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# Self-Organized Nanoscale Materials

Motonari Adachi and David J. Lockwood

Editors

With 197 Figures

 Springer

Motonari Adachi  
International Innovation Center  
Kyoto University  
Uji, Kyoto 611-0011  
Japan  
adachi@iae.kyoto-u.ac.jp

David J. Lockwood  
Institute for Microstructural Sciences  
National Research Council of Canada  
Ottawa, Ontario K1A 0R6  
Canada  
david.lockwood@nrc-cnrc.gc.ca

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# Preface

Novel system performance through nanostructuring has been recognized in many branches of science in the latter half of the 20th century. In computer science, the computational efficiency has improved by nearly four orders of magnitude in 30 years, using energy consumed per operation as a metric. To achieve further advances will require the reduction in size of electronic devices to the scale of molecules; that is, a totally different type of computational machinery is required: molecular electronics. The requirement for inventing a new technology paradigm has created research opportunities for scientists in a very wide range of disciplines.

Nature uses molecular self-assemblies composed of surfactant molecules in biomineralization to construct nanostructures regulated at the atomic scale. Advances in synthetic molecular biology have resulted in highly efficient biological systems, which perform elegant energy and mass conversions using hierarchical assemblies of microstructures, again regulated at the atomic scale (e.g., the structure of the photosynthetic reaction center of a purple bacterium and the structure and reaction mechanism of enzymes).

In order to realize the tremendous potential of nanostructure science and technology, the extremely important challenges are how to exploit synthetic methods for structures regulated at the atomic scale and to construct materials across the hierarchy of length scales from the atomic to mesoscopic and/or to macroscopic scale.

This book comprises a survey of different approaches to the synthesis of nanoscale materials and the hierarchical assemblies produced from them, which have been prepared using self-organized mechanisms via chemical and bio-inspired methods. These methods have two principal advantages. First, nanoscale materials can be synthesized under mild conditions. For example, the layer-by-layer adsorption method in the liquid phase can accumulate different layers consecutively at room temperature just like the multilayer formation by molecular beam deposition at high temperature. The prime advantage of mild conditions such as room-temperature formation is essential for the utilization of biomaterials and is also recommended from an environmental point of view. Second, synthesis using self-organized mechanisms can make nanosize materials at the

scale of Avogadro's number. For comparison, it is very difficult to make nanosize materials at the scale of Avogadro's number by fabrication methods using an individual atom or molecule, such as manipulating atoms or molecules with the atomic force microscope (AFM) tip. Thermal, chemical, and structural stabilization of the nanostructured materials and removal of defects are other challenges still for the future.

The growth and properties of semiconductor quantum dots have been studied extensively in the last decade. These novel nanostructures offer interesting prospects for the development of new electronic or optoelectronic devices. In particular, if the size, shape, and positioning of those structures can be controlled, they become very attractive for applications in areas such as telecommunication wavelength integrated photodetectors, tunable light sources, and single-photon light sources. In Chapter 1, "Self-Assembled  $\text{Si}_{1-x}\text{Ge}_x$  Dots and Islands," Jean-Marc Baribeau, Nelson L. Rowell, and David J. Lockwood review progress in our understanding of  $\text{Si}_{1-x}\text{Ge}_x$  island growth on (001) Si. The evolution of the island morphology with  $\text{Si}_{1-x}\text{Ge}_x$  coverage is particularly complex and understanding it has led to a better knowledge of strained heterosystems. The chapter summarizes the effect of various growth parameters or postgrowth treatments on the shape of the  $\text{Si}_{1-x}\text{Ge}_x$  islands, their composition and strain distribution, their spatial distribution, and their vertical correlation in multilayer stacks. The vibrational properties of these  $\text{Si}_{1-x}\text{Ge}_x$  nanostructures are presented along with a detailed review of their optical properties, which are of key importance in device applications. The self-organization of the  $\text{Si}_{1-x}\text{Ge}_x$  islands is a feature of special significance if they are to become building blocks of novel devices. Various approaches that have been used to engineer  $\text{Si}_{1-x}\text{Ge}_x$  islands and, in particular, to control their size and spatial distribution are described. Recent progress in the use of  $\text{Si}_{1-x}\text{Ge}_x$  island superlattices as fast telecommunication infrared photodetectors is detailed.

