WHAT CAN CHEMISTS DO FOR NANOSTRUCTURED MATERIALS?*

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Introduction

Nanostructured materials have now been investigated for more than a decade using a rather wide range of experimental methods [1-3]. The structures and properties of these new materials, which are artificially synthesized from nanometer-sized "building blocks", such as clusters, grains or layers, have been elucidated in a number of important areas and the relationships among these areas are beginning to be understood. Various investigations of their mechanical, chemical, electrical, magnetic, and optical behavior have demonstrated the possibilities to engineer the properties of nanostructured materials through control of the sizes of their constituent clusters, grains or layers and the manner in which these constituents are assembled [4-6]. There are, however, tremendous opportunities remaining for creative new tailored chemical synthesis and processing methods and for developing an understanding of the important role of surface and interface chemistry in the assembly and resulting properties of these materials. Some aspects of our present understanding of nanostructured materials and their properties are briefly presented here, along with some thoughts regarding a few critical future research needs in various areas of chemistry that would add greatly to the field of nanostructured materials.

Interest in the physics of condensed matter at size scales larger than that of atoms and smaller than that of bulk solids has grown rapidly because of the increasing realization that the properties of these mesoscopic atomic ensembles are different than those of conventional solids. Thus, interest in artificially assembling materials from nanometer sized building blocks arose from discoveries that, by controlling their sizes in the range of 1-100 nm and the assembly of such constituents, one could begin to alter and prescribe the properties of the assembled nanostructures. Nature had apparently already learned well the value of nanostructuring, since many examples of naturally created nanostructures, formed chemically under ambient conditions, can be found in biological systems from sea shells to the human body.

Nanostructured materials are modulated over nanometer length scales. They can be assembled with modulation dimensionalities of zero (atom clusters or filaments), one (multilayers), two (ultrafine-grained overlayers or coatings or buried layers), and three (nanophase materials), or with intermediate dimensionalities [5]. Thus, nanocomposite materials containing multiple phases can range from the most conventional case in which a nanoscale phase is embedded in a phase of conventional sizes to the case in which all the constituent phases are of nanoscale dimensions. All nanostructured materials share three features: atomic domains (grains, layers or phases) spatially confined to less than 100 nm in at least one dimension, significant atom fractions associated with interfacial environments, and interactions between their constituent domains.

Multilayered materials have had the longest history among the various artificially synthesized nanostructures, one that has already seen applications in semiconductor devices, strained-layer superlattices, and magnetic...
multilayers. The technological potential of multilayered quantum heterostructure semiconductor devices was recognized in the 1970s in the rapidly expanding electronics and computer industries and helped to drive advances in this exciting new field. Since the 1980s there has been a rapid expansion of research on isolated atom clusters and an increased understanding of their potential as the constituents of new materials [1].

A knowledge of the variation in cluster properties, both physical and chemical, with cluster size is important to both our fundamental understanding of condensed matter and our ability to use cluster-assembled materials in a variety of technological applications. The manner in which the structure and properties of collections of condensed atoms in a single cluster vary with cluster size, from atomic or molecular to bulk solid-state behavior, is a fundamental touchstone in the development of realistic theoretical models for condensed matter. Theoretical areas that are impacted by this variation include understanding the forces acting among atoms, the structures of atom collections, electronic effects (quantum size effects) caused by spatial confinement of delocalized valence electrons, and cooperative (many body) atom phenomena such as lattice vibrations or melting.

Synthesis and properties

A number of methods exist for the synthesis of nanostructured materials. They include synthesis from atomic or molecular precursors (chemical or physical vapor deposition; gas-condensation; chemical precipitation; aerosol reactions; biological templating), from processing of bulk precursors (mechanical attrition; crystallization from the amorphous state; phase separation), and from nature. It is generally preferable to synthesize nanostructured materials from atomic or molecular precursors, in order to gain the greatest control over a variety of microscopic aspects of the condensed ensemble, but other methodologies can often yield very useful results [4,7]. Novel chemical synthesis and processing methods for creating tailored nanostructures are sorely needed, especially ones that can carefully control the interface chemistry and ones that can be effected at ambient temperatures.

Foremost in importance in nanostructuring is the ability to control the size and size distribution of the constituent phases or structures. The desirable sizes are generally below 100 nm, since it is in this size range (and frequently below 10 nm) that various properties begin to change significantly owing to confinement effects. Spatial confinement can in general affect any property when the size of the atomic ensemble becomes comparable to or smaller than a critical length scale for the mechanism that is responsible for that property. Examples can be as diverse as the "blue" (high-frequency, short-wavelength) shifts of the optical absorption in semiconducting clusters when their sizes fall below the Bohr radii (ca. 5-50 nm) of the excitonic (electron-hole pair) states responsible for absorption and the increased strengthening of normally soft metals when their grain sizes fall below the critical length scales (ca. < 50 nm) for the sources of dislocations (the defect responsible for easy deformation) to easily operate at conventional applied stresses.

