

Nanoscale Materials in Chemistry

Edited by

KENNETH J. KLABUNDE

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NANOSCALE MATERIALS IN CHEMISTRY

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NANOSCALE MATERIALS IN CHEMISTRY

To Linda

PREFACE

Nanotechnology is almost a household word now-a-days, or at least some word with “nano” in it, such as nanoscale, nanoparticle, nanophase, nanocrystal, or nanomachine. This field now enjoys worldwide attention and a National Nanotechnology Initiative (NNI) is about to be launched.

This field owes its parentage to investigations of reactive species (free atoms, clusters, reactive particles) throughout the 1970s and 1980s, coupled with new techniques and instruments (pulsed cluster beams, innovations in mass spectrometry, vacuum technology, microscopes, and more).

Excitement is high and spread throughout different fields, including chemistry, physics, material science, engineering, and biology. This excitement is warranted because nanoscale materials represent a new realm of matter, and the possibilities for interesting basic science as well as useful technologies for society are widespread and real.

In spite of all this interest, there is a need for a book that serves the basic science community, especially chemists.

This book was written to serve first as a advanced textbook for advanced undergraduate or graduate courses in “nanochemistry”, and second as a resource and reference for chemists and other scientists working in the field. Therefore, the reader will find that the chapters are written as a teacher might teach the subject, and not simply as a reference work. Therefore, we hope that this book will be adopted for teaching numerous advanced courses in nanotechnology, materials chemistry, and related subjects.

The coverage of this volume is as follows: First, a detailed introduction of nanotechnology and a brief historical account is given. This is followed by masterful chapters on nanosize metals by Gunter Schmid, semiconductors by Marie Pileni, and ceramics by Abbas Khaleel and Ryan Richards. The next chapters deal more with properties, such as optical properties by Paul Mulvaney, magnetic properties by Chris Sorensen, catalytic and chemical properties by the editor and Ravi Mulukutla, physical properties by Olga Koper and Slawomir Winecki, and finally a short chapter on applications of nanomaterials by John Parker.

The editor gratefully acknowledges the contributing authors of these chapters, who are world renowned experts in this burgeoning field of nanotechnology. Their enthusiasm and hard work are very much appreciated. The editor also acknowledges the help of his students and colleagues, as well as his family for their patience and understanding.

Kenneth J. Klabunde

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1 Introduction to Nanotechnology

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1.1 INTRODUCTION TO THE NANOWORLD

It has been said that a nanometer is “a magical point on the length scale, for this is the point where the smallest man-made devices meet the atoms and molecules of the natural world.”¹

Indeed, “nanotechnology mania” is sweeping through essentially all fields of science and engineering, and the public is becoming aware of the quote of the chemist and Nobel Laureate, Richard Smalley: “Just wait—the next century is going to be incredible. We are about to be able to build things that work on the smallest possible length scales, atom by atom. These little nanothings will revolutionize our industries and our lives.”²

In a recent report of the National Science Foundation to the President’s Office of Science and Technology Policy it was stated that “Nanoscience and technology will change the nature of almost every human-made object in the next century.”³

So what are these “nanothings” that are going to change our lives? Perhaps the best way to begin to convey the possibilities is to list topical areas that nanotechnology promises to affect.

Pharmacy It may be possible to create biomolecules that carry out “pharmacy in a cell,”¹ that could release cancer-fighting nanoparticles or chemicals in response to a distress signal from an afflicted cell.

