International Technology Research Institute
World Technology (WTEC) Division

WTEC Panel Report on

NANOSTRUCTURE SCIENCE AND TECHNOLOGY

R&D Status and Trends in Nanoparticles, Nanostructured Materials, and Nanodevices

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International Technology Research Institute
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WTEC PANEL ON NANOPARTICLES, NANOSTRUCTURED MATERIALS, AND NANODEVICES

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WTEC at Loyola College (previously known as the Japanese Technology Evaluation Center, JTEC) provides assessments of foreign research and development in selected technologies under a cooperative agreement with the National Science Foundation (NSF). Loyola's International Technology Research Institute (ITRI), R.D. Shelton, Director, is the umbrella organization for WTEC. Paul Herer, Senior Advisor for Planning and Technology Evaluation at NSF's Engineering Directorate, is NSF Program Director for WTEC. Several other U.S. government agencies provide support for the program through NSF.

WTEC's mission is to inform U.S. scientists, engineers, and policymakers of global trends in science and technology in a manner that is timely, credible, relevant, efficient, and useful. WTEC's role is central to the government's effort to measure its performance in science and technology. WTEC assessments cover basic research, advanced development, and applications. Panels of typically six technical experts conduct WTEC assessments. Panelists are leading authorities in their field, technically active, and knowledgeable about U.S. and foreign research programs. As part of the assessment process, panels visit and carry out extensive discussions with foreign scientists and engineers in their labs.

The ITRI staff at Loyola College help select topics, recruit expert panelists, arrange study visits to foreign laboratories, organize workshop presentations, and finally, edit and disseminate the final reports.

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FINAL REPORT

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ABSTRACT

This report reviews the status of research and development in nanoparticles, nanostructured materials, and nanodevices worldwide, with particular focus on comparisons between the United States and other leading industrialized countries. Topics covered include particle synthesis and assembly, dispersions and coatings of nanoparticles, high surface area materials, functional nanoscale devices, bulk behavior of nanostructured materials, and biological methods and applications. The final chapter is a review of related government funding programs around the world. The report also includes site reports for visits conducted by the panel to leading research laboratories in Japan and Europe. The panel held workshops in the United States, Germany, Sweden, and Russia to gather additional information for this report on activities in those countries. The proceedings of the U.S. and Russia workshops are being published separately by WTEC. The panel's conclusions include the following: (1) In the synthesis and assembly area (Chapter 2), the U.S. appears to be ahead with Europe following and then Japan; (2) In the area of biological approaches and applications (Chapter 7), the U.S. and Europe appear to be rather on a par with Japan following; (3) In nanoscale dispersions and coatings (Chapter 3), the U.S. and Europe are again similar with Japan following; (4) For high surface area materials (Chapter 4), the U.S. is clearly ahead of Europe and then Japan; (5) In the nanodevices area (Chapter 5), Japan seems to be leading quite strongly with Europe and the U.S. following; In the area of consolidated materials (Chapter 6), Japan is a clear leader with the U.S. and Europe following. These and other conclusions are reviewed in detail in the panel's executive summary.

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Sincerely,

Geoffrey M. Holdridge
WTEC Division Director and ITRI Series Editor

Foreword

Timely information on scientific and engineering developments occurring in laboratories around the world provides a critical input to maintaining the economic and technological strength of the United States. Moreover, sharing this information quickly with other countries can greatly enhance the productivity of scientists and engineers. These are some of the reasons why the National Science Foundation (NSF) has been involved in funding science and technology assessments comparing the United States and foreign countries since the early 1980s. A substantial number of these studies have been conducted by the World Technology Evaluation Center (WTEC) managed by Loyola College through a cooperative agreement with NSF.

The purpose of the WTEC activity is to assess research and development efforts in other countries in specific areas of technology, to compare these efforts and their results to U.S. research in the same areas, and to identify opportunities for international collaboration in precompetitive research.

Many U.S. organizations support substantial data gathering and analysis efforts focusing on nations such as Japan. But often the results of these studies are not widely available. At the same time, government and privately sponsored studies that are in the public domain tend to be "input" studies. They enumerate inputs to the research and development process, such as monetary expenditures, personnel data, and facilities, but do not provide an assessment of the quality or quantity of the outputs obtained. Studies of the outputs of the research and development process are more difficult to perform because they require a subjective analysis performed by individuals who are experts in the relevant scientific and technical fields. The NSF staff includes professionals with expertise in a wide range of

disciplines. These individuals provide the expertise needed to assemble panels of experts who can perform competent, unbiased reviews of research and development activities. Specific technologies such as telecommunications, biotechnology, and nanotechnology are selected for study by government agencies that have an interest in obtaining the results of an assessment and are able to contribute to its funding. A typical WTEC assessment is sponsored by several agencies.

In the first few years of this activity, most of the studies focused on Japan, reflecting interest in that nation's growing economic prowess. Then, the program was called JTEC (Japanese Technology Evaluation Center). Beginning in 1990, we began to broaden the geographic focus of the studies. As interest in the European Community (now the European Union) grew, we added Europe as an area of study. With the breakup of the former Soviet Union, we began organizing visits to previously restricted research sites opening up there. Most recently, studies have begun to focus also on emerging science and technology capabilities in Asian countries such as the People's Republic of China.

In the past several years, we also have begun to substantially expand our efforts to disseminate information. Attendance at WTEC workshops (in which panels present preliminary findings) has increased, especially industry participation. Representatives of U.S. industry now routinely number 50% or more of the total attendance, with a broad cross-section of government and academic representatives making up the remainder. Publications by WTEC panel members based on our studies have increased, as have the number of presentations by panelists at professional society meetings.

The WTEC program will continue to evolve in response to changing conditions. New global information networks and electronic information management systems provide opportunities to improve both the content and timeliness of WTEC reports. We are now disseminating the results of WTEC studies via the Internet. Twenty of the most recent WTEC final reports are now available on the World Wide Web (http://itri.loyola.edu) or via anonymous FTP (ftp.wtec.loyola.edu/pub/). Viewgraphs from several recent workshops are also on the Web server.

As we seek to refine the WTEC activity, improving the methodology and enhancing the impact, program organizers and participants will continue to operate from the same basic premise that has been behind the program from its inception, i.e., improved awareness of international developments can significantly enhance the scope and effectiveness of international collaboration and thus benefit the United States and all its international partners in collaborative research and development efforts.

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Executive Summary

Richard W. Siegel [1]
Rensselaer Polytechnic Institute
Panel Chair

INTRODUCTION

Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

A worldwide study of research and development status and trends in nanoparticles, nanostructured materials, and nanodevices (or more concisely, nanostructure science and technology) was carried out during the period 1996-98 by an eight-person panel under the auspices of the World Technology (WTEC) Division of Loyola College. Led by the National Science Foundation, a wide range of U.S. government agencies commissioned and funded this study: the Air Force Office of Scientific Research, the Office of Naval Research, the Department of Commerce (including the National Institute of Standards and Technology and the Technology Administration), the Department of Energy, the National Institutes of Health, and the National Aeronautics and Space Administration. Their support indicates the breadth of interest in and the far-reaching potential of this burgeoning new field. The purpose of the study was to assess the current status and future trends internationally in research and development in the broad and rapidly growing area of nanostructure science and technology. The goals were fourfold:

1. provide the worldwide science and engineering community with a broadly inclusive and critical view of this field

[1] Although written by the panel chair, this summary includes contributions from the full panel and represents the consensus views of the panel as a whole.

2. identify promising areas for future research and commercial development
3. help stimulate development of an interdisciplinary international community of nanostructure researchers
4. encourage and identify opportunities for international collaboration

This report is the principal volume in a three-part publication of the activities and findings of the WTEC panel; it is an overview of the panel's observations and conclusions regarding nanostructure science and technology worldwide. It includes reviews of panel workshops held in Germany and Sweden, as well as site reports of panel visits to university, government, and industry laboratories in Europe, Japan, and Taiwan. An earlier volume, published in January 1998, reported the proceedings of a WTEC workshop on R&D Status and Trends in Nanoparticles, Nanostructured Materials, and Nanodevices in the United States (Baltimore: Loyola College, International Technology Research Institute, NTIS #PB98-117914). A third volume to be published by WTEC reports the proceedings of a workshop held in St. Petersburg, Russia on related work.

FINDINGS

There are two overarching findings from this WTEC study:

First, it is abundantly clear that we are now able to nanostructure materials for novel performance. That is the essential theme of this field: novel performance through nanostructuring. It represents the beginning of a revolutionary new age in our ability to manipulate materials for the good of humanity. The synthesis and control of materials in nanometer dimensions can access new material properties and device characteristics in unprecedented ways, and work is rapidly expanding worldwide in exploiting the opportunities offered through nanostructuring. Each year sees an ever increasing number of researchers from a wide variety of disciplines enter the field, and each year sees an ever increasing breadth of novel ideas and exciting new opportunities explode on the international nanostructure scene.

Second, there is a very wide range of disciplines contributing to the developments in nanostructure science and technology worldwide. The rapidly increasing level of interdisciplinary activity in nanostructuring is exciting and growing in importance, and the intersections between the various disciplines are where much of the novel activity resides.

The field of nanostructure science and technology has been growing very rapidly in the past few years, since the realization that creating new materials and devices from nanoscale building blocks could access new and improved properties and functionalities. While many aspects of the field existed well before nanostructure science and technology became a definable entity in the

past decade, it has only become a coherent field of endeavor through the confluence of three important technological streams:

1. new and improved control of the size and manipulation of nanoscale building blocks
2. new and improved characterization (spatial resolution, chemical sensitivity, etc.) of materials at the nanoscale
3. new and improved understanding of the relationships between nanostructure and properties and how these can be engineered

As a result of these developments, a wide range of new opportunities for research and applications in the field of nanotechnology now present themselves. Table ES.1 indicates some examples of present and potential applications with significant technological impact that were identified in the course of this study. Considerable resources are being expended around the world for research and development aimed at realizing these and a variety of other promising applications. Government funding alone approached half a billion dollars per year in FY 1997: $128 million in Western Europe; $120 million in Japan; $116 million in the United States; and $70 million altogether in other countries such as China, Canada, Australia, Korea, Taiwan, Singapore, and the countries of the former Soviet Union (see Chapter 8).

Table ES.2 presents an overall comparison of the current levels of activity among the major regions assessed (Europe, Japan, and the United States) in the various areas of the WTEC study. These broad areas—synthesis and assembly, biological approaches and applications, dispersions and coatings, high surface area materials, nanodevices, and consolidated materials—constitute the field of nanostructure science and technology. These are the areas around which the study was crafted.

In the synthesis and assembly area (Chapter 2), the United States appears to be ahead, with Europe following and then Japan. In the area of biological approaches and applications (Chapter 7), the United States and Europe appear to be rather on a par, with Japan following. In nanoscale dispersions and coatings (Chapter 3), the United States and Europe are again at a similar level, with Japan following. For high surface area materials (Chapter 4), the United States is clearly ahead of Europe, followed by Japan. On the other hand, in the nanodevices area (Chapter 5), Japan seems to be leading quite strongly, with Europe and the United States following. And finally, in the area of consolidated materials (Chapter 6), Japan is a clear leader, with the United States and Europe following. These comparisons are, of course, integrals over rather large areas of a huge field and therefore possess all of the inevitable faults of such an integration. At best, they represent only a snapshot of the present, and the picture is admittedly incomplete.

TABLE ES.1. Technological Impact: Present and Potential

Technology	Present Impact	Potential Impact
Dispersions and Coatings	Thermal barriers	Targeted drug delivery/gene therapy
	Optical (visible and UV) barriers	Multifunctional nanocoatings
	Imaging enhancement	
	Ink-jet materials	
	Coated abrasive slurries	
	Information-recording layers	
High Surface Area Materials	Molecular sieves	Molecule-specific sensors
	Drug delivery	Large hydrocarbon or bacterial filters
	Tailored catalysts	Energy storage
	Absorption/desorption materials	Grätzel-type solar cells
Consolidated Materials	Low-loss soft magnetic materials	Superplastic forming of ceramics
	High hardness, tough WC/Co cutting tools	Ultrahigh-strength, tough structural materials
	Nanocomposite cements	Magnetic refrigerants
		Nanofilled polymer composites
		Ductile cements
Nanodevices	GMR read heads	Terabit memory and microprocessing
		Single molecule DNA sizing and sequencing
		Biomedical sensors
		Low noise, low threshold lasers
		Nanotubes for high brightness displays
Additional Biological Aspects	Biocatalysis	Bioelectronics
		Bioinspired prostheses
		Single-molecule-sensitive biosensors
		Designer molecules

TABLE ES.2. Comparison of Activities in Nanostructure Science and Technology in Europe, Japan, and the United States

	Level 1 (Highest)	Level 2	Level 3
Synthesis & Assembly	U.S.	Europe	Japan
Biological Approaches & Applications	U.S./Eur	Japan	
Dispersions and Coatings	U.S./Eur	Japan	
High Surface Area Materials	U.S.	Europe	Japan
Nanodevices	Japan	Europe	U.S.
Consolidated Materials	Japan	U.S./Eur	

More detailed findings in each of these major areas are included in the individual chapters of this report, along with additional general findings and observations in Chapter 1. Chapter 8 compares the scope and funding levels for the relevant nanostructure science and technology R&D programs around the world. The appendices give details on the site visits and workshops of the panel: B contains the Europe site reports, C contains notes on workshops held in Germany and Sweden, D contains the Japan site reports, and E contains the Taiwan site reports. Appendix A lists the professional experience of panelists and other members of the traveling team.

CHALLENGES

We are now at the threshold of a revolution in the ways in which materials and products are created. How this revolution will develop, how great will be the opportunities that nanostructuring can yield, and how rapidly we progress, will depend upon the ways in which a number of challenges are met.

Among the challenges facing us are those concerned with making the necessary advances in enabling technologies in order for rapid progress to continue in this field. We must increase characterization capabilities in visualization and chemical analysis at ever finer size scales. We must be able to manipulate matter at ever finer size scales, and we must eventually

use computational approaches in directing this, if we are really going to take full advantage of the available opportunities. Experiment simply cannot do it alone. Theory and modeling are essential. Fortunately, this is an area in which the sizes of the building blocks and their assemblies are small enough that one can, with the ever increasing capabilities in computational sciences, now start doing very serious controlled modeling experiments to guide us in the nanostructuring of matter. Hence, multiscale modeling of nanostructuring and the resulting materials properties across the hierarchy of length scales from atomic, to mesoscopic, to macroscopic is an absolute necessity as we go down the road in the next decades to realizing the tremendous potential of nanostructure science and technology.

Furthermore, we need to understand the critical roles that surfaces and interfaces play in nanostructured materials. Nanoparticles have very high specific surface areas, and thus in their assembled forms there are large areas of interfaces. We need to know in detail not only the structures of these interfaces, but also their local chemistries and the effects of segregation and interaction between the nanoscale building blocks and their surroundings. We need to learn more about the control of nanostructure size and size distribution, composition, and assembly. For some applications, there are very stringent conditions on these parameters; in other applications less so. We must therefore understand the relationships between this stringency and the desired material or device properties.

We also need to be concerned with the thermal, chemical, and structural stability of nanostructured materials and the devices made therefrom, in the face of both the temperature and changing chemistries of the environments in which these nanostructures are asked to function. A nanostructure that is only a nanostructure at the beginning of a process is not of much use to anybody, unless the process is over in a very short time or the process itself is the actual nanostructure advantage. So for many applications, stability is an important consideration, and we must investigate whether natural stability is sufficient or whether we must additionally stabilize against changes that we cannot afford.