Second, the chemical compositions of the constituent phases in a nanostructured material are of fundamental importance, as they are also to the performance of conventional materials. This not only relates to average compositions, but also invariably to chemical gradients within the constituent phases or structures and especially those near surfaces and interfaces. Indeed, the chemistry of the surfaces of the constituents, as well as that of the subsequently formed interfaces on assembly, can often play a crucial role in the ability to use these materials. The third aspect of nanostructured materials
that one would like to be able to control in their synthesis is the nature of the interfaces created between constituent phases and, hence, the nature of the interactions across the interfaces. Both the local structure and chemistry of the interfaces are important in this regard.

The properties of nanostructured materials are determined by the interplay among these three features (domain size, composition, and interfaces). In some cases, one or more of these features may dominate the particular property in question. Thus, one wants to be able to synthesize nanostructured materials under controlled conditions, but with an eye toward the particular property or properties of interest. The degree of control available, of course, depends upon the particular synthesis method being used to create the given nanostructured material.

Examples

During the past several years, exciting progress has been made in the physics, chemistry, biology, and materials research communities in characterizing and understanding nanostructured materials, including multilayers, individual and assembled atom clusters, and cluster-consolidated nanophase materials. A few examples are given here.

In magnetic multilayers, such as those formed by alternating layers of ferromagnetic Fe and Cr, the material can be nanostructured so that its electrical resistance is significantly decreased (by up to a factor of 2 depending upon the Cr layer thickness) by the application of a magnetic field of 2 T\[^{181}\]. Such an effect, called giant magnetoresistance (GMR), occurs when the magnetic moments of the neighboring alternating layers (Fe) are arranged in an antiparallel fashion, so that application of the magnetic field overcomes the antiferromagnetic coupling and aligns the layers into a condition of parallel ferromagnetic ordering, strongly reducing the electron scattering in the system. Magnetoresistive materials are already being used in the magnetic recording industry as read heads, owing to their lower noise and improved signal handling capabilities. It is expected that nanostructured materials will have a significant future impact in this area as new materials are developed with stable GMR at room temperature that can operate at magnetic fields as low as about one mT. Discoveries that nanostructured materials other than multilayers (such as magnetic Co clusters embedded in a nonmagnetic matrix of Cu or Ag\[^{9,10}\] or magnetic plate-like NiFe deposits embedded in Ag\[^{113}\]) also exhibit GMR should hasten the advent of their useful application. It seems that the modulation dimensionality and the material architecture play important roles in the resulting magnetic behavior.

Optical properties of noninteracting assemblages of small semiconductor clusters have been found exciting from both the scientific and technological points of view. The optical absorption of CdS clusters with diameters in the nanometer size regime made by any of a variety of methods, including chemical precipitation in solutions or in zeolite supports, is rather different from that for bulk CdS. The absorption edge is blue shifted to appreciably shorter wavelengths, owing to the the effects of quantum confinement in these nanoscale clusters. However, when these clusters are synthesized in zeolite supports with increasing loading, such that they become close enough to begin to interact through quantum tunneling, the absorption edge begins to shift back toward bulk behavior\[^{12}\]. A similar effect can be created by changing the sizes of the clusters in colloidal suspensions and thereby changing the degree of quantum confinement\[^{13}\]. Hence, control of the average distance between clusters in the zeolite cages, even though they are not actually in contact, or control of the cluster sizes in a suspension can...
enable control over a macroscopic property of the assembled cluster ensemble. Thus, not only do such quantum size effects in clusters provide a basis for verifying our understanding of the electronic structure of condensed matter, they may also provide for engineered optical properties that will find useful future applications in optical and computing devices. Another example of this, which has gained much attention recently, is porous Si formed by chemical etching that creates a bicontinuous array of nanometer-sized pores and Si "wires" [14]. The remaining nanostructured Si has an increased band gap caused by quantum confinement and an enhanced photoluminescence. Nevertheless, important questions regarding this latter property remain to be answered related to the surface chemistry of this material.