One of the most active trends in modern materials chemistry is the development of synthetic methods to obtain size- and shape-controlled inorganic nanocrystals. The shape and size of inorganic nanocrystals determine their widely varying electrical and optical properties. As reported in Chapter 2, "Synthesis of Titania Nanocrystals: Application for Dye-Sensitized Solar Cells" by Motonari Adachi, Yusuke Murata, Fumin Wang, and Jinting Jiu, titania nanocrystals, which have a large surface area with controlled surface structure and high electron transport properties, are important for producing high-efficiency dye-sensitized solar cells (DSCs). DSCs have significant potential as a low-cost alternative to conventional  $p$ - $n$  junction solar cells. Morphological control and high crystallinity are key properties needed in titanium oxide materials for such cells. A promising way to increase the efficiency of titanium oxide DSCs is to improve the properties of the semiconductor electrode using a network structure of single-crystalline anatase nanowires instead of a porous titania film composed of nanosize particles. In this chapter, the formation of a network structure of single-crystalline  $\text{TiO}_2$  nanowires by an "oriented attachment" mechanism is presented in detail. Methods are given for the morphological control of anatase nanocrystals using dodecanediamine as a surfactant, and the formation mechanism is discussed together with the synthesis

of nanosheets of quasi-anatase phase. Finally, the application of a TiO<sub>2</sub> network of single-crystalline anatase nanowires in DSCs is considered.

Nanosized building blocks with low dimensionality such as nanowires, nanorods, nanotubes, and nanosheets have emerged as technically important systems, which provide fundamental scientific opportunities for investigating the influence of size and dimensionality on their optical, magnetic, and electronic properties as well as potential components for nanodevices. In Chapter 3, “Soft Synthesis of Inorganic Nanorods, Nanowires, and Nanotubes” by Shu-Hong Yu and Yi-Tai Qian, the latest developments on new mild soft-solution-based strategies for the fabrication of low-dimensional nanocrystals are reviewed. Examples of such approaches are the hydrothermal/solvothermal process, the solution–liquid–solid mechanism, capping agent/surfactant-assisted synthesis, the bio-inspired approach, and the oriented attachment growth mechanism. Current developments show that soft-solution synthesis provides alternative strategies for the rational synthesis of a variety of low-dimensional nanorods, nanowires, nanosheets, and nanotubes with a controllable size, shape, length scale, and structural complexity. This new growth mechanism could offer an additional tool to design advanced materials with anisotropic material properties and could be used for the synthesis of more complex crystalline three-dimensional structures.

Porous inorganic materials such as zeolites and zeolite-like crystalline molecular sieves are of great interest due to their range of commercial applications in traditional areas such as catalysis, adsorption/separation, and ion exchange and the more specialized fields of MRI contrast agents and blood-clotting agents. The term *zeolite* refers to the specific class of aluminosilicate molecular sieves, although the term is frequently used more loosely to describe compounds other than aluminosilicates that have frameworks similar to known zeolites. Here, in Chapter 4, “Assembly of Zeolites and Crystalline Molecular Sieves” by Jennifer L. Anthony and Mark E. Davis, various aspects of the assembly processes for synthesizing zeolites and other crystalline molecular sieves are overviewed. Topics covered include the thermodynamics and kinetics of the crystallization process, the possible self-assembly mechanisms in the crystallization, and the roles that the various components of the synthesis play in determining the ultimate structure that is formed. The importance of understanding how zeolites and zeolite-like molecular sieves are assembled from a molecular/atomic point of view is emphasized and the knowledge gained is applied to designing a chiral molecular sieve.

As discussed in Chapter 5, “Molecular Imprinting by the Surface Sol-Gel Process” by Seung-Woo Lee and Toyoki Kunitake, molecular imprinting is a fairly representative method of template synthesis and it has been recognized as a means for preparing specific binding sites for given molecules in appropriate matrices. In this approach, the shape and functionality of organic molecules as the template are transcribed onto microporous materials. The configuration of the functional groups in the template can be fixed within the matrix. In comparison with the more conventional sol-gel procedures, the characteristics of the surface sol-gel process, which was developed as a means for preparation of ultrathin metal oxide films, are presented. This process gives rise to oxide gel films of nanosize thickness, and

the individual metal oxide layers have a thickness close to 1 nm under carefully controlled conditions. Recent progress in molecular imprinting in metal oxide matrices is summarized together with the application of the surface sol-gel process to mixtures of organic carboxylic acids and titanium alkoxide, which provides ultrathin layers of titania gel. Many substances such as aromatic carboxylic acids, amino acid derivatives, peptides, saccharide monomers, phosphonic acid derivatives, mercaptans, and metal ions are examined as templates. Possible practical applications and unsolved problems of this technique are presented and discussed.

Nanotubes offer some important advantages for biotechnological and biomedical applications because of their tremendous versatility in terms of materials that can be used, sizes that can be obtained, and the chemistry and biochemistry that can be applied. The template method might prove to be a particularly advantageous approach for preparing nanotubes for such applications. However, this field of nanotube biotechnology is in its infancy, and there is much work still to be done before products based on this technology are brought to fruition. In Chapter 6, "Fabrication, Characterization, and Applications of Template-Synthesized Nanotubes and Nanotube Membranes," Punit Kohli and Charles R. Martin report on the synthesis, characterization, and applications of nanotubes and nanotube membranes synthesized using template synthesis. They discuss in detail the applications of nanotube and nanotube membranes in biosensing, bioseparation, and bioanalytical areas such as drug detoxification using functionalized nanotubes, enzyme- and antibody-immobilized nanotubes for biocatalysis and bioextractions, synthesis of nano test tubes, DNA-functionalized nanotube membranes with single-nucleotide mismatch selectivity, and the fabrication of an artificial ion channel using a single-conical nanotube membrane.