To effectively commercialize and utilize the nanostructuring of matter we also need enhancements in statistically driven process control. Achieving reproducibility and scalability of nanoparticle synthesis and consolidation processes in nanostructuring are paramount if successful scale-up is to be effected and if what we do in the laboratory is to contribute to the society that pays for this research. Given a commercial need, the viability of nanostructure production and utilization is wrapped up in the costs of precursors or raw materials, processing costs, and also the costs of dealing with effluent. It is the total integrated cost, in terms of raw materials, synthesis of the building blocks, manufacture of parts from those building

blocks, and effluent clean-up costs, that is important and that will ultimately determine commercial viability.

Finally, in order for the field of nanostructure science and technology to truly reach fruition, it is an absolute necessity to create a new breed of researchers who can work across traditional disciplines and think "outside the box." Educating this new breed of researchers, who will either work across disciplines or know how to work with others in the interfaces between disciplines, is vital to the future of nanostructure science and technology. People must start thinking in unconventional ways if we are to take full advantage of the opportunities in this new and revolutionary field.

Chapter 1

Introduction and Overview

Richard W. Siegel
Rensselaer Polytechnic Institute

BACKGROUND

The field of nanostructure science and technology is a broad and interdisciplinary area of worldwide research and development activity that has been growing explosively in the past few years. While an understanding of the range and nature of functionalities that can be accessed through nanostructuring is just beginning to unfold, its tremendous potential for revolutionizing the ways in which materials and products are created is already clear. It is already having a significant commercial impact, and it will very certainly have a much greater impact in the future.

During the years 1996-98, an eight-person panel under the auspices of the World Technology Evaluation Center (WTEC) conducted a worldwide study of the research and development status and trends in nanoparticles, nanostructured materials, and nanodevices, or more concisely, nanostructure science and technology. The study was commissioned and sponsored by a wide range of U.S. government agencies led by the National Science Foundation (NSF), which included the Air Force Office of Scientific Research, Office of Naval Research, Department of Commerce (including the National Institute of Standards and Technology and the Technology Administration), Department of Energy, National Institutes of Health, and National Aeronautics and Space Administration. Additional participating U.S. government agencies for the study were the Army Research Office, Army Research Laboratory, Defense Advanced Research Projects Agency, and the Ballistic Missile Defense Organization. The uniquely broad sponsor

list for this WTEC study mirrors the broadly based interests in and, in fact, the reality of the field of nanostructure science and technology.

The panel study began in 1996, when panel co-chair Prof. Evelyn L. Hu (University of California at Santa Barbara) and I came to Washington to present our thoughts to WTEC and the sponsors on how the study could best be configured and carried out, given the available resources (time, people, and money). After an extensive discussion with sponsors and potential sponsors of the study, we assembled a team of experts for the panel from industry and university, including Dr. Donald M. Cox (Exxon Research and Engineering Company), Dr. Herb Goronkin (Motorola), Prof. Lynn Jelinski (Cornell University during most of this study, now at Louisiana State University), Prof. Carl Koch (North Carolina State University), John Mendel (Eastman Kodak Company), and Prof. David T. Shaw (State University of New York at Buffalo). Two of us on the panel, Prof. Koch and I, although presently in universities, had spent large fractions of our careers at Oak Ridge and Argonne National Laboratories, respectively, lending national laboratory perspectives to the study, as well. Biographical sketches of the panel members and other study participants are included in Appendix A of the present volume.

The purposes of this study, which the panel determined in conjunction with its sponsors, were to assess the current status and future trends internationally in research and development in the broad and rapidly growing area of nanostructure science and technology. The study had the following four goals:

1. to provide the worldwide science and engineering community with a broadly inclusive and critical view of this field
2. to identify promising areas for future research and commercial development
3. to help stimulate development of an interdisciplinary international community of nanostructure researchers
4. to encourage and identify opportunities for international collaboration

Based on these goals, the panel formulated a number of questions, for which we sought answers during our study:

- What are the scientific drivers (new properties and phenomena, instruments, theory, and simulation methods) and advantages (applications) to be gained from control at the nanostructure level?
- What are the critical parameters to control in nanostructured material synthesis and device manufacturing?
- What are the likelihood of and the time scale for bringing these new technologies to fruition?

- What are the underlying research and development and educational concepts and directions driving nanostructure science and technology development?
- What are the expected financial dimensions of this effort over the next five to ten years, and are there national programs in force or planned?
- Which areas of nanostructure science and technology would be most fruitful for international collaboration?

These questions were posed in advance to the various workshop participants and hosts of our panel visits so that answers could be considered and prepared. In every case, our hosts went to great lengths and considerable efforts to prepare for our visits and to make our study both effective and comfortable. The various activities of the WTEC panel, in addition to considerable reading, thinking, discussing, and writing, included the following:

- a U.S. workshop on 8-9 May 1997 with presentations by 26 invited expert participants from universities, industry, and national laboratories, and by 23 U.S. government agency sponsors
- visits by panel members to 42 universities, industrial companies, and national laboratories in Europe (France, Germany, Belgium, the Netherlands, Sweden, Switzerland, and the United Kingdom), Japan, and Taiwan
- three round-table workshops involving 27 additional institutions in Germany, Sweden, and Russia

These activities represent a rather broad base of information for the study from which the panel derived the findings and conclusions that appear in this volume. One must emphasize, however, that even though we visited many places, listened to many presentations, and read much material, there is no way that this study is, or could have been with the available resources, encyclopedic. The field of nanostructure science and technology is simply too large, too geographically dispersed, and changing too rapidly to cover exhaustively. What this volume presents are only examples, the best examples the panel could find, to describe what the field encompasses, its current breath and depth, and where it appears to be heading. The choices of the places that we visited, and even the types of visits, were made from lists and suggestions generated by all the panel members, with useful sponsor input. The final priorities were made according to where we felt the most exciting research and development activities in nanostructure science and technology were going on, overlayed with a realistic evaluation of which sites and how many of them could be logically visited in the time allotted. Unfortunately, this means that panel members on our limited schedule could not visit many interesting institutions and could not accommodate visits to entire countries that make significant contributions to nanostructure science

and technology—Australia, Canada, China, Finland, India, Israel, Italy, Mexico, Spain, and the Ukraine, to name just a few.

The initial public report of the findings of the WTEC study panel was presented in Arlington, Virginia (http://itri.loyola.edu/nano/views/top.htm) on 10 February 1998. Full site reports from the panel's visits in Europe, Japan, and Taiwan are included as Appendices B to E in this volume. A separate volume covering the U.S. workshop has already been published by WTEC under the title *R&D Status and Trends in Nanoparticles, Nanostructured Materials, and Nanodevices in the United States* (see bibliography at the end of this chapter). WTEC will soon publish a third volume of this study that consists of papers presented at its workshop in St. Petersburg, Russia.

An introduction to and overview of the study and its conclusions are presented in this chapter, including some of the technical highlights of nanostructure science and technology that the panel observed.

The WTEC panel would like to take this opportunity to thank all of the study participants around the world for their conscientious help and contributions and for their generous hospitality. We would also like to extend our thanks to Dr. Mike Roco of NSF for the wonderful support he has given us throughout the study and for his active participation in many of the visits that we made around the world. In addition, we would like to thank Mr. Geoff Holdridge (WTEC Director) and his staff for their excellent support, without which the study could not have been accomplished.

FINDINGS

There are two overarching findings from this WTEC study. First, it is now abundantly clear that we are able to nanostructure materials for novel performance. This is the essential theme of this field: novel performance through nanostructuring. Nanostructuring represents the beginning of a revolutionary new age in our ability to manipulate materials for the good of humanity. The synthesis and control of materials in nanometer dimensions can access new material properties and device characteristics in unprecedented ways. Panelists had seen the tip of the iceberg or the pinnacle of the pyramid before starting this study, but only since undertaking the study do we fully appreciate just how broad the field really is and begin to understand what its exciting potential and impact may really be. It is now clear that work is rapidly expanding worldwide in exploiting the opportunities offered through nanostructuring.

The second major finding is that there is a wide range of disciplines contributing to the developments in nanostructure science and technology

worldwide. Each year sees an ever increasing number of researchers from diverse disciplines enter the field and an increasing breadth of novel ideas and exciting new opportunities explode on the international nanostructure scene. The rapidly mounting level of interdisciplinary activity in nanostructuring is truly exciting. The intersections between the various disciplines are where much of the novel activity resides, and this activity is growing in importance.

If nothing else, these are the two basic findings that you need to carry away from this study.

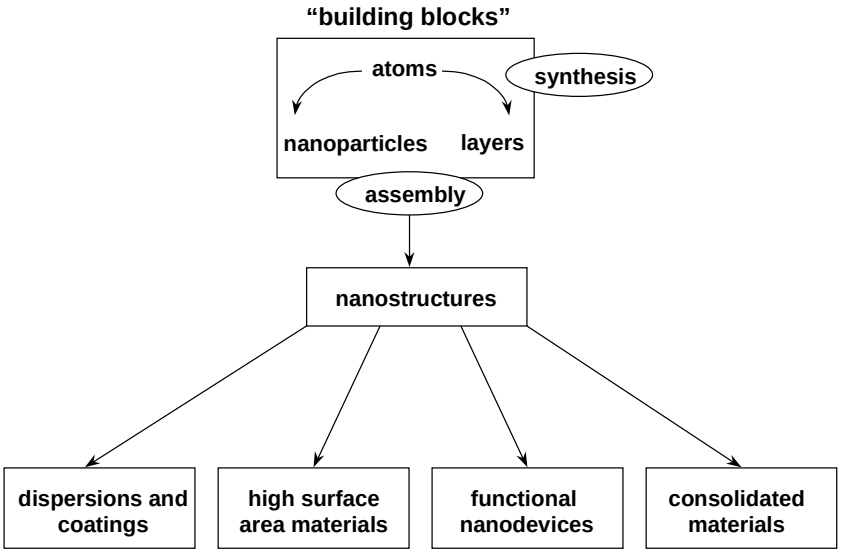

Figure 1.1. Organization of nanostructure science and technology and the WTEC study.

The broad field of nanostructure science and technology can be most conveniently organized according to the chart shown in Figure 1.1, which indicates its tremendous breadth and potential impact. The WTEC study was organized along the same lines as Figure 1.1, as is this final report, which has a separate chapter focused on each major area shown in the figure. The basis of the field is any type of material (metal, ceramic, polymer, semiconductor, glass, composite) created from nanoscale building blocks (clusters or nanoparticles, nanotubes, nanolayers, etc.) that are themselves synthesized from atoms and molecules. Thus, the controlled synthesis of those building blocks and their subsequent assembly into nanostructures is one fundamental theme of this field. This is the subject of Chapter 2 by Evelyn Hu and David Shaw. This theme draws upon all of the materials-related disciplines from physics to chemistry to biology and to essentially all

of the engineering disciplines as well. In fact, there is a very strong thread from all these disciplines running throughout the fabric of this study; the biological aspects are so pervasive that special attention is given to them in Chapter 7 by Lynn Jelinski.

The second and most fundamentally important theme of this field is that the nanoscale building blocks, because of their sizes below about 100 nm, impart to the nanostructures created from them new and improved properties and functionalities heretofore unavailable in conventional materials and devices. The reason for this is that materials in this size range can exhibit fundamentally new behavior when their sizes fall below the critical length scale associated with any given property. Thus, essentially any material property can be dramatically changed and engineered through the controlled size-selective synthesis and assembly of nanoscale building blocks. Four broadly defined and overlapping application areas that cover the tremendous range of challenges and opportunities for nanostructure science and technology are dispersions and coatings, high surface area materials, functional nanodevices, and consolidated materials.

In the synthesis and assembly area (Chapter 2) we see that atoms, molecules, clusters and nanoparticles can be used as building blocks for nanostructuring. However, the useful size of these building blocks depends upon the property to be engineered, since the critical length scales for which one is designing these building blocks depends upon the particular property of interest. For multifunctional applications, more than one property and one length scale must be considered. Every property has a critical length scale, and if a nanoscale building block is made smaller than that critical length scale, the fundamental physics of that property starts to change. By altering the sizes of those building blocks, controlling their internal and surface chemistry, and controlling their assembly, it is possible to engineer properties and functionalities in unprecedented ways.

The characteristics of the building blocks, such as their size and size distribution, composition, composition variation, and morphology, must be well controlled. Also, the interfaces between the building blocks and their surroundings can be critical to performance. It is not sufficient simply to make the building blocks; one must also worry about the structure and chemistry of their surfaces and how they will interact one with another or with a matrix in which they are embedded. There is a very wide range of diverse synthesis and assembly strategies being employed in nanostructuring, all the way from fundamental biological methods for self-assembling molecules to sophisticated chemical precipitation methods to a variety of physical and chemical aerosol techniques for making clusters or nanoparticles and then dispersing them or bringing them together in consolidated forms. All of these strategies contribute in essential ways to the

growth of this field. Each may have unique capabilities that will benefit a particular property, application, or process. The most generally applicable of them are likely to have significant technological impact and commercial potential.

In the area of dispersions and coatings, covered in Chapter 3 by John Mendel, a wide range of new and enhanced functionalities are now becoming available by means of nanostructuring. They cover the whole set of properties that are of interest in optical, thermal, and electrical applications. This is the most mature area of nanoscale science and technology. The many current commercial applications include printing, sunscreens, photography, and pharmaceuticals. Some examples of the present technological impact of nanostructuring are thermal and optical barriers, imaging enhancement, ink-jet materials, coated abrasive slurries, and information-recording layers. From our vantage point at present, there appears to be very strong potential impact in the areas of targeted drug delivery, gene therapy, and multifunctional coatings. Nevertheless, certain central issues must be addressed if work in this area is going to continue to affect society in meaningful new ways in the coming years. Successful nanoscale dispersions require freedom from agglomeration and surface control. Process controls are required to ensure reproducibility, reliability, and scalability. There is also a need to develop process models that lead to shorter cycle times in manufacturing, if commercialization is to be truly effective.

In the area of high surface area materials, reviewed by Donald Cox in Chapter 4, it is of primary importance to realize that nanostructured material building blocks have inherently high surface areas unless they are consolidated. For example, a nanoparticle 5 nm in diameter has about half of its atoms on its surface. If the nanoparticles are then brought together in a lightly assembled way, this surface area is available for a variety of useful applications. In fact, there is a wide range of new applications in high capacity uses for chemical and electrical energy storage, or in sensors and other applications that take copious advantage of this feature. Already there are numerous commercial applications in porous membranes or molecular sieves, drug delivery, tailored catalysts, and absorption/desorption materials. Clearly, what is required to optimize the impact of nanostructures to be really useful to society in high surface area material applications is to create materials that combine high selectivity, high product or function yield, and high stability. Thus, the major challenges in this area are critical dimensional control and long-term thermal and chemical stability. When these problems are solved, considerable future technological potential is seen in the areas of molecule-specific sensors, large hydrocarbon or bacterial filters, energy storage, and Grätzel-type solar cells.