Therapeutic Drugs It is now possible to produce new solid state medicines by simply producing them in nanoparticle form. The high surface areas of these small particles allow them to be solubilized into the bloodstream where normal micro

particles or larger particles cannot.³ Since over 50% of new drug formulations are never brought to market because of solubility problems, this simple transformation into a nano-form opens up broad new possibilities for drug synthesis and utilization.³

Tagging of DNA and DNA Chips Nanoparticle assay of DNA has been possible by coating gold nanoparticles with DNA strands. When these are exposed to complementary DNA, binding (hybridization) occurs, and this causes the colloidal gold particles to aggregate, and as a result a color change takes place.^{4,5}

Microarrays to detect and help identify DNA samples have been built by creating devices with up to 100,000 different known DNA sequences. When the unknown target DNA sequences match with any of the DNA chip arrays, then binding (hybridization) occurs and the unknown sequence is identified by its position on the array.³

Information Storage Ultrafine dye particles often yield higher quality inks in terms of color, coverage, and color-fastness.⁶ Also, “nanopens” (atomic force microscope tips) can write letters with features as small as 5 nm.¹

Actually, nanoparticles have already found their way into modern audio and videotapes and disks, which are dependent on magnetic and optical properties of fine particles. Further advances will be made with smaller and smaller sizes and with control of magnetic coercivity and optical absorption, so that much denser storage media should be possible.⁶

Refrigeration On a small scale it has been demonstrated that an entropic advantage can be gained in magnetic particle field reversal. Thus, upon application of a magnetic field, the entropy of a magnetic species changes, and if adiabatic conditions are maintained, the application of the field will result in a temperature change. This ΔT is the magnetocaloric effect, and the magnitude of this effect depends on the size of the magnetic moment, heat capacity, and temperature dependence of the magnetization. If nanoparticles with large magnetic moments and adequate coercivity can be obtained, the magnetocaloric effect may allow refrigeration on a practical scale.⁷

The promise of magnetic nanoparticle refrigerators, with no need for refrigeration fluids (Freons, HFC, etc.), has enticed many researchers, and success would mean tremendous benefits for society and the environment.

Chemical/Optical Computers Organized two-dimensional or three-dimensional arrays of metal or semiconductor nanoparticles exhibit special optical and magnetic properties. These materials hold promise in numerous applications in the electronics industry, including optical computers.^{8,9}

Improved Ceramics and Insulators The compression of nanoscale ceramic particles yields more flexible solid objects, apparently because of the multitude of grain boundaries that exist.^{3,10} After further development of compression techniques, so

that highly densified nonporous materials can be prepared, these new materials may find uses as replacements for metals in many applications.

Harder Metals Nanoparticulate metals when compressed into solid objects exhibit unusual surface hardness, sometimes as high as five times that of the normal microcrystalline metal.^{3,10}

Film Precursors Similar to their use in inks, nanoqueous metallic colloidal solutions have proven useful as precursors for thin metallic film formation when used as spray paint.¹¹ In particular, gilding of silver artifacts with gold has been accomplished with gold–acetone colloids.^{12,13}

Environmental/Green Chemistry

- *Solar Cells.* Semiconductor nanoparticles, with size-tunable bandgaps, hold the potential for more efficient solar cells for both photovoltaics (electricity production) and water splitting (hydrogen production).^{14,15}
- *Remediation.* Photoexcitation of fine particles of semiconductors leads to electron–hole pairs that are useful for both oxidation and reduction of pollutants, for use in decontaminating water.^{14–16}
- *Water Purification.* Reactive metal fine powders (Fe, Zn) show high reactivity toward chlorocarbons in an aqueous environment. These results have led to the successful implementation of porous metal powder–sand membranes for groundwater decontamination.¹⁷
- *Destructive Adsorbents.* Nanoparticulate metal oxides exhibit high intrinsic surface reactivities and high surface areas, and strongly chemisorb acidic gases and polar organics. Since dissociative chemisorption is usually observed, these new materials have been dubbed “destructive adsorbents,” and are finding use in anti-chemical/biological warfare,¹⁸ in air purification,¹⁹ and as an alternative to incineration of toxic substances.²⁰

Catalysts Successful catalytic processes developed over the last six decades have led to a vital industry that contributes to the economy at least 20% of the GDP.²¹

What is significant in the context of nanostructural materials in chemistry is that heterogeneous catalysis is dependent on nanoparticles of metals, and research on the effect of particle size (percent dispersion as a measure of the fraction of metal atoms on the surface and thus available to incoming reactants) and shape (crystal faces, edges, corners, defects that lead to enhanced surface reactivity) has been and continues to be a vigorous field.

