AND THE MATERIALS ENTERPRISE

Billions of dollars are being invested in opportunities centered around materials that exist on the scale of a billionth of a meter. The National Science Foundation has made the bold prediction that the business impact of nanotechnology will be \$1 trillion by 2015. Some 800,000 to 2 million new jobs, in a field where the estimates of current number of workers range from 20,000 to 40,000, will be required to reach this level.¹⁶ Pundits claim that within the next decade, nanotech will have huge effects on many practical industries, including manufacturing, health care, energy, agriculture, communication, transportation, and electronics.¹⁷ Just issued, *The Nanotech Report 2004* produced by Lux Research¹⁸ highlights the magnitude of financial resources being put into nanotechnology. Specifically, the report notes:

- Governments, corporations, and venture capitalists will spend more than \$8.6 billion worldwide on nanotechnology R&D in 2004.
- National and local governments across the world will invest more than \$4.6 billion in nanotechnology R&D in 2004. Roughly 35% of this investment is in North America, 35% in Asia, 28% in Europe, and 2% in the rest of the world.
- The U.S. government will spend nearly twice as much on nanotechnology this year as it did on the Human Genome Project (HGP) in its peak year. In 2005, the National Nanotechnology Initiative will surpass the HGP on a cumulative basis. The United States has

appropriated more than \$3.16 billion for nanotechnology R&D since 2000 and is proposing \$982 million in new funding for 2005.

- Established corporations will spend more than \$3.8 billion globally on nanotechnology R&D in 2004.

It is not an exaggeration to say that nanotechnology is the biggest thing to happen to the physical sciences for quite some time. It is estimated that worldwide

Once poorly understood as an ill-defined amalgamation of disparate atomic level sciences, nanotechnology is now coming of age as sophisticated investors and corporate executives grasp that this is no passing fad.¹⁸

Lux Research, 2004

government funding in nanotechnology increased by seven times from 1997 to 2003, exceeding \$3 billion in 2003.¹⁹

In the United States, the 21st Century Nanotechnology Research and Development Act, signed in December 2003, will provide \$3.7 billion for four years beginning in 2005. The funding request for \$982 million in 2005 is an increase of more than 500% compared to 2001. A key component of this funding is for five user facilities, called the Nanoscale Science Research Centers, which are now under construction at Department of Energy laboratory sites. These research facilities will focus on synthesis, processing, and fabrication of nanoscale materials. They will be co-located with existing user facilities to provide sophisticated characterization and analysis capabilities. Also included is funding for addressing so-called grand

challenge areas. Three of these areas, Nanostructured Materials by Design, Manufacturing at the Nanoscale, and Nano-Electronics, -Photonics, and -Magnetics, have a materials focus.²⁰

Another indicator of the potential in nanotechnology is indicated by the growth in patent activity. In the United States, for example, the number of patents issued in areas such as atomic force microscopy and quantum dots increased ten-fold from 1994–2003. The U.S. Patent and Trademark Office has been prompted to create a classification system for nanotechnology (as the Japanese Patent Office has already) so that it can track the number, pendency, and assignment of nanotechnology patent applications. While at present there is a classification for fullerene-related patent applications there are no separate classes for areas such as nanotubes or nanowires.²¹

Also harkening the transition from laboratory to commercialization is the presence of organizations such as the NanoBusiness Alliance (www.nanobusiness.org), which claims to be the first industry association founded to advance the emerging business of nanotechnology and micro-systems. The NanoBusiness Alliance's mission is to create a collective voice for the emerging small-tech industry and develop a range of initiatives to support and strengthen the nanotechnology business community.

The business prospects of nanotechnology have caught the attention of Wall Street, where brokerage firm Merrill Lynch has been promoting a nanotech stock index. A nanotechnology company, Nanosys, contemplated an initial public offering of stock but withdrew it, which was viewed in a *Wall Street Journal* article as “less an indictment of nanotechnology than a sign of how tough it is for any company in an early stage of development right now.” The article goes on to note, however, that “nanotechnology remains difficult to define, causing additional uncertainties for investors. . . . Some companies have used the nanotechnology label to hype unrelated products, while many real advances are occurring inside big companies such as Intel, where the developments have only a modest impact on stock prices.”²²

Nanomaterials are one area where

real revenues are being realized currently. It is estimated that sales of nanomaterials were \$1.5 million in 1999 and grew to \$430 million by the end of 2003. With this annual growth rate of 300%, the market size would be projected to be \$1.3 billion in 2004 and \$5 billion in 2005.¹⁶ A more conservative estimate of \$1 billion in revenue in 2007 is provided by a recent study by the Freedonia Group.²³

Nanotechnology is already having an impact on the structure of the scientific community. The intersection of physics, chemistry, and materials science at the nanoscale has required a broadening of the educational process, which will be required to meet the need for future nanotechnologists. More than 300 academic programs in nanotechnology exist today, with at least 200 in the United States and 100 internationally.¹⁸ There are implications for professional societies as well, and it has been noted that the scientific and engineering communities should create new means of interdisciplinary training and communication, reduce the barriers that inhibit individuals from working across disciplines, develop links to a variety of other technical and medical organizations, and address ethical issues related to technological developments.²⁴

Nanotechnology is gaining awareness beyond the scientific community. The number of times terms related to "nano" appeared in the popular press has risen from 190 in 1995 to a projection of more than 12,000 in 2004.¹⁷ Recent studies carried out both in the United States²⁵ and United Kingdom³ indicated that the public is not as aware yet of nanotechnology while only 29% in the United States, 71% had heard "little" or "nothing" about nanotechnology while only 29% in the United Kingdom had heard of it. Of that 29%, only 19% were able to offer some sort of definition. These same studies indicated that a majority of those polled in both countries are encouraged by the prospects of nanotechnology to improve life in the future.

As nanotechnology grows into the public consciousness, its potential societal implications are beginning to be

seriously addressed. On one level, attention is being directed to the environmental, safety, and health issues that may develop (see the sidebar "The Double-Edged Sword of Nanomaterials"). In addition, the potentially disruptive nature of nanotechnology, particularly if visions of the radical technology are realized, is beginning to be addressed by groups such as the Foresight Institute (www.foresight.org/).

CONCLUSION

Nanomaterials are here now—in some cases as incremental but significant improvements of development efforts before the nanotechnology label was applied—and are finding application in a wide range of markets. Substantial funding along with intense government, business, and media attention promises to accelerate R&D and implementation, although significant challenges exist for large-scale nanomaterials for structural applications. While the emergence of nanotechnologies has greatly broadened the disciplines involved, the structure-processing-property framework that materials science and engineering brings will be a vital component in ultimate technical and commercial success.

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