The area of functional nanoscale devices, covered in Chapter 5 by Herb Goronkin and his Motorola colleagues, is largely driven by the need for ever smaller devices, which necessitate both new device and new circuit architectures. It is not very useful to make nanoscale devices if they cannot be assembled in a circuit with interconnects that are themselves nanoscale. Thus, a complete rethinking of this area is required. The major research and development effort worldwide in functional nanoscale devices is focused on the single electron transistor (SET) using a variety of nanostructuring approaches. However, there is also considerable worldwide activity on magnetic devices using giant magnetoresistance (GMR) of nanostructures with architectures of various modulation dimensionalities. In fact, it is the nanostructuring with various modulation dimensionalities that has created an expanding range of different functionalities that can be engineered into these GMR devices. There is also exciting carbon nanotube research being actively pursued in areas of high-field-emission displays and several other nanoscale electronic devices. This is an area still very early in its development, since nanotubes and their derivatives are a relatively recent discovery, but one with tremendous potential.

While there is little technological impact already present in the nanoscale device area other than GMR read heads, several potential areas of significant impact do appear on the horizon. These include terabit memory and microprocessing; single molecule DNA sizing and sequencing; biomedical sensors; low-noise, low-threshold lasers; and nanotubes for high brightness displays. Nevertheless, a major challenge looms in the efficient manipulation of these nanoscale building blocks and their eventual commercial scaleup, if any of this is really going to affect society as we know it. One shining example that indicates probable success in overcoming such obstacles in the future is the ability to now translate SET devices made by individual atomic manipulation into arrays of similarly functional devices created by the biological self-assembly of large molecular arrays. Such cross-disciplinary transfers of nanostructuring ideas and capabilities can be expected to increasingly impact the future successful implementation of nanostructure science and technology.

In the area of consolidated materials, reviewed by Carl Koch in Chapter 6, we have known for about a decade that the bulk behavior of materials can be dramatically altered when constituted of, or consolidated from, nanoscale building blocks. This can significantly and favorably affect the mechanical properties, magnetic properties, and optical properties of a range of engineering materials. We already know that the hardness and strength of nanophase metals can be greatly increased by nanostructuring, for example. On the other hand, the ductility and superplastic forming capabilities of nanophase ceramics have now become possible generically,

leading to new processing routes that will be more cost-effective than present methods. Nanoparticle fillers in metal, ceramic, or polymer matrices can yield a very wide range of nanocomposites with unique properties. This is an area that in some cases is just beginning to be researched seriously, but it could have huge technological impact in the future. Nanostructuring can also uniquely create both soft and hard magnetic materials with greatly improved performances. These materials are already having technological impact in the areas of low-loss magnets, high-hardness and tough cutting tools, and nanocomposite cements. Potential technological applications with high commercial impact can be expected in the areas of superplastic forming of ceramics, ultrahigh-strength and tough structural materials, magnetic refrigerants, a wide range of nanoparticle-filled polymer nanocomposites based on elastomers, thermoplastics and thermosets, and ductile cements.

In Chapter 7 Lynn Jelinski describes nanoparticles, nanostructured materials, and nanodevices from the point of view of biological applications and biological analogies. Current research directed toward biological synthesis and assembly is highlighted as it pertains to the building blocks of nanotechnology, and examples are presented of state-of-the-art research on the biological aspects of dispersions and coatings, high surface area materials, and functional nanostructures. A primary finding is that although biological applications of nanostructure science and technology may not be as well developed currently as non-biological ones, they nevertheless present a very promising research and development frontier that is likely to have tremendous future impact.

Funding and research programs in nanotechnology around the world are reviewed by Mike Roco in Chapter 8. It is noteworthy that these funding levels have been increasing very rapidly in recent years as the number of researchers worldwide who are excited about this field have multiplied and funding agencies have responded accordingly. The various ways in which nanostructure science and technology research is funded in the countries the panel surveyed had often appeared quite different from a distance, but are actually quite similar to one another at closer view. Some countries, most notably Japan, have tended to primarily fund their nanostructure research through large national programs, with a rather monolithic appearance from afar, centered at national laboratories or at major national universities. On the other hand, with some exceptions, most of the nanostructure research funding in the United States and Europe tends to be based upon competition among individual research groups for smaller amounts of support. In both types of nanostructure funding schemes, however, it seems that the individual researchers actually dominate how the work proceeds. In most cases, any significant interactions among researchers occur through normal personal and professional contacts; large-scale institutionalized cooperative

research efforts in this field have often not been particularly effective. A particularly impressive national funding effort in nanostructure science and technology occurs in France under the auspices of the Centre National de la Récherche Scientifique (CNRS). There, an extensive multidisciplinary network of laboratories in universities, industries, and national laboratories, funded partly by the CNRS and partly by industry, appear to interact successfully. It could be a very useful model to follow.

CONCLUSIONS

Table ES.2 (p. xvii) compares the current levels of activity of the major regions assessed in this WTEC study (Europe, Japan, and the United States), for the broad areas of synthesis and assembly, biological approaches and applications, dispersions and coatings, high surface area materials, nanodevices, and consolidated materials. These comparisons are, of course, integrals over rather large areas of a huge field and therefore possess all of the inevitable faults of such an integration. At best, they represent only a snapshot of the present. Nevertheless, the panel drew the following general conclusions. In the synthesis and assembly area, the United States appears to be somewhat ahead, with Europe and then Japan following. In the area of biological approaches and applications, the United States and Europe appear to be on a par, with Japan following. In nanoscale dispersions and coatings, the United States and Europe are again at a similar level, with Japan following. In the area of high surface area materials, the United States is clearly ahead of Europe, which is followed by Japan. On the other hand, in the nanodevices area, Japan seems to be leading quite strongly, with Europe and the United States following. Finally, in the area of consolidated nanomaterials, Japan appears to be a clear leader, with the United States and Europe following.

Nanostructure science and technology is clearly a very broad and interdisciplinary area of research and development activity worldwide. It has been growing explosively in the past few years, since the realization that creating new materials and devices from nanoscale building blocks could access new and improved properties and functionalities. While many aspects of the field existed well before nanostructure science and technology became a definable entity during the past decade, it has really only become a coherent field of endeavor through the confluence of three crucial technological streams:

1. new and improved control of the size and manipulation of nanoscale building blocks

2. new and improved characterization (e.g., spatial resolution, chemical sensitivity) of materials at the nanoscale
3. new and improved understanding of the relationships between nanostructure and properties and how these can be engineered

These developments have allowed for an accelerating rate of information transfer across disciplinary boundaries, with the realization that nanostructure scientists can and should borrow insights and techniques across disciplines, and for an increased access to common enabling tools and technologies. We are now at the threshold of a revolution in the ways in which materials and products are created. How this revolution will develop, and how great will be the opportunities that nanostructuring can yield in the future, will depend upon the ways in which a number of challenges are met.

Among the challenges facing nanostructure scientists and engineers in order for rapid progress to continue in this field are the necessary advances that must be made in several enabling technologies. We need to increase the capabilities in material characterization, be it in visualization or analytical chemistry, at ever finer size scales. We also need to be able to manipulate matter at finer and finer size scales, and we must eventually use computational approaches in directing this. Experiment simply cannot do it alone; theory and modeling are essential. Fortunately, this is an area in which the sizes of the building blocks and their assemblies are small enough that it is possible, with the ever increasing capabilities of computational sciences, to start doing very serious controlled modeling experiments to guide researchers in the nanostructuring of matter. Hence, multiscale modeling, across atomic, mesoscopic, and macroscopic length scales, of nanostructuring and the resulting hierarchical structures and material properties is an absolute necessity as we attempt in the coming decades to utilize the tremendous potential of nanostructure science and technology.

Another challenge is to fully understand the critical roles that surfaces and interfaces play in nanomaterials, owing to the very high specific surface areas of nanoparticles and the large areas of interfaces in the assembled nanophase forms. We need to know in detail not only the structures of these interfaces, but also their local chemistries and the effects of segregation and interaction between the nanoscale building blocks and their surroundings. We also need to learn more about the control parameters of nanostructure size and size distribution, composition, and assembly. For some applications of these building blocks, there are very stringent conditions on these parameters; in other applications considerably less so. We must therefore understand the relationships between the limits of this stringency and the desired material or device properties if efficient utilization of nanostructuring is to be achieved.

Since nanostructures are often inherently unstable owing to their small constituent sizes and high chemical activity, a further challenge is to increase the thermal, chemical, and structural stability of these materials and the devices made therefrom, in the various temperatures and chemistries of the environments in which the nanostructures are asked to function. A nanostructure that is only a nanostructure at the beginning of a process is not of much use unless the process is over in a very short time or unless the process itself is the actual nanostructure advantage. So, stability is a real concern in many applications. Researchers must determine whether natural stability or metastability is sufficient or if we must additionally stabilize against the changes that we cannot afford. Fortunately, it appears that many nanostructures possess either a deeply metastable structure or they can be readily stabilized or passivated using rather traditional strategies.

Reproducibility and scalability of nanoparticle synthesis and consolidation processes in nanostructuring are paramount for successful utilization of nanostructure research and development. What is accomplished in the laboratory must eventually benefit the society that pays the bills for the research, or the field will simply die. Also, significant enhancements in statistically driven process controls are required if we are to be able to effectively commercialize and utilize the nanostructuring of matter. New thinking is needed, not only about the materials, not only about the processing and assembly of these materials, but also about the manufacture of products from these materials and the economic impact of dealing with effluents. Given the commercial promise of net-shape forming of nanoscale ceramics, for example, the viability of such nanostructure production and utilization depends upon the total integrated costs of precursors or raw materials, synthesis of the building blocks, manufacturing of parts from those building blocks, and finally, disposition of the effluents. Higher than normal up-front costs for the nanoparticles or building blocks may be affordable if the processing steps save more than that. It is the total integrated costs, along with societal needs, that will determine commercial viability

Education is also of tremendous importance to the future of the field of nanostructure science and technology. The creation of a new breed of researchers working across traditional disciplines and thinking "outside the box" is an absolute necessity for the field of nanostructure science and technology to truly reach fruition and to impact society with full force. The education of this new breed of researchers, who will either themselves work across disciplines or know how to work with others across disciplinary lines in the interfaces between disciplines, is necessary to make this happen in the future. People will need to start thinking in truly unconventional ways, if we are to take full advantage of this excitingly new and revolutionary field.

It appears that nanostructure science and technology at present resembles only the tip of a pyramid that has recently been uncovered from the sands of ignorance. As the new and expanding research community of nanostructure scholars worldwide digs away at these sands and uncovers more and more of the exciting field of nanostructure science and technology, we will eventually learn how truly important the field will have become and how great its impact will be on society. From our present vantage point, this future looks very exciting.

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Chapter 2

Synthesis and Assembly

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INTRODUCTION

The common theme of this WTEC study is the engineering of materials with novel (i.e., improved) properties through the controlled synthesis and assembly of the material at the nanoscale level. The range of applications is extremely broad, and these will be described in further detail in subsequent chapters in this report. The corresponding means of synthesis and assembly are similarly wide-ranging. But however multifaceted the synthesis approaches and the ultimate applications, there are common issues and unique defining features of these nanostructured materials.

First, there is the recognition of critical scale lengths that define the material structure and organization, generally in the nanometer range, and that ultimately determine the fundamental macroscopic properties of the material. Research in nanostructured materials is motivated by the belief that ability to control the building blocks or nanostructure of the materials can result in enhanced properties at the macroscale: increased hardness, ductility, magnetic coupling, catalytic enhancement, selective absorption, or higher efficiency electronic or optical behavior.

Synthesis and assembly strategies accommodate precursors from liquid, solid, or gas phase; employ chemical or physical deposition approaches; and similarly rely on either chemical reactivity or physical compaction to integrate nanostructure building blocks within the final material structure. The variety of techniques is shown schematically in Figure 2.1.

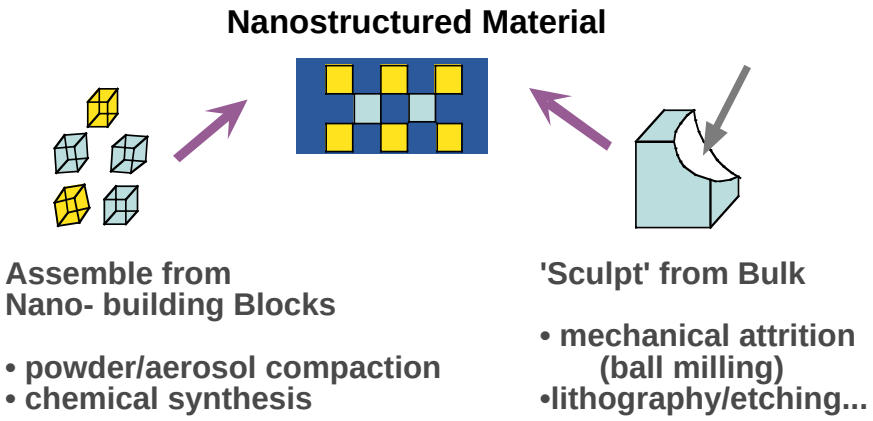

Figure 2.1. Schematic of variety of nanostructure synthesis and assembly approaches.

The "bottom-up" approach first forms the nanostructured building blocks and then assembles them into the final material. An example of this approach is the formation of powder components through aerosol techniques (Wu et al. 1993) and then the compaction of the components into the final material. These techniques have been used extensively in the formation of structural composite materials. One "top-down" approach begins with a suitable starting material and then "sculpts" the functionality from the material. This technique is similar to the approach used by the semiconductor industry in forming devices out of an electronic substrate (silicon), utilizing pattern formation (such as electron beam lithography) and pattern transfer processes (such as reactive ion etching) that have the requisite spatial resolution to achieve creation of structures at the nanoscale. This particular area of nanostructure formation has tremendous scope, warranting its own separate study, is a driving issue for the electronics industry, and will not be a principal theme of this study. Another top-down approach is "ball-milling," the formation of nanostructure building blocks through controlled, mechanical attrition of the bulk starting material (Koch 1989). Those nano building blocks are then subsequently assembled into a new bulk material.

In fact, many current strategies for material synthesis integrate both synthesis and assembly into a single process, such as characterizes chemical synthesis of nanostructured materials (Murray et al. 1993; Katari et al. 1994). The degree of control required over the sizes of the nanostructure components, and the nature of their distribution and bonding within the fully formed material varies greatly, depending on the ultimate materials application. Achieving selective optical absorption in a material (e.g., UV-blocking dispersions) may allow a wide range of sizes of the component nanostructure building blocks, while quantum dot lasers or single electron

transistors require a far tighter distribution of size of the nanostructure components. Compaction methods may provide excellent adhesion for nanocomposite materials of improved structural performance (e.g., ductility), but such interfaces may be unsatisfactory for electronic materials.

The intention of this chapter of the report is not to recapitulate in detail the various synthesis and assembly techniques that have been and are being employed in the fabrication of nanostructured materials; that detail can be found in succeeding chapters as well as in excellent summary descriptions provided in the May 8-9, 1997 WTEC workshop proceedings (Siegel, Hu, and Roco 1998). Rather, in attempting to capture the salient features of a new impetus for and interest in a field of nanostructure science and technology, it is more useful to identify the emerging commonalities than the differences among synthesis and assembly approaches.