Sensors Porous aggregates of semiconductor nanoparticles can be prepared by low-load compression. These materials maintain their high surface areas, and when they undergo adsorption of various gases, their electrical conductivity changes. Since more of the gas to be detected (such as sulfur dioxide) is adsorbed per unit

mass compared with normal compressed powders, the electrical changes are more pronounced. Thus, the use of nanoparticles yields a considerable advantage in sensor technology.

Defect-tolerant Chemically Assisted Architectures Size reduction of electronic devices, if continued apace, will reach the size of *molecules* in a few decades. However, when entering the molecular scale or nanoscale, the fact that these are quantum mechanical objects means that the physics upon which the devices are based will be dramatically changed. Manufacturing processes will also have to change dramatically. One concept of making such a dramatic shift is through molecular electronics; molecules will have to serve as quantum electronic devices, and be synthesized and allowed to self-assemble into useful circuits. Recent efforts have shown some promise; for example, electrical properties of a single immobilized benzene-1,4-thiol molecule have been measured.²² Also, a molecular switch based on the rotaxane molecule has been experimentally demonstrated.^{9,23}

Nanostructured Electrodes Nanoscale metal crystallites can be grown by rapid electrodeposition due to very high nucleation rates and thereby reduced crystallite (grain) growth. Magnetic metals such as iron can then form dense magnetic solids with soft magnetic properties (low coercivity and high saturation magnetization). These materials are useful for transformers.^{24,25}

Improved Polymers There are almost magical effects produced when nanopowders are added to polymer matrices. The nanopowders can be in the form of fine particles, needlelike structures, or platelets. There is a reinforcing effect such that strength of the composite is greatly increased.

The mechanism by which this reinforcement takes place is poorly understood at present. However, with further work and better understanding, the potential outcomes of improved polymers and plastics are easy to imagine. Stronger, lighter materials, wear-resistant tires, tougher coatings, replacements for body parts, flame-retardant plastics, replacements for metals, and more can be imagined.³

Self-cleaning and Unusual Coloring in Paints It has been demonstrated that when paints are doped with light-absorbing nanoparticles, such as TiO_2 , the paints are self-cleaning.³ The mechanism by which this happens is related to photooxidation of contaminants by TiO_2 in water discussed earlier. Organic greasy materials that adhere to paint can be oxidized by the electron-hole pair formed when TiO_2 nanoparticles absorb sunlight. Thus, the organic materials are cleaned off the paint film. It is perhaps surprising that the paint itself is not attacked by this powerful oxidation/reduction couple, and it may be found that such paints are not as long-lived as those that are not doped with TiO_2 nanoparticles.

Another interesting development is the use of gold nanoparticles to give paints a beautiful metallic reddish color, due to the special optical properties of such particles.²⁶

Smart Magnetic Fluids Ferrofluids are colloidal solutions containing small magnetic particles stabilized with surfactant ligands. These have been known since the 1960s and are important as vacuum seals, viscous dampers, and contamination exclusion seals. With improvements, other applications may become important, such as their use as cooling fluids, nanoscale bearings, magnetically controlled heat conductors, and magnetic acids in separation of ores in mining and scrap metal separation.^{3,27}

Better Batteries Nanostructural materials in lithium ion batteries have proven to be very advantageous. For example, researchers at Fuji found that by placing nanocrystalline tin (7–10 nm) within an amorphous glass-forming matrix yielded nanocrystalline islands of tin enclosed by an amorphous oxide network. Electrical conductivity can be maintained within such an electrode. The advantage of such a nanostructural material is that the rather open structure of the glass helps to accommodate strain associated with the volume expansion during insertion and removal of lithium from tin. Also, it is believed that the nanocrystalline nature of the tin precludes formation of bulk phases of Li–Sn alloys, which are deleterious to the battery.^{3,28}

Other advantages have been gleaned from nanostructural materials, such as the rapid reaction of Li_2CO_3 and NiO to form a desired mixed oxide.²⁹ Dragieva and coworkers have prepared a series of nickel–metal–hydride (Ni–M–H) batteries through the preparation of nickel nanoparticles by borohydride reduction in water.³⁰

In general, the ability to prepare metallic nanocrystals that can be consolidated into high-surface-area electrodes has certain inherent advantages, and further progress is sure to come.