The chemical reactivity of nanostructured materials, with their potentially high surface areas compared to conventional materials, can also be significantly enhanced, a property long utilized in the catalysis community. Since clusters can be assembled by means of a variety of methods, there can be an excellent degree of control over the total available surface area in the resulting self-supported nanostructured ensembles. Thus, one can maximize porosity for obtaining very high surface areas, remove most of it via consolidation, but retain some to facilitate low-temperature doping or other processing, or fully densify the nanophase material. Also, control of chemical composition can be readily achieved, since rapid atomic diffusion paths are plentiful and diffusion distances are short in the clusters. Measurements of the decomposition of hydrogen sulfide over lightly consolidated, high surface area nanophase titanium dioxide with a rutile crystal structure have clearly demonstrated the potential for enhanced chemical reactivity of nanophase materials [15]. Nanophase rutile is far more reactive initially than other available forms of titanium dioxide and, more importantly, remains so even after extended exposure to the hydrogen sulfide at 500°C. This enhanced activity results from a combination of unique and controllable features of the nanophase material, its high surface area combined with its rutile structure and its oxygen deficient composition. Such behavior should have significant future impact in a variety of catalytic and sensor applications.

Chemical reactivity has also played a role in the study of atom clusters. The structure of individual atom clusters is difficult to characterize owing to the very small size scale involved. Direct observation methods, such as electron microscopy, are useful in probing the structure of clusters larger than about 2 nm containing hundreds of atoms or more. Methods with greater resolution, such as field-ion or scanning-tunneling microscopy, which might be used to observe smaller clusters, suffer from the necessity of placing the clusters on a substrate that may alter their structure. However, the structures of isolated small clusters containing tens of atoms have been successfully characterized by using their chemical reactivity as a probe. As atoms are individually added to a cluster, the ability of the cluster to react chemically with surrounding gas molecules changes depending upon the particular atomic structure of its surface. For example, the selective chemical reactivity with ammonia or water molecules has been used to characterize the atomic structure of clusters of the transition metals Ni and Co containing fewer than about 200 atoms [16]. It was found that the cluster structure changes with the addition of metal atoms, but not in a monotonic fashion and differently for the two metals. Atoms are arranged in an icosahedral structure for some size ranges and more close-packed structures typical of bulk metals at other sizes. However, the propensity for forming the icosahedral structure is greater in Ni clusters, consistent with the decrease in d-electron bonding in Ni relative to Co. Theoretical modeling of this selective reactivity using molecular
dynamics has been successful in reproducing the experimental results and in extending them to other cluster-reactant systems.

The assembly of larger atom clusters into bulk nanophase materials can also have dramatic effects upon properties. In this case, the clusters interact fully with one another, yet the effects of cluster size are still very important. Clusters of metals or ceramics have been consolidated to form ultrafine-grained polycrystals that have mechanical properties remarkably different and improved relative to their conventional coarse-grained counterparts [17]. For example, nanophase Cu and Pd assembled from clusters with diameters in the range 5 to 7 nm can have hardness and yield-strength values up to 500% greater than in the conventionally produced metal. This greatly increased strength arises from the increased difficulty in the spatially confined grains of nanophase metals in creating and moving dislocations, the defect normally responsible for the relatively easy deformation process in metals. In ceramics, on the other hand, which are normally difficult to deform and hence very brittle, cluster assembly yields a different benefit. Ceramics and conventionally brittle intermetallics can be rendered ductile (capable of easier deformation) by being synthesized from clusters with sizes below about 15 nm. This ductility results from the increased ease with which the ultrafine grains created by the clusters can slide by one another in a process called grain-boundary sliding, owing to the short diffusion distances required for the necessary local healing of incipient cracks that could otherwise form during this grain-over-grain sliding process. Nanocomposites consisting of metallic phases, ceramic and metallic phases (cermets), and ceramic phases in a variety of modulation dimensionalities also have considerably enhanced mechanical properties including increased strength and fracture toughness. It is very early in the development of these new materials, but the increased ductility exhibited by nanophase ceramics and intermetallics and the increased strength observed in nanophase metals and nanocomposites should find use in a variety of future technological applications, including those for which wear or corrosion resistance are important design criteria.

Future needs

There are tremendous opportunities for synthesizing nanostructured materials with new architectures at nanometer length scales from atomic or molecular precursors via the assembly of atom layers and clusters and by a myriad of other techniques now becoming available, such as nanoscale lithography and biological templating. Important keys to the future of nanostructured materials will be (i) our ability to continue to significantly improve the properties of materials by artificially structuring them on these nanometer length scales and (ii) developing the methods for producing these materials in commercially viable quantities. There are, thus, very significant opportunities for developing creative new chemical synthesis and processing routes for the tailored nanostructuring of materials with new engineered properties in a manner not unlike that so successfully applied to polymer synthesis and processing. It is also imperative that an understanding of the important role of surface and interface chemistry in the assembly and resulting properties of these materials be developed. Because of the nanometer scales involved, new or improved experimental probes with accessible lateral length scales in the nanometer regime will certainly need to be developed.

Various aspects of our present understanding of nanostructured materials and their properties have been briefly presented here, along with some thoughts regarding a few critical future research needs in various areas of chemistry that would add greatly to the field of nanostructured materials.