CRITICAL ISSUES FOR NANOSTRUCTURE SYNTHESIS AND ASSEMBLY

However broad the range of synthesis approaches, the critical control points fall into two categories:

1. control of the size and composition of the nanocluster components, whether they are aerosol particles, powders, semiconductor quantum dots, or other nanocomponents
2. control of the interfaces and distributions of the nanocomponents within the fully formed materials

These two aspects of nanostructure formation are inextricably linked; nevertheless, it is important to understand how to exercise separate control over the nucleation of the nanostructure building blocks and the growth (for example, minimizing coagulation or agglomeration) of those components throughout the synthesis and assembly process. This latter issue is related to the importance of the following:

- the chemical, thermal, and temporal stability of such formed nanostructures
- the ability to scale-up synthesis and assembly strategies for low-cost, large-scale production of nanostructured materials, while at the same time maintaining control of critical feature size and quality of interfaces (economic viability is a compelling issue for any nanostructure technology)

All researchers in this area are addressing these issues.

COMMON ENABLING TECHNOLOGIES

There has been steady technological progress in all fields of nanostructure synthesis and assembly, in no small part because of the more general availability of characterization tools having higher spatial, energy, and time resolution to clearly distinguish and trace the process of nanostructure formation. As transmission electron microscopy and X-ray diffraction techniques helped in an earlier period to relate the improved properties of "age-hardened" aluminum alloys to their nanostructure (Koch 1998), today's technological advances in materials characterization are providing new insights into the role of the nanostructure in determining macroscopic properties. The tightly-coupled iteration between characterizing the nanostructure, understanding the relationship between nanostructure and macroscopic material properties (Figure 2.2), and improved sophistication and control in determining nanostructure size and placement have accelerated the rate of progress and helped to define the critical components of this "new" field of nanostructure science and technology. Tightly focused (1-2 μm), high brightness synchrotron X-ray sources provide detailed structural information on colloids, polymers, alloys, and other material structures, highlighting the inhomogeneities of the material with suitable spatial resolution (Hellemans 1998).

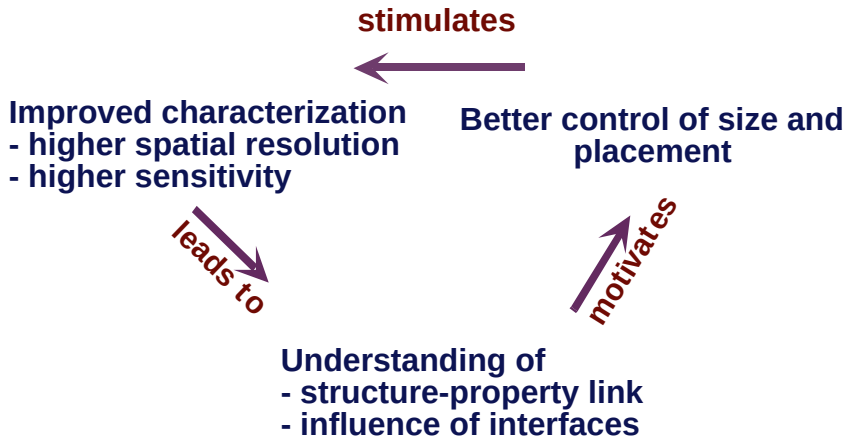

Figure 2.2. Interactive cycle of characterization, understanding and enhanced control in the synthesis and assembly of nanostructures.

Another important enabling technology has been the now widely available scanning probe technology, including scanning tunneling microscopy and atomic force microscopy. The power of these techniques has provided impetus for developing even higher performance scanning

probe tips, fabricated through microfabrication techniques. Development of different tip structures in various materials has given rise to an entire family of powerful scanning probe techniques that encompass such a wide range of characterization capabilities that one can envision "a laboratory on a tip" (Berger et al. 1996). The development of a tip technology also impacts the synthesis and assembly processes themselves: scanning probe technologies have been used as the basis of materials patterning and processing at nanometer scales (Held et al. 1997; Snow et al. 1997; and Wilder et al. 1997) and have provided information on the mechanical and thermal properties of materials at the nanoscale (Nakabeppu et al. 1995; Tighe et al. 1997; and Zhang et al. 1996).

More sophisticated in situ monitoring strategies have provided greater understanding and control in the synthesis of nanostructured building blocks, particularly those formed in vacuum environments. Molecular beam epitaxy (MBE) represents a physical vapor (gas phase) deposition technique where sub-monolayer control can be imposed on the formation of two-dimensional and, more recently, three-dimensional nanostructured materials (Leonard et al. 1993). A great deal of the understanding and control derives from the ability to carry out sensitive monitoring of the growth process in situ: reflection high energy electron diffraction (RHEED) details the nature of the surface and surface bonding, and oscillations of the RHEED intensity provide information on the growth rate (Neave et al. 1983).

The improvements brought about by these advances in technology have been substantial, but perhaps of greater importance for this nascent field of nanostructure science and technology has been the development of strategies and technologies that have been formed across the former disciplines. More reliable means of controlling nanostructure size and placement, with an end view of being able to scale up the production of such materials while maintaining the control over the nanostructure, have given impetus to a common search for novel synthesis and assembly strategies. In that search, it is apparent that the naturally occurring synthesis and assembly of biological materials can provide us with some critical insights.

NANOPARTICLE SYNTHESIS STRATEGIES

Gas Phase Synthesis and Sol-Gel Processing

Major efforts in nanoparticle synthesis can be grouped into two broad areas: gas phase synthesis and sol-gel processing. Nanoparticles with diameters ranging from 1 to 10 nm with consistent crystal structure, surface derivatization, and a high degree of monodispersity have been processed by

both gas-phase and sol-gel techniques. Typical size variances are about 20%; however, for measurable enhancement of the quantum effect, this must be reduced to less than 5% (Murray et al. 1993).

Initial development of new crystalline materials was based on nanoparticles generated by evaporation and condensation (nucleation and growth) in a subatmospheric inert-gas environment (Gleiter 1989; Siegel 1991, 1994). Various aerosol processing techniques have been reported to improve the production yield of nanoparticles (Uyeda 1991, Friedlander 1998). These include synthesis by combustion flame (Zachariah 1994, Calcote and Keil 1997, Axelbaum 1997, Pratsinis 1997); plasma (Rao et al. 1997); laser ablation (Becker et al. 1997); chemical vapor condensation (Kear et al. 1997); spray pyrolysis (Messing et al. 1994); electrospray (de la Mora et al. 1994); and plasma spray (Berndt et al. 1997).

Sol-gel processing is a wet chemical synthesis approach that can be used to generate nanoparticles by gelation, precipitation, and hydrothermal treatment (Kung and Ko 1996). Size distribution of semiconductor, metal, and metal oxide nanoparticles can be manipulated by either dopant introduction (Kyprianidou-Leodidou et al. 1994) or heat treatment (Wang et al. 1997). Better size and stability control of quantum-confined semiconductor nanoparticles can be achieved through the use of inverted micelles (Gacoin 1997), polymer matrix architecture based on block copolymers (Sankaran et al. 1993) or polymer blends (Yuan et al. 1992), porous glasses (Justus et al. 1992), and ex-situ particle-capping techniques (Majetich and Canter 1993; Olshavsky and Allcock 1997).

Other Strategies

Additional nanoparticle synthesis techniques include sonochemical processing, cavitation processing, microemulsion processing, and high-energy ball milling. In sonochemistry, an acoustic cavitation process can generate a transient localized hot zone with extremely high temperature gradient and pressure (Suslick et al. 1996). Such sudden changes in temperature and pressure assist the destruction of the sonochemical precursor (e.g., organometallic solution) and the formation of nanoparticles. The technique can be used to produce a large volume of material for industrial applications.

In hydrodynamic cavitation, nanoparticles are generated through creation and release of gas bubbles inside the sol-gel solution (Sunstrom et al. 1996). By rapidly pressurizing in a supercritical drying chamber and exposing to cavitational disturbance and high temperature heating, the sol-gel solution is mixed. The erupted hydrodynamic bubbles are responsible for nucleation, growth, and quenching of the nanoparticles. Particle size can be controlled

by adjusting the pressure and the solution retention time in the cavitation chamber.

Microemulsions have been used for synthesis of metallic (Kishida et al. 1995), semiconductor (Kortan et al. 1990; Pileni et al. 1992), silica (Arriagada and Osseo-Assave 1995), barium sulfate (Hopwood and Mann 1997), magnetic, and superconductor (Pillai et al. 1995) nanoparticles. By controlling the very low interfacial tension ($\sim 10^{-3}$ mN/m) through the addition of a cosurfactant (e.g., an alcohol of intermediate chain length), these microemulsions are produced spontaneously without the need for significant mechanical agitation. The technique is useful for large-scale production of nanoparticles using relatively simple and inexpensive hardware (Higgins 1997).

Finally, high energy ball milling, the only top-down approach for nanoparticle synthesis, has been used for the generation of magnetic (Leslie-Pelecky and Reike 1996), catalytic (Ying and Sun 1997), and structural (Koch 1989) nanoparticles. The technique, which is already a commercial technology, has been considered dirty because of contamination problems from ball-milling processes. However, the availability of tungsten carbide components and the use of inert atmosphere and/or high vacuum processes have reduced impurities to acceptable levels for many industrial applications. Common drawbacks include the low surface area, the highly polydisperse size distributions, and the partially amorphous state of the as-prepared powders.

Other Synthesis Issues

Means to Achieve Monodispersity

One of the most challenging problems in synthesis is the controlled generation of monodispersed nanoparticles with size variance so small that size selection by centrifugal precipitation or mobility classification is not necessary. Among all the synthesis techniques discussed above, gas-phase synthesis is one of the best techniques with respect to size monodispersity, typically achieved by using a combination of rigorous control of nucleation-condensation growth and avoidance of coagulation by diffusion and turbulence as well as by the effective collection of nanoparticles and their handling afterwards. The stability of the collected nanoparticle powders against agglomeration, sintering, and compositional changes can be ensured by collecting the nanoparticles in liquid suspension. For semiconducting particles, stabilization of the liquid suspension has been demonstrated by the addition of polar solvent (Murray et al. 1993); surfactant molecules have been used to stabilize the liquid suspension of metallic nanoparticles.

Alternatively, inert silica encapsulation of nanoparticles by gas-phase reaction and by oxidation in colloidal solution has been shown to be effective for metallic nanoparticles (Andres et al. 1998).

New approaches need to be developed for the generation of monodisperse nanoparticles that do not require the use of a size classification procedure. An example of this is a process developed in Japan where very monodispersed gold colloidal nanoparticles with diameters of about 1 nm have been prepared by reduction of metallic salt with UV irradiation in the presence of dendrimers (Esumi et al. 1998). Poly(amidoamine) dendrimers with surface amino groups of higher generations have spherical 3-D structures, which may have an effective protective action for the formation of gold nanoparticles. Although the specific role of dendrimers for the formation of monodispersed nanoparticles has yet to be defined, good monodispersity is thought to come from the complex reaction accompanying the decomposition of dendrimers, which eventually leads to the conversion of solution ions to gold nanoparticles.

Scaleup

Scaleup production is of great interest for nanoparticle synthesis. High energy ball milling, already a commercial high-volume process, as mentioned above, has been instrumental in generating nanoparticles for the preparation of magnetic, structural, and catalytic materials. However, the process produces polydispersed amorphous powder, which requires subsequent partial recrystallization before the powder is consolidated into nanostructured materials. Although gas-phase synthesis is generally a low production rate process (typically in the 100 milligrams per hour range) in research laboratories, higher rates of production (about 20 grams per hour) are being demonstrated at Ångström Laboratory at Uppsala University in Sweden (see Appendix C of this report). Even higher production rates (about 1 kg per hour) are now being achieved commercially. For sol-gel processing, the development of continuous processing techniques based on present knowledge of batch processing has yet to be addressed for economical scaleup production of nanoparticles. Other related sol-gel issues concern the cost of precursors and the recycling of solvent. Overall, sol-gel processing is attractive for commercial scale-up production.

Building Nanoparticle Chains or Wires

A recent paradigm shift envisioned for optoelectronics and computational devices involves the assembly of molecular or quantum wires (Chidsey and Murray 1986). Large polymeric molecules have been used as nano building

blocks for nanoporous molecular sieves, biocompatible materials, optical switching, data processing, and other nonlinear optical components. Chain aggregates of nanoparticles can be considered as polymer-like units with their primary particles composed of a few hundred to a few thousand molecules. Thus, these chain aggregates can be considered "heavy" quantum wires. In fact, nanoparticle chain aggregates have been studied extensively as magnetic materials (Zhang and Manthiram 1997), as reinforced elastomers (Pu et al. 1997), and as additives in concrete (Sabir 1997). These aggregates have been shown to have chemical and mechanical properties different from those of individual primary particles (Friedlander et al. 1998). Depending on the particle size and its compositional material, the bonding force responsible for holding the aggregates together varies from weak van der Waals force for micrometer particles to strong chemical bonds for nanometer particles to very strong magnetic dipolar bonds for nanosized magnetic particles. The mechanical, optical, and electronic transport properties can be varied by controlling the diameter and the monodispersity of the primary particles, the crystalline structure and morphology, aggregate length, interfacial properties, and material purity. These chain aggregates can be formed by allowing agglomeration of nanoparticles generated by any of the synthesis techniques discussed above, with the exception of high energy ball milling, which generates particles with low surface area and high anisotropic morphologies, both of which are detrimental for the formation of chain aggregates. Depending on the magnetic and electric charging properties of the nanoparticles, an external applied magnetic or electric field can be used to control the fractal dimension of aggregates. For optical applications of chain aggregates, lower fractal dimensions (i.e., relatively straight chain aggregates with few branches) are desirable.

Building Nanometer Fibers or Tubes

Recent advances in the fabrication of nanometer fibers or tubes offer another form of building blocks for nanostructured materials. An effective way to generate nanometer fibers (or tubes) is based on the use of membrane-template techniques (Martin 1994). Membranes, with nanochannels generated by fission-fragment tracks or by electrochemical etching of aluminum metal, are used as templates for either chemical or electrochemical deposition of conductive polymers (Pathasarathy and Martin 1994), metal (van de Zande et al. 1997), semiconductor (Klein et al. 1993), and other materials for the generation of nanofibers or tubes. Since the nanochannels on membranes are very uniform in size, the diameter and the aspect ratio of the nanofibers (or tubes) synthesized by the membrane-template technique can be precisely controlled. This greatly facilitates the

interpretation of optical data and the processing of these fibers (or tubes) into 2-D nanostructured materials (de Heer et al. 1995). Single-crystal semiconductor nanofibers can also be grown catalytically by metalorganic vapor phase epitaxy and laser ablation vapor-liquid-solid techniques (Hiruma et al. 1995; Morales and Lieber 1998). The synthesis of these one-dimensional structures with diameters in the range of 3 to 15 nm holds considerable technological promise for optoelectronic device applications, such as the p-n junctions for light emission at Hitachi Central Research Laboratory in Japan (see Appendix D of this report).

The advent of carbon-based nanotubes has created yet another way to fabricate nanometer fibers and tubes. These nanotubes have been used as templates for the fabrication of carbide and oxide nanotubes (Dai et al. 1995; Kasuga et al. 1998). Synthesis of nanotubes based on BN, BC3 and BC2N have also been reported (Chopra et al. 1995; Miyamoto et al. 1994). These nanotubes potentially possess large third-order optical non-linearity and other unusual properties (Xie and Jiang 1998). Metallic nanofibers synthesized by carbon-nanotube-template techniques are useful in the design of infrared absorption materials. The carbon nanotubes can now be catalytically produced in large quantities and have been used for reinforcement of nanostructural composite materials and concrete (Peigney et al. 1997).