Improved National Security The use of high-surface-area reactive nanoparticles as destructive adsorbents for decontamination of chemical and biological warfare agents has proven quite effective, and allows rapid response with few logistical problems.^{31,32}

Sensors for toxic airborne and waterborne materials are also possible through the unique adsorbent properties of consolidated nanocrystals. Indeed, there appear to be numerous areas where national security can be improved through advances in nanotechnology in electronics, optics, catalysts, and sorbents.³

Summary It is quite apparent that there are innumerable potential benefits for society, the environment, and the world at large. Some of them have been briefly described, but the list is longer still.³

Before presenting greater detail, as Chapters 2–9 will do regarding nanomaterials in chemistry and related fields, it is appropriate now to describe in a more academic sense why nanoparticles are so unique.

1.2 A NEW REALM OF MATTER THAT LIES BETWEEN CHEMISTRY AND SOLID STATE PHYSICS

After considering the current interest in nanotechnology, it seems appropriate to place the nanoworld in the context of basic sciences. Chemistry is the study of atoms and molecules, a realm of matter of dimensions generally less than one nanometer, while condensed matter physics deals with solids of essentially an infinite array of bound atoms or molecules of dimensions greater than 100 nm. A significant gap exists between these regimes. Figure 1.1 illustrates this gap, which deals with particles of 1 to 100 nm, or about 10 to 10^6 atoms or molecules per particle.^{33,34}

In this nanoscale regime neither quantum chemistry nor classical laws of physics hold.² In materials where strong chemical bonding is present, delocalization of valence electrons can be extensive, and the extent of delocalization can vary with the size of the system. This effect, coupled with structural changes with size variation, can lead to different chemical and physical properties, *depending on size*. Indeed, it has now been demonstrated that a host of properties depend on the size of such nanoscale particles, including magnetic properties, optical properties, melting points, specific heats, and surface reactivity. Furthermore, when such ultrafine particles are consolidated into macroscale solids, these bulk materials sometimes exhibit new properties (e.g., enhanced plasticity).

It is clear that a huge new field of science has been born. Think of the multitude of combinations of two, three, or more elements with particles of varying sizes! Each change in composition or size can lead to different physical and chemical properties. It is evident that an almost infinite number of possibilities present themselves. And this new field of clusters/nanophase materials, lying between the traditional fields of chemistry and solid-state physics, touches upon disciplines such as electronics, astronomy, mathematics, and engineering. Therefore, interdisciplinary research is required for progress to be made. The most important aspects are synthesis, physical properties, and chemical properties, but the most important of these at this time is *synthesis*. The nanoparticles of interest are almost always prepared in the laboratory (as opposed to occurring naturally), are sometimes reactive with oxygen and water, and are difficult to produce in a monodisperse (one size only) form. Thus creative synthesis schemes that lead to gram or kilogram quantities of pure materials are absolutely essential before this new field of science can be developed for the benefit of humankind.

Atoms/ Molecules	Nanoscale Particles		Condensed Matter	
1	125	70,000	6×10^6	∞N^0 Atoms
	1	10	100	∞ Diameter (nm)
Quantum Chemistry	?		Solid State Physics	

FIGURE 1.1 Size relationships of chemistry, nanoparticles, and condensed matter physics.

Another way to calibrate the nanocrystalline size range is to compare it with other small things in our world. Figure 1.2 compares the size of bacteria, viruses, nanocrystals, and the Buckminsterfullerene molecule. Note that bacteria are huge in comparison and it is helpful to realize that the volume of one *Bacillus cereus* bacterium could hold a million 5 nm nanoparticles.