Metal nanoparticles have been intensively studied in the past from the points of view of scientific interest and practical applications. These nanoparticles, with their diameters of 1–10 nm, consist of several tens or thousands of metal atoms in each cluster. These nanoparticles can be considered as a new class of material in the nanotechnology field. Specific aspects of interest include their spectroscopic and magnetic properties, the synthesis and catalysis of polymer-stabilized or ligand-coated metal nanoparticles, and the nonlinear optical properties of metal nanoparticle-doped metal oxides. Thanks to the size limit of these nanoparticles, they are expected to show novel properties, which can be explained by a "nanoscopic effect." This size limit introduces quite a high population of surface atoms that control their properties. The synthesis of monodispersed nanoparticles is of prime importance because their properties vary strongly by their dimensions, and economical mass production of monodispersed metal nanoparticles is now a very important issue. One solution to improving the unique properties of metal nanoparticles is the addition of another element. This is especially so in the field of catalysis, where the addition of second and third elements to the principal monometallic nanoparticle is a common way to improve catalytic properties of selectivity and/or activity. Studies of bimetallic nanoparticles have been intensively carried out for more than a decade and many preparative methods have been proposed, such as the successive reduction of the corresponding two metal precursors. Thanks to improvements

in analytical methods and nanosize analyses, detailed characterizations of such complex material systems have been carried out. In Chapter 7, “Synthesis and Characterization of Core-Shell Structured Metals” Tetsu Yonezawa focuses on the synthesis and characterization of “core-shell”-type bimetallic nanoparticles, reporting especially on recent progress in this field.

The emergence of new methods and concepts for the organization of nanoparticles has induced great expectations in the field of magnetism. The organization of nanoscale ferromagnetic particles opens up a new field of technology through the controlled fabrication of mesoscopic materials with unique magnetic properties. In particular, these ferromagnetic nanoparticles are potential candidates for magnetic storage, where the idea is that each ferromagnetic particle corresponds to one bit of information. However, there are several problems to be solved before their application to magnetic storage media becomes feasible. Devices based on magnetic nanocrystals are limited by thermal fluctuations of the magnetization and by the dipolar magnetic interaction between nanocrystals ordered in arrays. A detailed understanding of the magnetic properties of assemblies of nanocrystals is, therefore, essential to the future development of magnetic recording technology. In Chapter 8, “Cobalt Nanocrystals Organized in Mesoscopic Scale,” Marie-Paule Pileni describes how cobalt nanocrystals can be organized into one-, two-, and three-dimensional superlattices forming mesostructures. The collective magnetic properties, due to dipolar interactions and nanocrystal organization, of such assembled magnetic nanocrystals are reported. In spite of the long-range length scale of dipolar interactions, structural and intrinsic properties due to the self-organization are observed to affect the magnetic behavior.

Anodic porous alumina, which is formed by the anodization of Al, is a typical self-organized material that is eminently suitable for the fabrication of several types of functional nanodevices. The geometrical structure of anodic porous alumina can be described as a closed-packed array of uniform-sized cylindrical units called cells, each of which has central straight pores perpendicular to the surface. Compared with other nanomaterials, anodic porous alumina has an important advantage: The geometrical structure, pore size, pore interval, and pore depth can be controlled easily by the anodizing conditions. Anodic porous alumina has been applied in a wide variety of fields for many years due to its unique nanostructural geometry. Chapter 9, “Synthesis and Applications of Highly Ordered Anodic Porous Alumina” by Hideki Masuda and Kazuyuki Nishio describes the synthesis of highly ordered anodic porous alumina and its application to the fabrication of functional nanodevices. Anodic porous alumina formed under appropriate anodizing conditions has a naturally occurring long-range order, and this, in combination with a pretexturing process before anodization, yields the ideally ordered perfect pore arrangement. This highly ordered anodic porous alumina is applicable as a template in several nanofabrication methods producing various kinds of ordered nanostructures (e.g., nanocomposites, nanocylinder arrays, nanodot arrays, and nanohole arrays).

In conclusion, it is apparent that this book covers many of the exciting and recent developments in the field of self-assembly of nanostructures from basic research to

applications. We expect it to attract a broad community of researchers in physics, chemistry, biology, engineering, and materials science and hope that established scientists and technologists as well as graduate students will find much relevant and interesting information contained between these covers. The extensive references appearing at the end of each chapter are also valuable resources in themselves. In the preparation of this book, we have had the opportunity to see how far this field has developed, but we are sure that much exciting work lies ahead of us still in this field!

Motonari Adachi  
Kyoto, Japan  
David J. Lockwood  
Ottawa, Ontario, Canada

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