BIOGENIC STRATEGIES

The elegant complexity of biological materials represents the achievement of structural order over many length scales, with the full structure developed from the “nested levels of structural hierarchy” (Aksay et al. 1992), in which self-assembled organic materials can form templates or scaffolding for inorganic components. These notions of a multilevel material structure with strong interactions among levels and an interplay of perfection and imperfection forming the final material was discussed earlier by Cyril Stanley Smith (1981). Along with characteristic length scales, there are characteristic relaxation times of the material, bringing in the consideration of the temporal stability of the structured materials (Zener 1948).

A more detailed discussion of the role of biological materials as both paradigm and tool for the fabrication of nanostructured materials is given in Chapter 7 of this report. It is interesting how many of the synthesis and assembly approaches seek out and adapt two key features of biogenic fabrication: that of “self-assembly,” and the use of natural nanoscaled templates.

Self-Assembly as a Deliberate Strategy

"Self-assembly" is a term that by now figures prominently in the literature of nanostructured materials and nanofabrication. The term therefore carries a variety of implicit or explicit meanings, and we cite the definition given by Kuhn and Ulman: "Self-assembly is a process in which supermolecular hierarchical organization is established in a complex system of interlocking components." The mechanisms that produce the hierarchical organization are determined by competing molecular interactions (e.g., interactions between hydrophobic versus hydrophilic components, van der Waals, Coulombic, or hydrogen bonding), resulting in particular microphase separation or surface segregation of the component materials. Thus, the use of a hierarchy of bond strengths and/or chemical specificity can produce a hierarchy of lengths in the final nanostructured material (Muthukumar et al. 1998; Stupp and Braun 1998).

As one example of such self-assembled or self-organized materials, McGehee et al. (1994) have mixed silica precursors with surfactants that have self-ordered to form various surfactant-water liquid crystals, producing various structures built from walls of amorphous silica, organized about a repetitive arrangement of pores up to a hundred angstroms in diameter. A range of such structures is shown in Figure 2.3. In the "natural" formation of inorganic nanostructures, the addition of organic molecules can strongly influence the resulting structure of inorganic components. Such strategies have been adopted in synthetic formation of nanostructures, such as in the formation of networks of gold clusters (Andres et al. 1998).

Gold clusters 3.7 nm in diameter, formed in the vapor phase, are encapsulated in organic surfactants, such as dodecanethiol, forming a colloidal suspension. The surfactants prevent the agglomeration of the gold clusters. Addition of small amount of dithiol precipitates out a 3-D cluster network, which can in turn be deposited onto another solid substrate. Figure 2.4 shows a transmission electron microscope (TEM) image of a cluster array spin-cast onto MoS_2.

The methodology of self-assembly has even been extended to physical vapor deposition processes where it would seem more difficult to control the nucleation and growth of three-dimensional nanostructures. Utilizing the strain inherent in the epitaxial growth of lattice-mismatched materials, and the expected strain-induced transition from two-dimensional (layered) to three-dimensional (islanded) growth, together with careful monitoring of the growth process through RHEED analysis, researchers have been able to form arrays of semiconductor quantum dots, ~200-300 Å in diameter, ~1011 cm^{-2} in density, and with a size variation of about ±7% (Leonard et al. 1993). An example of such "self-assembled" semiconductor quantum dots is shown in

Figure 2.5. The achievement of arrays of several billions of quantum dots of these dimensions with such a size variation is beyond the capability of standard high resolution lithographic and pattern transfer processes. Moreover, the controlled formation of critical surfaces and interfaces without the intercession of ion-assisted processing that can introduce potential defects into the materials has produced a rich source of optically and electronically efficient quantum structures. A number of researchers have already incorporated such self-assembled dots into laser structures (Bimberg et al. 1998).

Chemical specificity may provide the most robust means of ensuring control of size and placement of nanostructured building blocks, and recent work in the synthesis of compound semiconductor quantum dots from chemical precursors have provided even tighter distributions of size variation (±5%) than those shown in the strain-induced self-assembled dots (Katari et al. 1994; Murray et al. 1993). The size-dependent and energy-selective optical absorption properties of such chemically synthesized quantum dots are shown in Figure 2.6.

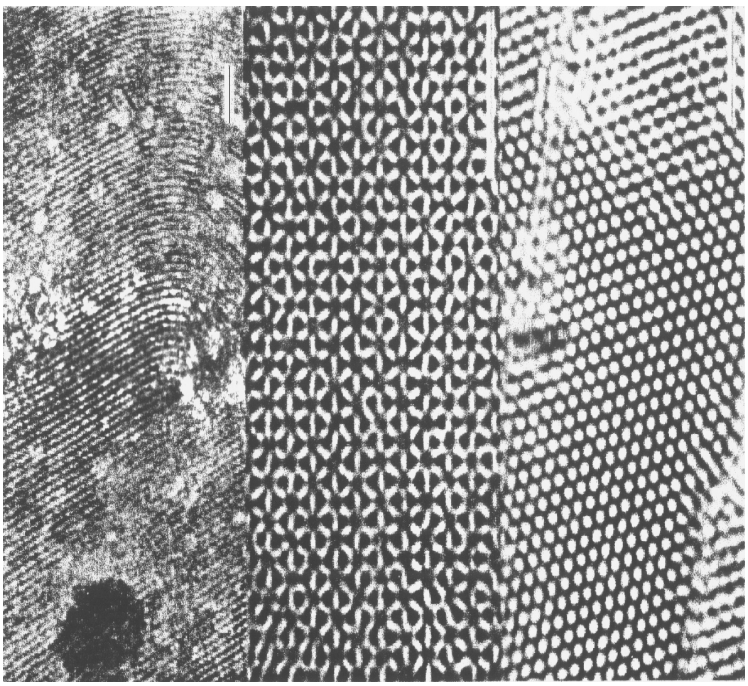

Figure 2.3. TEM images of (a) the lamellar morphology, (b) the cubic phase with Ia3d symmetry viewed along its [111] zone axis, and (c) the hexagonal phase viewed along its [001] zone axis of thesilica/surfactant nanostructured composites by co-assembly (McGehee et al. 1994) (bars = 30 nm).

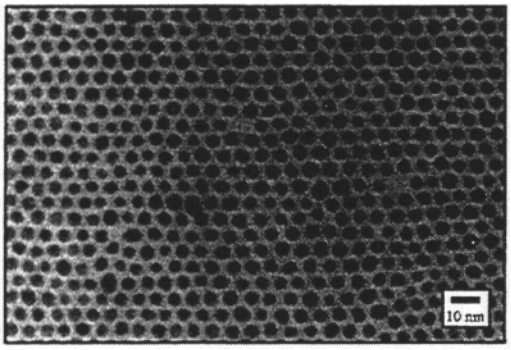

Figure 2.4. TEM image of unlinked cluster array of 3.7 nm Au clusters encapsulated by dodecanethiol (Andres et al. 1998).

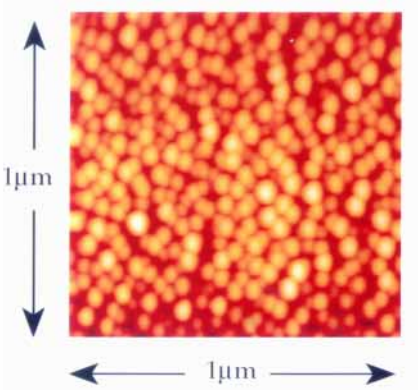

Figure 2.5. Array of InAs quantum dot structures grown on GaAs substrates (Mirin et al. 1996).

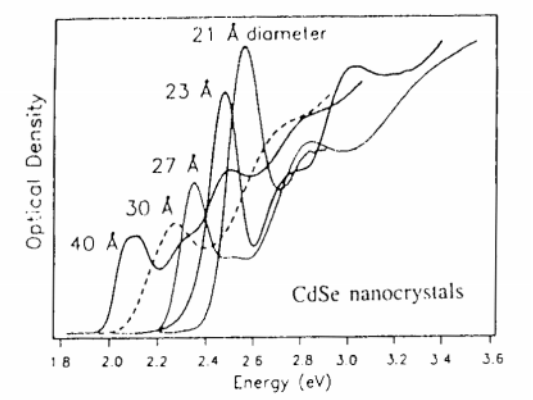

Figure 2.6. Variation of optical transparency with diameter of chemically synthesized CdSe nanocrystals (Alivisatos 1996).

Natural Templates or "Scaffolds"

Biogenic systems employ natural templates or scaffolding in the construction of nanoscaled materials, where the templates and scaffolding can help set the proper, critical dimensions that are characteristic of the final material. The templates can be formed "artificially," through the use of lithographically defined patterning and processing of the substrate material in order to achieve selective nucleation and growth of the nanostructured materials. However, there are also a host of "natural" templating materials that researchers can avail themselves of. The zeolites have for a long time been utilized as the basis of high surface area materials that enable catalysis. Recent work has taken these natural cage structures and formed large cage structures with varying pore sizes (Estermann et al. 1991; Ying and Sun 1997; Bu et al. 1998). When zeolite cages are "loaded" with various materials, the controlled proximity enforced by the cage structure can result in various magnetically active or nonlinear optical materials. More recently, the C-based fullerenes and C-nanotubes have provided a tremendously rich basis for nanostructure research; the impact of such materials is further described in Chapters 4 and 5. The by now "easy" formation of such structures and ready availability of such materials provide a rich source of nanostructures with nearly immediate applications for electronic devices, storage, and enhancement of structural materials. Further, these materials can serve as the nanostructured precursors of nanostructure synthesis approaches (such as the starting material for cluster or aerosol deposition), or can provide an avenue for the synthesis of templates of varying sizes. Such templates can be electronically "doped" and filled with other materials. Recent work reported the synthesis of "nanorods" of GaN through confined reactions in carbon nanotubes (Han et al. 1998).

OUTSTANDING ISSUES: OPPORTUNITIES AND CHALLENGES

The broad explorations of this WTEC study have shown a great diversity of impressive work on nanostructured materials. One could argue that many aspects of the work on nanostructured materials have been long-established efforts, with well-developed techniques that have been brought forth into the manufacturing arena. How do we then explain the current excitement and interest in nanostructured materials as a promising new endeavor? Part of the answer lies in the recognition of common scientific issues and common enabling technologies that link this group of researchers together. Ready availability of ever more sophisticated characterization methods that allow

us to visualize and probe materials at the nanoscale has accelerated the pace of activities in this field; at the same time, recognition of the common critical issues of control over nanostructure size and placement motivates sharing of solutions over the boundaries of conventional disciplines. Thus, some of the most exciting findings of this study manifest the cross-fertilization of techniques and ideas; for example, aerosol particles are being integrated with more traditionally fabricated electronic nanostructures, with placement achieved through the manipulation of STM tips, in order to explore ideas of electronic device enhancement at the nanostructure level (Junno et al. 1998). A sample structure is shown in Figure 2.7. The ordered assembly of diblock copolymers define three-dimensional nanostructures, and those structures are transferred into electronic (semiconductor) substrates through high resolution pattern transfer processes (Möller 1998).

Recognizing the need for effective utilization of ideas across disciplines brings the responsibility of establishing the educational infrastructure that will adequately train young scientists to more fully develop the concepts and applications of nanostructured materials in the future. Such an infrastructure will require researchers and educators who are familiar with the properties of a broad range of materials, including polymers, biomolecular materials, metals, ceramics, and semiconductors. It will benefit from an informed perspective on critical applications, and must provide access to a wide range of synthesis and assembly techniques and characterization methods that currently reside separately in the disciplines of physics, chemistry, electrical engineering, biology, etc. Finally, a critical enabler for the future of this field and for its educational infrastructure is further development of computational tools that encompass the full range of atomistic calculations to macroscopic materials properties. This will require a “systems approach” (Olson 1997) that will span a variety of different computational models, addressing the different critical length scales, starting with solutions of the Schrodinger and Poisson equations, solving interatomic forces, and scaling all the way up to simulations of macroscopic properties and behavior (Goddard 1998).

Increased appreciation of and access to the diverse means of nanoparticle synthesis and assembly that have been developed within many different disciplines, and a common development of enabling tools and technologies, will enhance the pace of accomplishments in this new area of nanoscale synthesis and assembly.

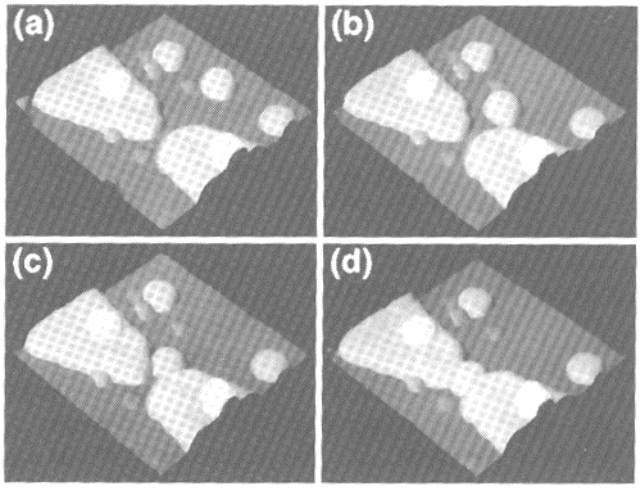

Figure 2.7. A sequence of 670 nm by 670 nm AFM images taken during the manipulation of a 50 nm Au particle into the gap between two Au/Ti electrodes (Junno et al. 1998).

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Chapter 3

Dispersions and Coatings

John Mendel
Eastman Kodak

INTRODUCTION

The object of the controlled assembly of nanoparticulates is to make materials with new properties and assemble them with practical applications. A unique value of nanoparticulates is their extremely high particle surface area; having many more sites for achieving property enhancements makes them ideal for a wide variety of applications as dispersions and coatings. Dispersive and coating applications of nanoparticles include optical, thermal, and diffusion barriers. Significant work on nanoscale dispersions and coatings is underway worldwide in the areas of ceramics, cosmetics, biosensors, colorants, and abrasion-resistant polymers. Other applications include imaging ink jet materials, electrophotography, pharmaceuticals, flavor enhancers, pesticides, lubricants, and other proprietary applications specific to industry. Still another application is in a new, post-silicon generation of electronic devices that includes nanotubes and fullerenes as constituent units of carbon nanoelectronic devices; here, dispersion takes on a more quantum consideration in which the number of atoms in a cluster is compared to the number of surface atoms to determine its dispersion function. Also in the semiconductor industry, a monolayer or thin film coating of atoms or molecules is deposited on foils, metal sheets, or glass to enhance storage capacity and accelerate responses from the electronic component.

All these applications deal with dispersions or coatings of particles that enhance specific features. Also, ability to manufacture smaller functional systems enhances performance, cost, and efficiency. These considerations power the drive towards miniaturization and precision finishing.

PROPERTY AMPLIFICATION

What's particularly exciting in the study of nanoparticles, nanostructured materials, and nanodevices is their ability to also add value to materials and products through enhancement of specific properties, such as the following:

- Mechanical strength. Nanostructured powders have been produced by plasma processing where the reactor vaporizes coarse metal particles (Froes 1998, 105-6); by combustion synthesis where redox reactions take place at elevated temperatures, followed by quenching; and by mechanical alloying with gas atomization. When nanocrystalline powders achieved by these means are compacted and applied as a coating, they lend significant strength and ductility to a variety of conventional materials such as ceramic, composites, and metal alloys.
- Superconductivity. Brus (1996) describes the nature of the superconductivity effect in detail. It involves a deposition of nanocrystals on substrates, leading to improved optical and electrical properties.
- Covering power. Because nanostructuring increases the number of active sites—there are many more atoms per grain boundary—the enhanced surface area leads to a reduced material requirement, which in turn can lower cost (Solomaon and Hawthorne 1983).
- Ability to incorporate high cost materials. Expensive materials such as colorants and drugs may be effectively dispersed in small and controlled quantities through nanostructuring (Schnur 1994).
- Environmental value. Improvements in environmental impact are achieved by utilizing nanostructure particulates in coatings and thus eliminating the requirement for toxic solvents. By eliminating hazardous wastes, nanocoatings can both reduce a company's disposal costs and improve its environmental position.