These illustrations help make the point that nanocrystals, particularly in the 1–10 nm range (100 to 70,000 atoms) serve as bridges from molecules to condensed matter. In this size range intrinsic properties change due to size alone. For semiconductors such as ZnO, CdS, and Si, *bandgaps* (the energy needed to promote an electron from the valence band to the conduction band) change. In some cases, for bandgaps in the visible spectrum, this means that colors can change with size change in the 1–10 nm range. Furthermore, *melting points* change in this size regime, and *specific heats* change. For magnetic materials such as Fe, Co, Ni, Fe_3O_4 , and others, magnetic properties are size-dependent. In particular the coercive force (or “magnetic memory”) needed to reverse an internal magnetic field within the particle is size-dependent. Further, the strength of a particles’ internal magnetic field can be size-dependent.

Of particular importance for chemistry, surface energies and surface morphologies are also size-dependent, and this translates to enhanced intrinsic surface reactivities. Added to this are huge surface areas for nanocrystalline powders, and this also affects their chemistry in substantial ways. Consider, for example, that a 3 nm iron particle has 50% of its atoms on the surface, whereas a 10 nm particle has just 20% on the surface, and a 30 nm particle only 5%. There are several important ramifications of large fractions of surface atoms, not the least of which is the fact that such materials can chemically react as nearly stoichiometric reagents.

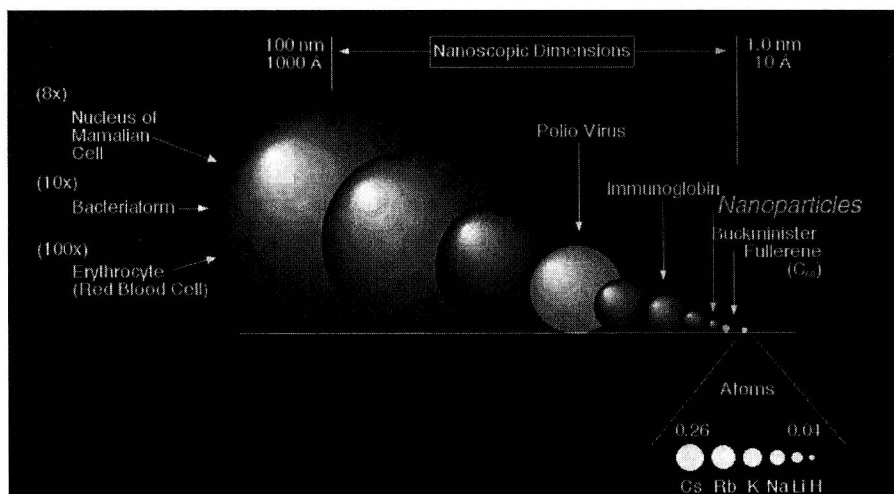


FIGURE 1.2 Size comparisons of nanocrystals with bacteria, viruses, and molecules.

1.3 HISTORICAL PERSPECTIVE ON NANOMATERIALS

As mentioned above, heterogeneous catalysis can be considered as one of the first uses of nanoscale materials. However, the broad field of colloid chemistry can also be viewed as an early integral part of nanotechnology.³⁵ Indeed, several decades have passed since catalysts and colloids were the true pioneering aspects of nanotechnology. So why is it that this topic has “heated up” only in recent years?

The answer undoubtedly lies in the invention of numerous techniques for characterization and analysis of such materials. It is now possible to actually see atoms, a development that was hard even to imagine only a few years ago. In fact there are numerous technological developments that tend to amaze even scientists working in this area of investigation. Some of these developments are briefly described below.