Thus, nanostructured dispersions and coatings can significantly reduce material costs and improve performance and functionality in a large variety of applications. In all of the sites the WTEC panel visited in Europe, Russia, and Japan, research groups were interested in achieving one or more of the properties listed above.

ENABLERS

For nanoparticulate dispersions and coatings, certain enablers must be present to achieve success: (1) effective particle preparation, (2) stabilization of the dispersed phase, (3) scaleup and control of the process, and (4) the

existence of excellent analytical capabilities. The main methods or issues for each are described below.

1. Particle preparation. Wet chemical methods such as liquid phase precipitation or sol-gel methods are of high interest in particle preparation (Friedlander 1993). In the area of hybrid methods, both spray pyrolysis and flame hydrolysis are utilized. Numerous physical methods such as mechanical size reduction are also often employed.

2. Stabilization of the dispersed phase. For stabilization of the dispersed phase, it is necessary to understand how particles can be kept as distinct entities. Either a charged stabilized system or a sterically stabilized approach is required. A successful preparation for use as a dispersion should be free from agglomeration in the liquid state so as to maintain particle integrity. The dry-coated format of nanoparticles should also minimize any presence of particle aggregation

3. Scaleup and control of the process. The scaleup and control of nanoparticle processing is well described by Kear (1998). Here, the issue in achieving a high rate of production of powder is the effective pyrolysis of the gas stream containing the precursor. Issues such as scaling and reproducibility from one run of nanoparticle material or dispersions to another are all inherent in the concept of precision engineering or invariant process control.

4. Analytical capabilities. Analytical capabilities are absolutely essential for characterizing dispersions and coatings (Angstrom 1995). Particle size determinations, assay analysis, and interfacial properties are all important. Transmission electron microscopes, atomic force microscopy, nuclear magnetic resonance, and scanning tunneling microscopy are just some of the tools utilized in characterizing nanoparticle dispersions and coatings, particularly at the very small end of the nanoscale.

APPLICATIONS

Below are some general examples of the vast array of applications of nanoparticulate dispersions and coatings. There are a number of applications in all of the categories below that are already in the public domain; however, most are still highly proprietary, especially drug delivery applications.

Cosmetics. An area of nanoparticle technology that has incredible commercial potential is the cosmetic industry (Crandall 1996, 251-267). Here there is a great demonstrated demand, and the technology can be made simple, since properties of color and light fastness are achieved by component mixing in the cosmetic preparation. A survey in 1990 indicated a worldwide gross volume of $14-18 billion for toiletries (Crandall 1996, 61),

i.e., traditional hygiene products such as powders, sprays, perfumes, and deodorants. The large markets for sunscreens and skin rejuvenation preparations promise additional revenues.

The diet industry is said to gross $33 billion annually (Crandall 1996, 61). One way that nanoparticle technology is addressing this market is through introducing nanoparticulate taste enhancers into low-calorie substrates.

Medicine/Pharmacology. In the area of medical applications, finely dispersed pharmaceuticals offer rapid drug delivery and reduced dosages for patients (POST 1995). Dispersions of strong and resilient biocompatible materials suggest opportunities for artificial joints. These generally are ceramic materials containing nanoparticulates.

Overall, much of the demand for nanoparticulate dispersions and coatings comes from the cosmetic and pharmaceutical industries; in particular, liquid dispersion preparations will be widely used to apply topical coatings to the human epidermis because they can be absorbed faster and more completely than conventional coatings.

Microelectromechanical systems (MEMS). Although MEMS technologies will support the semiconductor industry in particular, there are many other applications being explored, such as in medicine, ceramics, thin films, metal alloys, and other proprietary applications. In the United States a particular focus is applying sputtering coatings to achieve MEMS technology in concert with these applications.

Printing. In the areas of image capture/image output addressed by ink jet technology, nanoscience can help control the properties of the inks themselves. The production and use of nanoengineered ink products benefits from such complimentary technology as laser-assist delivery of the ink jet droplet to maintain an accurate deposit of the ink on its target (POST 1996). Another application in this field is using nanoscale properties to tailor the inks to achieve ideal absorption and drying times for desired color properties and permanency.

Semiconductors. One form of “bottom up” technology that is receiving considerable attention is thin films for the semiconductor industry (POST 1996). Here single atoms or molecules are deposited by physical vapor deposition, which could be achieved through sputtering, molecular beam epitaxy, or chemical vapor deposition. Sputtering is used on a large scale to coat metal sheets, glass, polymer substrates and other receptive materials in order to produce enhanced electronic properties for information storage and processing speed.

Sensors. Chemical or physical sensors often use nanoparticles because they provide high surface area for detecting the state of chemical reactions, because the quality of detection signals is improved, and because earlier and

more accurate determination of leakage reduces waste. Some commercial sensors and actuators composed of thin films are already used for environmental vapor monitoring in reactors, for example.

Other likely applications of nanotechnology involving dispersions and coatings include nanofabricated surface coatings for keeping windows and surfaces clean (POST 1996). Here, the transparent nanocoating on a surface prevents fog and dirt particles from depositing on the substrate. Commercial products (achieved through gas phase condensation) also include aluminum oxide/epoxy dispersions yielding 19 times more wear resistance than conventional products.

ONGOING R&D / PREPARATION ISSUES

During the course of this study, the WTEC panelists were privileged to hear of and to observe a wide variety of current work on nanostructured dispersions and coatings in various laboratories around the world. Descriptions follow of a number of research projects and the preparation issues being addressed in the United States and in some of the foreign laboratories that panelists visited. Table 3.1 outlines some of the nanoparticle preparation techniques that are currently in use, many of which will be discussed in the paragraphs that follow.

Work in the United States

Significant work on coatings of dispersions is underway in the United States, as described in the proceedings of the 1997 WTEC workshop report, *R&D status and Trends in Nanoparticles, Nanostructured Materials, and Nanodevices in the United States* (Siegel et al. 1998). Some of the highlights of that volume are summarized below. Similar work is ongoing in other countries.

TABLE 3.1. Nanoparticle Preparation for Dispersions/Coatings

Liquid Chemical Methods	Physical Methods	Elevated Temperature Methods
Sol-Gel *	Size reduction by mechanical means (low energy)	Aerosol
Chemical Precipitation		Flame
Ag-X (Eastman Kodak) †		
Colloidal Micelles *		Vapor phase condensation

* Wiltzius 1998; † Trivelli and Smith 1930.

I.A. Aksay describes a ceramic thin film structure that would mirror-image a self-assembly process in many materials (Aksay et al. 1992). Here silica precursors when mixed with surfactants yield polymerized templates having structures similar to surfactant-water liquid crystals; what results are highly controlled pores on the 10 to 100 Å scale. Controlling the pore structure and synthesizing the building blocks are two technical challenges facing future work in this area. However, Aksay has shown that he can grow silicate films onto a wide variety of substrates. The layer structure of the bound surfactant molecules is key. Atomic force microscopy can reveal some details on the morphology of these films. The nanostructural patterns obtained in processing ceramics that contain organic/inorganic composites allow self-assembly to take place at lower temperatures.

Another example of thin films or coating is the work of Gell (1998, 124-130), focused on improving both the physical and the mechanical properties of materials. Nanostructured coating can lead to high diffusivity, improved toughness and strength, and better thermal expansion coefficients, with lower density, elastic modulus, and thermal conductivity. In comparisons of nanostructures and conventional materials, use of nanostructured WC/cobalt composites have resulted in as much as a two-fold increase in abrasion resistance and hardness. Deposition is often accomplished by utilizing a sputtering chamber where the nanomaterial is coated on substrates. This can lead to such benefits as resistance to oxidation and cracks in addition to resistance to wear and erosion.

An area that offers exciting possibilities in the area of dispersions is the sol-gel process described by P. Wiltzius (1998, 119-121). Here, a concentrated dispersion of colloids is chemically converted into a gel body. Drying followed by sintering produces a ceramic or glass product. This process can create nanoparticles, fibers, film, plates, or tubes. All processing is at low temperatures. Lucent Technologies has developed a silica casting process that is reproducible for making tubes of pure silica of one meter in length for use in manufacturing optical fibers. Technical challenges include obtaining pure starting materials, removing refractory particles that lead to breakage in the fiber drawing process, and achieving very tight dimensional tolerances. Colloidal dispersions of this type play a critical role in chemical mechanical polishing. To obtain good yield and high quality, it is necessary to achieve very tight process control.

R. Brotzman at Nanophase Technologies Corporation describes the gas phase condensation process for synthesizing inorganic and metallic powders (Brotzman 1998, 122-123). Such a process was invented by R. Siegel and his colleagues at Rensselaer Polytechnic Institute in New York (Siegel et al. 1994). The process involves production of physical vapor from elemental or reacted material followed by sudden condensation and reaction of the vapor

into small nanometer particles. The condensation process is rapid and involves dilution to prevent the formation of hard agglomerates and coalescence.

Nanophase Technologies has developed a production system where forced convection flow controls the particle/gas stream and enhances particle transport from the particle growth region so as to generate more metal vapor (Parker et al. 1995). The convection flow helps in forming oxides and nitrides from metal crystallites. This process produces commercial quantities of nanosized inorganic powders that have a spherical shape with narrow size distributions. Table 3.2 shows some properties of these particles, and Figure 3.1 shows their transparency as a function of particle size.

Nanophase Technologies Corporation has developed a coating process that encapsulates nanoparticles with a surface treatment that ensures individual integrity of the particles in subsequent coating steps. Applications span their use in low dielectric media all the way to water and, if needed, steric stabilizers.

Nanophase also has directed efforts in the electronics and industrial catalyst areas. Friedlander (1998, 83-8) describes in good detail aerosol reaction engineering where attention is paid to design of the process and the importance of material properties and process conditions. Key process parameters include time, temperature, and volume concentration. Most commercially produced particles have polydispersity. Important full-scale processes are flame reactors for preparing pigments and powdered materials for optical fibers. Pyrolysis reactors have long been used to prepare carbon blacks.

Kear and Skandan (1998, 102-4) have discussed two divergent approaches toward fabrication of bulk materials. The first is a powder processing route involving preparations by physical or chemical means followed by condensation and sintering. Materials for cutting tools such as tungsten carbide/cobalt powders were prepared in a controllable way to about 50 nm. Liquid phase sintering completes the formation of the solid dispersion phase. However, a gap in fabrication technology remains that of controlling grain growth during liquid phase sintering.

A second approach to fabrication of bulk materials is spray forming. This procedure avoids contamination and coarsening of the dispersion and its particles when the process has a controlled atmosphere of inert gas at low pressure. In this approach there is need to establish process/product co-design where we understand cause-effect relationships between processing parameters and properties of nanophase spray/deposited materials.

TABLE 3.2. Particle Properties

Particle Properties	TiO_2	ZnO	Fe_2O_3
Refractive Index	2.40	2.01	3.01
Density (gm/cc)	3.95	5.61	5.30
Molecular Weight (μ)	80	81	160
Particle Sizes (see Figure 3.1 below)			
Optical Density (D) = Absorbance (A) = log 10 (lo/l = ε Cl) C = concentration l = optical path length ε = molar absorption coefficient/2.303			

Source: R. Brotzman, Nanophase Technologies

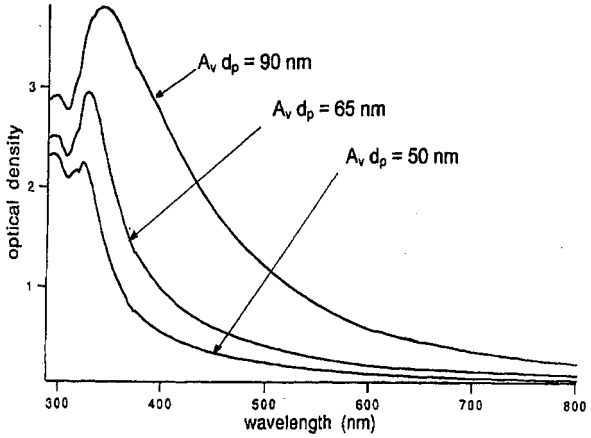

Figure 3.1. Transparency as a function of particle size (Nanophase).

In summary, particle preparation in the United States utilizes a wide variety of methods—both chemical and physical, at both high and low temperatures—all having unique considerations for scale-up and process control. Researchers in other countries are tackling many of these same issues.

Work in Europe and Japan

Due to time constraints, the WTEC panel was able to visit only a few labs in Europe and Japan that deal with issues associated with dispersions and coatings. Cited below are a visit to the Institute for New Materials at Saarbrücken in Germany and a visit to Japan's Industrial Research Institute

of Nagoya, both of which are exploring direct applications of nanostructured dispersions and coatings.

Drs. Rudiger Nass and Rolf Clasen at the Institute for New Materials at Saarbrücken make specific use of the sol-gel process in which liquid starting materials are utilized at low temperatures for nanoscale metal, ceramic, glass, and semiconductor nanoparticles (Clasen 1990). The advantages, besides temperature, include the isolation of high purity powders. The institute has focused on four basic areas for spin-off and adaptation towards commercialization:

1. New functional surfaces with nanomers. Properties such as corrosion protection, wettability, coloration, micropatterned surfaces, porosity, and the ability for selective absorption of molecules produce multifunctionality.
2. New materials for optical applications. This area combines properties of lasers and ceramics with polymers. Such features as optical filters, transparent conducting layers, materials for optical telecommunications, photochromic layers, and holographic image storage are under investigation.
3. Ceramic technologies. In this area, a simple precipitation process such as sol-gel provides for pilot-scale production of agglomerate-free powder.
4. Glass technologies. Chemical incorporation of metal colloids with intelligent properties into glasslike structures is clearly possible.

During the WTEC team's site visits to the Industrial Research Institute of Nagoya, S. Kanzaki and M. Sando described methods for preparing synergy ceramics using nanoporous silica particles that are used to fabricate thin films with one-dimensional throughput channels (Kanzaki et al. 1994). The channels had 10-20 nm sizes. High temperature Fe_2SiO_4 oxides were prepared as both molecular sieves and particulate fibers. Japan plans to pursue the preparation of nanoporous materials for absorbing oil and identified particulates.

ALTERNATIVE PREPARATION METHODS

The quest for low temperature nanoparticle preparation methods has spanned a wide range of systems. One that has been in existence for decades but has not been put into use in other industries is the method of preparing silver halide particles. Eastman Kodak in France, England, and the United States has utilized solution precipitation technology with well-controlled mixing and nucleation control to produce a wide range of grain sizes. "Lippmann"-type grains have a size of about 50 nm. Some of the properties of these fine-grain systems are discussed by Trivelli and Smith (1939).

There are other methods of creating nanoparticles of organic materials such as filter dye applications in photographic films and spectral sensitizing dyes for use in silver halide grains. Ultrafine grinding media are used to almost sandpaper organic crystals to nanoparticle ranges of 20-80 nm (Czekai et al. 1994). Similar technology by Bishop has been utilized in both pharmaceutical preparations and ink jet applications with good success (Bishop et al. 1990).

One other exciting area is in polymer science, where dendrimer molecules, often 10 nanometers in diameter, are prepared synthetically. These molecules have been studied in gene therapy, as aids in helping to detect chemical or biological agents in the air, and as a means to deliver therapeutic genes in cancer cells (Henderson 1996). The preparation of dendritic starburst molecules is described by Salamone (1996, 1814). One can imagine applications for coatings in which these molecules with their highly reactive surfaces participate in either classical (sub-nanoscopic chemistry) or novel nanoscopic conversions.

OPPORTUNITIES AND CHALLENGES

There are some outstanding opportunities and challenges that face the nanoscience community. For dispersions and coatings these include four areas:

1. The foremost area of opportunity is controlling the particle preparation process so that size is reproducible and scaleable. This requires creation of narrow size range particles that can be prepared by processes mentioned in the study such as vapor phase condensation, physical size reduction, or flame and pyrolysis aerosol generators. These same processes must respond to good reproducibility and scaling. In most studies to date, the size of primary particles depends on material properties and the temperature/time history. Two processes, collision and coalescence, occur together, and the processes need to be controlled in order to favorably influence final particle size distribution (Wu et al. 1993).
2. The second area of opportunity is process control (Henderson 1996). In the concept of a process control methodology, the nature of chemical processes makes it imperative to have means of effectively monitoring and initiating change in the process variables of interest. Accordingly, those involved with production of nanoparticles would monitor outputs, make decisions about how to manipulate outputs in order to obtain desired behaviors, and then implement these decisions on the process. Control system configuration will necessarily have a feeding process from the output such that information can be fed back to the controller. It may also have an

opportunity to base controller decision-making on information that is being fed forward; decisions could be made before the process is affected by incoming disturbances. Such would apply to process parameters like temperature, flow rate, and pressure.

In many chemical setups, product quality variables must be considered, and such measurements often take place in the laboratory. An objective analysis is needed of any observed deviation of a process variable from its aim, and an objective decision must be made as to what must be done to minimize any deviation. Here process understanding leads to well behaved reactors in manufacturing that allow for true process verification with data feedback and analysis. This concept of process control requires the application of statistical methodologies for product and process improvements. Current interest in statistical process control (SPC) is due to several factors, in particular, interest in realizing consistent high quality so as to sustain the business and obtain greater market share. Most manufacturing zones are moving toward inline/online sensor technologies coupled with process software and user-friendly computer hardware for factory operators.

The benefits of process control are many. They include achieving reduced variability and higher quality, safety enhancement, reduction of process upsets, and in many cases, environmental improvements due to achieving mass balance in processes with material in/product out. Poor process design can be inherently overcome through SPC. Reduction in sampling and inspection costs results.

3. A third area of opportunity is the process/product relationship that leads to continuous uniformity—that is, the specification setting by product users that must be available to relate to process control in manufacturing. Here, nanoparticle formulation and the process used to prepare the particles must be linked and interactive.

4. A fourth technical opportunity is to develop process models for various dispersions and coatings that lead to shorter cycle time in manufacturing. Table 3.3 shows a comparison of enablers and opportunities in Europe, Japan, and the United States.

These four areas of opportunity, then, represent what lies ahead for advancement in nanotechnology with respect to dispersions and coatings. Achieving implementation in the industrial market will require close attention to resolving the challenges in the four areas summarized above. In addition, there remains a large gap between the cost of preparing conventional materials and the cost of preparing nanoparticles. This will remain a challenge for the future if nanomaterials are to be competitive.

TABLE 3.3. Dispersions and Coatings—Nanotechnology Comparisons Between the United States, Europe, and Japan

LEVEL	1 (Highest)	2	3	4
Enablers				
Particle Preparation	U.S./Europe	Japan		
Stabilization	U.S./Europe	Japan		
Scaleup				
Characterization	U.S./Europe	Japan		
Coating	U.S./Japan/ Europe			
Opportunities				
Process Control			U.S.	Japan/Europe
Process/Product Co-Design			U.S.	
Modeling		U.S./Japan		

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Chapter 4

High Surface Area Materials

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INTRODUCTION

The trend to smaller and smaller structures, that is, miniaturization, is well known in the manufacturing and microelectronics industries, as evidenced by the rapid increase in computing power through reduction on chips of the area and volume needed per transistor (Roher 1993). In the materials area this same trend towards miniaturization also is occurring, but for different reasons. Smallness in itself is not the goal. Instead, it is the realization, or now possibly even the expectation, that new properties intrinsic to novel structures will enable breakthroughs in a multitude of technologically important areas (Siegel 1991; Gleiter 1989).

Of particular interest to materials scientists is the fact that nanostructures have higher surface areas than do conventional materials. The impact of nanostructure on the properties of high surface area materials is an area of increasing importance to understanding, creating, and improving materials for diverse applications. High surface areas can be attained either by fabricating small particles or clusters where the surface-to-volume ratio of each particle is high, or by creating materials where the void surface area (pores) is high compared to the amount of bulk support material. Materials such as highly dispersed supported metal catalysts and gas phase clusters fall into the former category, and microporous (nanometer-pored) materials such as zeolites, high surface area inorganic oxides, porous carbons, and amorphous silicas fall into the latter category.

There are many areas of current academic and industrial activity where the use of the nanostructure approach to high surface area materials may have significant impact:

- microporous materials for energy storage and separations technologies, including nanostructured materials for highly selective adsorption/separation processes such as H_2O, H_2S, or CO_2 removal; high capacity, low volume gas storage of H_2 and CH_4 for fuel cell applications and high selectivity; high permeance gas separations such as O_2 enrichment; and H_2 separation and recovery
- thermal barrier materials for use in high temperature engines
- understanding certain atmospheric reactions
- incorporation into construction industry materials for improved strength or for fault diagnostics
- battery or capacitor elements for new or improved operation
- biochemical and pharmaceutical separations
- product-specific catalysts for almost every petrochemical process

In catalysis the key goal is to promote reactions that have high selectivity with high yield. It is anticipated that this goal will be more closely approached through tailoring a catalyst particle via nanoparticle synthesis and assembly so that it performs only specific chemical conversions, performs these at high yield, and does so with greater energy efficiency. In the electronics area one may anticipate manufacture of single electron devices on a grand scale. Manufacture of materials with greatly improved properties in one or more areas such as strength, toughness, or ductility may become commonplace. In separations science new materials with well defined pore sizes and high surface areas are already being fabricated and tested in the laboratory for potential use in energy storage and separations technologies. In addition, many laboratories around the world are actively pursuing the potential to create novel thermal barrier materials, highly selective sensors, and novel construction materials whose bonding and strength depend upon the surface area and morphology of the nanoscale constituents. Many are also engaged in developing molecular replication technologies for rapid scaleup and manufacturing.

The nanoscale revolution in high surface area materials comes about for several reasons. First, since the late 1970s the scientific community has experienced enormous progress in the synthesis, characterization, and basic theoretical and experimental understanding of materials with nanoscale dimensions, i.e., small particles and clusters and their very high surface-to-volume ratios. Second, the properties of such materials have opened a third dimension to the periodic table, that is, the number of atoms, N (for a recent example see Rosen 1998). N now becomes a critical parameter by which the properties for “small” systems are defined. As a simple example, for metals

we have known for decades that the atomic ionization potential (IP) is typically about twice the value of the bulk work function (Lide 1993). It is only relatively recently that experiments have shown that the IP (and electron affinity) for clusters containing a specific number N of (metal) atoms varies dramatically and non-monotonically with N for clusters containing less than 100-200 atoms. (For examples see Taylor et al. 1992; Rademann et al. 1987; and Rohlfing et al. 1984.) Other properties such as chemical reactivity, magnetic moment, polarizability, and geometric structure, where they have been investigated, are also found to exhibit a strong dependence on N. Expectations for new materials with properties different from the atom or the bulk material have been realized (e.g., see Jena 1996 and reports therein). The opportunity is now open to precisely tailor new materials through atom-by-atom control of the composition (controlling the types as well as the numbers of atoms) in order to generate the clusters or particles of precision design for use in their own right or as building blocks of larger-scale materials or devices—that is, nanotechnology and fabrication at its ultimate.

Such precision engineering or tailoring of materials is the goal of much of the effort driving nanoscale technology. Scientists and engineers typically have approached the synthesis and fabrication of high surface area nanostructures from one of two directions:

1. The “bottom up” approach in which the nanostructures are built up from individual atoms or molecules. This is the basis of most “cluster science” as well as crystal materials synthesis, usually via chemical means. Both high surface area particles and micro- and mesoporous crystalline materials with high void volume (pore volume) are included in this “bottom up” approach.
2. The “top down” approach in which nanostructures are generated from breaking up bulk materials. This is the basis for techniques such as mechanical milling, lithography, precision engineering, and similar techniques that are commonly used to fabricate nanoscale materials (see Chapter 6), which in turn can be used directly or as building blocks for macroscopic structures.

A fundamental driving force towards efforts to exploit the nanoscale or nanostructure is based upon two concepts or realizations: (1) that the macroscopic bulk behavior with which we are most familiar is significantly different from quantum behavior, and (2) that materials with some aspect of quantum behavior can now be synthesized and studied in the laboratory. Obviously, quantum behavior becomes increasingly important as the controlling parameter gets smaller and smaller. There are numerous examples of quantum behavior showing up in high surface materials: the fact introduced above that clusters are found to exhibit novel (compared to the

bulk) electronic, magnetic, chemical, and structural properties; the fact that the diffusivity of molecules through molecular sieving materials cannot be predicted or modeled by hard sphere molecule properties or fixed wall apertures; and the fact that catalysts with one, two, or three spatial dimensions in the nanometer size range exhibit unique (compared to the bulk) catalytic or chemical activity.

OPPORTUNITIES FOR CLUSTERS AND NANOCRYSTALLINE MATERIALS[1]

Clusters are groups of atoms or molecules that display properties different from both the smaller atoms or molecules and the larger bulk materials. Many techniques have been developed to produce clusters, beams of clusters, and clusters in a bottle (see Chapter 2) for use in many different applications including thin film manufacture for advanced electronic or optical devices (see Chapters 3 and 5), production of nanoporous structures as thermal barrier coatings (Chapter 3), and fabrication of thin membranes of nanoporous materials for filtration and separation (see Chapters 3 and 7). Figure 4.1 depicts an apparatus developed at the University of Göteborg to measure cluster reactivity and sticking probability as a function of the number of metal atoms in the cluster.

The unique properties of nanoparticles make them of interest. For example, nanocrystalline materials composed of crystallites in the 1-10 nm size range possess very high surface to volume ratios because of the fine grain size. These materials are characterized by a very high number of low coordination number atoms at edge and corner sites which can provide a large number of catalytically active sites. Such materials exhibit chemical and physical properties characteristic of neither the isolated atoms nor of the bulk material. One of the key issues in applying such materials to industrial problems involves discovery of techniques to stabilize these small crystallites in the shape and size desired. This is an area of active fundamental research, and if successful on industrially interesting scales, is expected to lead to materials with novel properties, specific to the size or number of atoms in the crystallite.

[1] For examples see conference proceedings such as: ISSPIC 1, *J. Phys*. 38 (1977); ISSPIC 2, *Surf. Sci*. 106 (1981); ISSPIC 3, *Surf. Sci*. 156, (1985); ISSPIC 4, Z. *Phys. D*. 12, (1989); ISSPIC 5, Z. *Phys. D*, 19, (1991); ISSPIC 6, *Z. Phys.* D 26, (1993): ISSPIC 7, *Surf. Rev. and Lett*. 3, (1996); ISSPIC 8, *Z. Phys. D*., (1997). For background information, see Prigogine and Rice 1998; Averback et al. 1991; Jena et al. 1996; and Chapter 2 of this report.

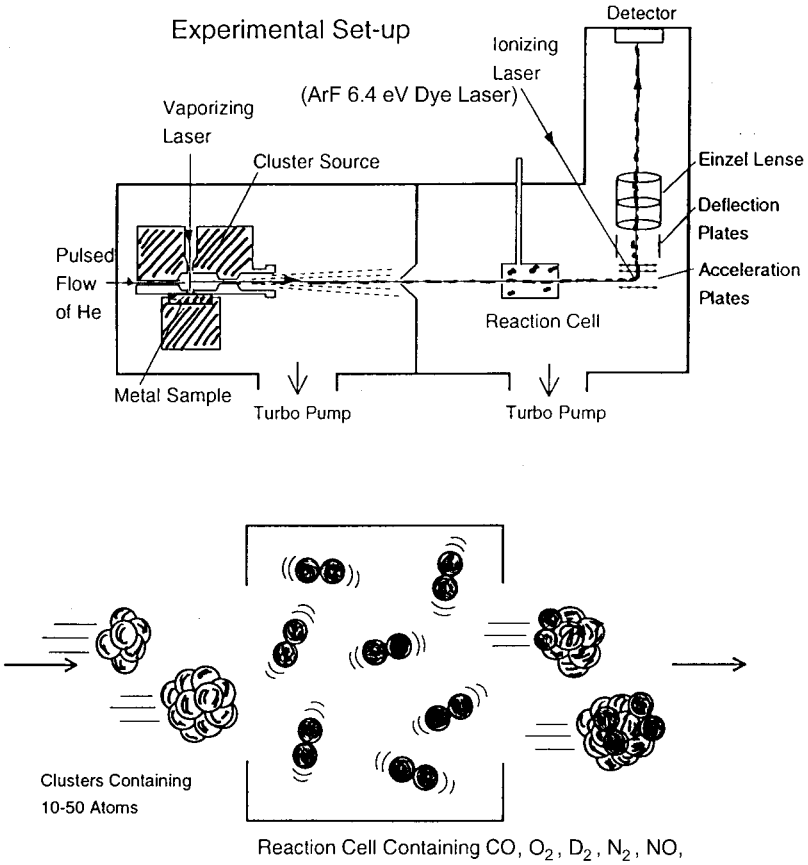

Figure 4.1. Schematic drawing of the experimental setup used in Göteborg for studies of chemical reactivity and/or sticking probability of various molecules with the clusters. The production of clusters is via laser vaporization of metal substrates and detection via photo-ionization time-of-flight mass spectrometry (A. Rosen, University of Göteborg, Sweden).

A typical objective of nanoscale catalyst research is to produce a material with exceedingly high selectivity at high yield in the reaction product or product state, i.e., chemicals by design, with the option of altering the product or product state simply by changing the surface functionality, elemental composition, or number of atoms in the catalyst particle. For instance, new catalysts with increasing specificity are now being fabricated in which the stoichiometry may be altered due to size restrictions or in which only one or two spatial dimensions are of nanometer size.

Five recent examples where nanocrystalline metallic and ceramic materials have been successfully investigated for catalytic applications are discussed below (Trudeau and Ying 1996).

Novel Catalytic Properties of Nanostructured Gold Catalysts

In the study of transition metal catalytic reactions the group at Osaka National Research Institute has discovered that nanoscale gold particles display novel catalytic properties (Haruta 1997). Highly selective low temperature catalytic activity is observed to switch on for gold particles smaller than about 3-5 nanometers in diameter. Accompanying this turn on in catalytic activity is the discovery that these nanoscale gold particles (crystals) also have icosahedral structure and not the bulk fcc structure, again a nanoscale phenomena not available with bulk samples.