High-resolution Transmission Electron Microscopy (HRTEM) A high-voltage electron beam passes through a very thin sample, and the sample areas that do not allow the passage of electrons allow an image to be presented. Due to advances in electronics, computers, and sample preparation techniques, modern high-voltage instruments have resolution in the 0.1 nm range; thus it is possible to image heavy atoms in some cases, and nanoparticle sizes and shapes are easily imaged. Sample preparation is crucial, and usually involves placing very dilute particle suspensions onto carbon-coated copper grids. Another useful technique is imbedding the particle in a solid organic polymer, slicing very thin sections, and passing the electron beam through the section.

*Scanning Probe Microscopy (SPM; also called Scanning Tunneling Microscopy, STM) and Related Atomic Force Microscopy (AFM)*³⁶ Discovery of the SPM technique took place in the 1980s. It involves dragging a very sharp needlelike probe across a sample very close to the sample surface. For conducting samples a tunneling current between the sample and probe tip can be monitored and held constant. As the probe approaches an elevated portion of the sample, the probe moves up and over, and by rastering over an area of the sample, a surface map can be produced. With proper sample preparation and using a high-quality instrument in a vibration-free environment, it is sometimes possible to image down to atomic resolution. In fact, it has been possible to probe electronic structure and single atoms by Scanning Tunneling Microscopy (STM).³⁷

When the sample is nonconducting, the atomic force (AFM) mode can be used, where the probe tip is essentially touching the surface, and the surface can be mapped by the weak interaction force between tip and sample. In the AFM mode, resolution is substantially poorer than for the tunneling mode. There continue to be developments in this area, and magnetic mapping is also possible.

Powder X-Ray Diffraction (XRD) Although XRD has been useful for crystalline powders for several decades, modern improvements in electronics, computers, and X-ray sources have allowed it to become an indispensable tool for identifying nanocrystalline phases as well as crystal size and crystal strain. Other aspects include

small angle X-ray scattering to characterize particle sizes in nano-, micro-, and macroscale in compressed powders.^{38,39}

Differential Scanning Calorimetry (DSC) Heating nanostructured materials can lead to crystal growth by amalgamation (exothermic), melting (endothermic), or crystal phase changes (exo- or endothermic). When the nanoparticles are ligated—for example, thiol coatings on gold—chemical reactions and ligand displacements can occur, which can be exo- or endothermic. By use of DSC, these transformations can be monitored and the extent of exo- or endothermicity determined, which can be very helpful in characterization.

Superconducting Quantum Interference (SQUID) Magnetometry For magnetic nanomaterials, the very sensitive SQUID can yield information on blocking temperatures, Néel temperatures, coercivity, saturation magnetization, ferromagnetism, and superparamagnetism. The device is cooled with liquid helium, and the sample can be studied at near liquid helium temperature or up to well above room temperature.

Laser Desorption Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (LD-FTICR-MS) The field of mass spectrometry is in rapid transition with the development of numerous new sample ionization techniques, better electronics, and data processing. Electrospray ionization now allows very high mass “molecules” to be analyzed. In addition, laser desorption coupled with ion cyclotron resonance allows probing of surface compositions and structure of surface adsorbed species.⁴⁰

Brunauer–Emmett–Teller Gas Adsorption Surface Area Measurement and Pore Structure Analysis (BET Method) Another technique that has been well known for many decades is the determination of surface areas of powders by nitrogen gas adsorption at near liquid nitrogen temperature. Physisorption of a monolayer of N₂ allows calculation of surface area, by plotting pressure versus gas uptake. In recent years great improvements have allowed not only rapid surface area determinations but also pore size distributions, pore volumes, and in general the ability to more thoroughly characterize morphologies and even fractal dimensions.⁴¹

This brief summary of important characterization techniques for nanostructural materials is far from complete. Advances in scanning electron microscopy (SEM), dynamic light scattering, surface techniques for obtaining IR and UV–visible spectra, X-ray photoelectron spectroscopy, Auger spectroscopy, and many more are of considerable importance as well.

In addition to advances in characterization methods, there have also been striking advances in the synthetic arena. Perhaps it is obvious that nanostructural materials are for the most part synthetic chemicals, and their synthesis has to precede everything else.