In fabricating these novel catalytic materials several issues appear to be crucial. For instance, the Osaka group has shown that (a) the preparation method plays a crucial role for generating materials with high catalytic activity and selectivity; that (b) the catalytic activity, selectivity and temperature of operation is critically dependent on the choice of catalyst support, and that (c) water (moisture) even in parts per million (ppm) levels dramatically alters the catalytic properties. Figure 4.2 shows the effect of moisture on the conversion profiles for CO oxidation for nanoscale gold catalysts supported on cobalt oxide.

Examples of novel catalytic behavior of nanoscale gold particles include the following:

- CO oxidation at temperatures as low as -70°C, as illustrated in Figure 4.2
- very high selectivity in partial oxidation reactions, such as 100% selectivity at 50°C for oxidation of propylene to propylene oxide as well as near room temperature reduction of nitric oxide with H_2 using alumina-supported gold nanoparticles

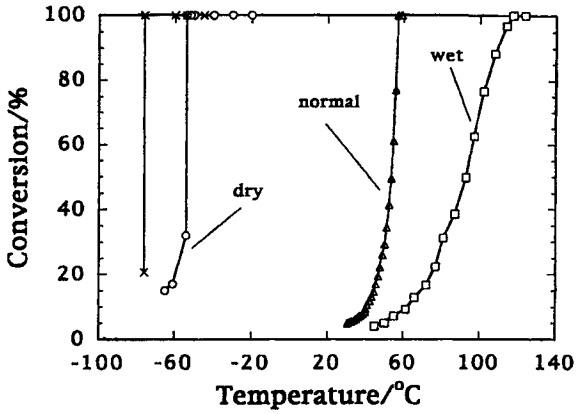

Figure 4.2. Effect of moisture on conversion profiles for CO oxidation over Co_3O_4 and Au/Co_3O_4.

The fundamental work on gold catalysts has led to "odor eaters" for the bathroom, based on nanoscale gold catalysts supported on a-Fe_2O_3, a recent commercialization from Osaka National Research Institute in Japan.

Demonstration of the Importance of Controlling at Least One Dimension in the Nanoscale Size Range for the Industrially Important HDS Reaction[2]

For catalysts based on the layered compound MoS_2, maximum hydrodesulfurization (HDS) activity is obtained only on well-crystallized nanosized materials, while HDS selectivity is determined by the number of layers or "stack height" of the nanocrystalline MoS_2. In the hydrodesulfurization reaction, illustrated in Figure 4.3, cyclohexylbenzene occurs only on the MoS_2 "rim sites," or those around the edges of the stack, whereas the pathway to biphenyl requires both "rim" and "edge" sites. Thus, the reaction selectivity can be controlled by controlling the aspect ratio of the nanoparticles of MoS_2. Such control of one- and two-dimensional nanostructures for selective chemical advantage is an exciting new area of research. Of course, a major industrial challenge will be to fabricate such nanocrystals in a commercializable form (Chianelli 1998).

Generation of Nanocrystalline, Non-Stoichiometric CeO_{2-X} by Controlled Post-Oxidation of Cerium Nanoclusters Produced Via Inert Gas Condensation Synthesis[3]

The cerium oxide (CeO_{2-x}) materials have been found to possess a significant concentration of Ce^{3+} and oxygen vacancies, even after high temperature (500°C) calcination. Such nanoclusters give rise to a substantial reduction in the temperature of selective SO_2 reduction by CO and exhibit excellent poisoning resistance against H_2O and CO_2 in the feed stream compared to that for conventional high surface area cerium oxide.

Electrochemical Reduction of Metal Salts[4]

Electrochemical reduction of metal salts is yet another option available to control the size of nanoscale catalyst particles. This has been successfully used to prepare highly dispersed metal colloids and fix the metal clusters to the substrate. Control of the current density during the electrochemical

[2] Chianelli et al. 1994
[3] Tschope and Ying 1994; Tschope et al. 1995
[4] Reetz et al. 1995

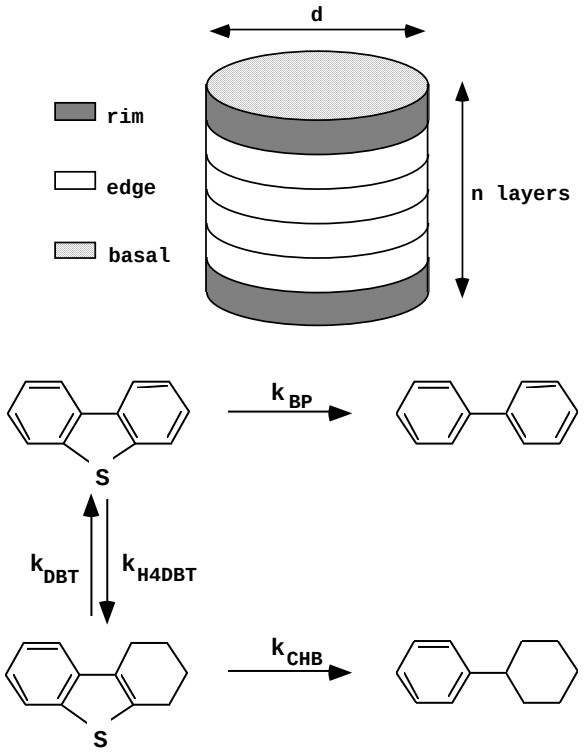

Figure 4.3. Hydrodesulfurization reaction. Selective catalysis is controlled by either the edge or rim of MoS_2 (Chianelli 1998).

synthesis process allows one to control the size of nanoscale transition metal particles. A combination of scanning tunneling microscopy (STM) and high-resolution transmission electron microscopy (TEM) has allowed surfactant molecules to be visualized on nanostructured palladium clusters.

Energy Storage Enhanced by Catalytic Dissociation of H_2

Materials with higher hydrogen storage per unit volume and weight are considered by many to be an enabling technology for vehicular fuel cell applications. Scientists at Los Alamos National Laboratories have developed an approach that enables materials such as Mg to be used for hydrogen storage (Schwartz 1998). Magnesium is of interest because it can store about 7.7 wt % hydrogen, but its adsorption/desorption kinetics are slow, i.e., the rate of charge (hydrogen dissociation and hydride formation) is much slower than in metal hydrides. At Los Alamos, high surface area mixtures of nanoscale Mg and Mg_2Ni particles are produced by mechanical means, ball milling. The addition of Mg_2Ni catalyzes the H_2 dissociation

such that the rate of hydrogen adsorption increases to a rate comparable to that of $LaNi_5$. Once a hydride is formed, the hydrogen "spillover" leads to magnesium hydride formation.

Figure 4.4 illustrates the hydrogen adsorption/desorption characteristics of the mixture of Mg with 23 atomic % Ni. As can be seen, a low pressure plateau at about 1500 torr is obtained for this particular sample. Experiments show that the pressure plateau can be tailored through such alloying. Studies with other nanoscale materials, including other catalysts such as FeTi and $LaNi_5$, are presently ongoing to further improve both the capacity and the rate of hydrogen storage.

OPPORTUNITIES IN SELF-ASSEMBLY

In self-assembly large molecular structures are obtained from the organization of a large number of molecules or atoms into a given shape, typically through specific interactions of the molecules among themselves and with a template. The interaction of the different bonding mechanisms is an area of strong fundamental research interest. Only two areas will be highlighted here: zeolites and carbon materials. Both of these materials exhibit characteristics of self-assembly, namely novel and reproducible structures that can be fabricated in industrially significant quantities.

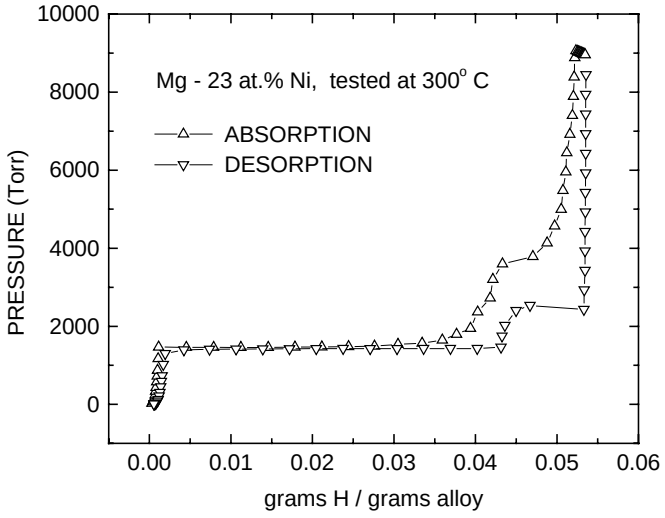

Figure 4.4. Hydrogen absorption-desorption characteristics for mixture of Mg and Mg_2Ni prepared by mechanical alloying.

Zeolitic Materials

Aluminosilicates (e.g., zeolites) are crystalline porous nanostructures with long range crystalline order with pore sizes which can be varied from about 4 Å to 15 Å in conventional zeolites. Figure 4.5 shows a 3-dimensional (e.g., MFI) zeolite cage structure together with a depiction of the straight and ziz-zag channels and a 2-dimensional zeolite with channels only in 2 directions. The vertices in the stick drawing denote position of the O atoms in the crystalline lattice. This particular zeolite has 10 atoms in the zeolite "window." The size of the window is determined by the number of oxygens in the ring. Table 4.1 gives approximate window dimensions for zeolites as a function of the number of oxygens in the ring.

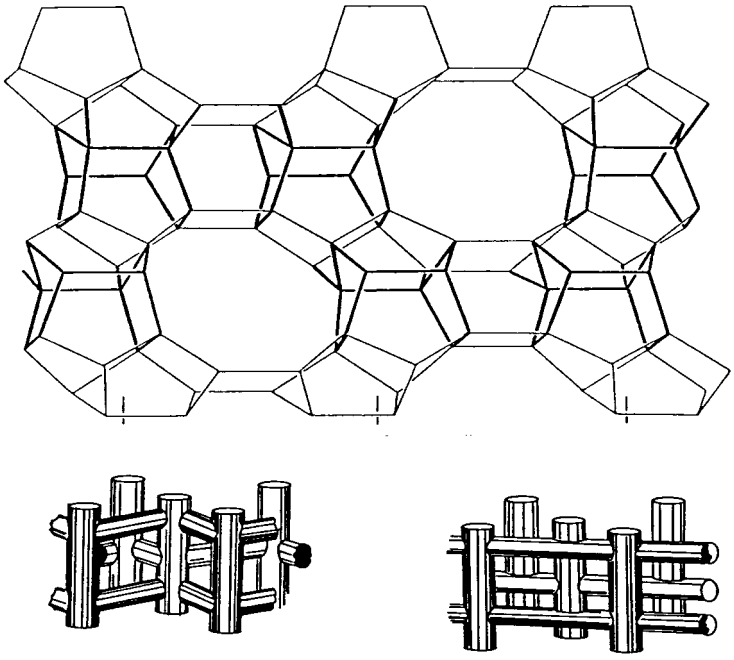

Figure 4.5. Typical zeolite structures together depicting the positions of the O atoms (vertices in upper figure) and two different zeolitic structures one (lower left) with a three dimensional structure and (lower right) a zeolite with a two dimensional channel structure.

TABLE 4.1. Zeolite Channel "Window" Dimension for Number of Oxygens in Ring

Number of Oxygens in Ring	Ring Diameter (Å)
4	1.2
5	2.0
6	2.8
8	4.5
10	6.3
12	8.0

As can be seen by examination of Table 4.1, molecules can pass through or be blocked from transport through or into the zeolite depending on the zeolite. For example normal hexane with a kinetic molecular diameter of about 5.1 Å can pass through a 10 ring or larger, whereas cyclohexane with a kinetic molecular diameter of 6.9 Å would be hard pressed to pass through a 10 ring. Thus all other things being equal, a 10-ring zeolite could be used to separate mixtures of normal hexane and cyclohexane. It is this property together with the ability to chemically modify the acidity of zeolitic materials that makes them extremely valuable as selective sorbants, as membranes and for use in selective catalytic reactions.

In 1992, a new family of aluminosilicates (M41S) with pores sizes between 20 and 100 Å in diameter were reported by Mobil researchers (Beck et al. 1992; Kresge et al. 1992). One of particular interest is MCM-41, which consists of hexagonal arrays of uniform 2 to 10 nanometer-sized cylindrical pores. Not only can such materials be synthesized, but novel structures such as "tubules-within-a-tubule" have been fabricated as mesoporous molecular sieves in MCM-41 (Lin and Mou 1996). Of particular interest is the possibility of expanding the so-called "liquid crystal templating" mechanism (Chen et al. 1993) to non-aluminum dopants within the silicate MCM-41 framework (Tanev et al. 1994) and to derive non-siliceous MCM-41 type of materials (Braun et al. 1996).

Another approach to synthesizing large pore and large single crystals of zeolytic materials is being pioneered by Geoffrey Ozin and his group at the University of Toronto, who have demonstrated that crystals as large as 5 mm can be synthesized (Kupperman et al. 1993). The ability to synthesize such large crystals has important implications for discovery of new sensors (selective chemical adsorbants) and membrane devices (selective transport of molecular species), since large single crystals can now be available to the laboratory researcher to carry out fundamental studies of adsorption and diffusion properties with such materials. These materials are expected to create new opportunities for applications in the fields of separations science, for use directly as molecular sieves or as new molecular sieving sorbant materials; in catalysis, as heterogeneous catalysts; and as supports for other

catalytic materials as well as other novel applications (Bowes et al. 1996; Brinker 1996; Sayari 1996). The ability to synthesize zeolitic materials of precise pore size in the range between 4 and 100 Å continues to expand the possibilities for research and technological innovation in the catalytic, separations, and sorption technologies (Ruthven et al. 1994; Karger and Ruthven 1992).

Carbon Materials

The carbon-based materials of interest from a molecular self-assembly point of view include fullerenes and their relatives, including endohedral fullerenes and metal-coated fullerenes, carbon nanotubes, carbon nanoparticles, and porous carbons. Since 1990 with the discovery of techniques to produce soluble carbon in a bottle (for examples, see Krätschmer et al. 1990 and references therein), research on and with carbon materials has skyrocketed (Dresselhaus et al. 1996; Dresselhaus and Dresselhaus 1995). Not only can the molecular forms of carbon (the fullerenes and their derivatives) be synthesized, characterized, and studied for applications, but many other new carbon materials such as multi- and single-walled carbon nanotubes can now be produced in macroscopic quantities. Figure 4.6 illustrates the broad variety of carbon nanotube structures whose properties are now being examined both theoretically and experimentally. A rich literature on these new carbon materials now exists. This report will only attempt to highlight a few important recent examples in the area of high surface area materials.

Of particular interest for future catalytic applications is the recent report that not only can C_{60} be coated with metal atoms, but that the metal coating can consist of a precise number of metal atoms. For example, $C_{60}Li_{12}$ and $C_{60}Ca_{32}$ have been identified mass spectroscopically (Martin, Malinowski, et al. 1993; Martin, Naher, et al. 1993; Zimmerman et al. 1995). C_{60} has been coated with a variety of different metals, including Li, Ca, Sr, Ba, V, Ta and other transition metals. Interestingly, addition of more than 3 Ta atoms to C_{60} breaks the C_{60} cage. Replacement of one carbon atom in C_{60} by a transition metal atom such as Co or Ir is being studied for possible catalytic applications. The future technological challenge will be to discover techniques to fabricate large quantities of such materials, so that such catalyst materials can be put in a bottle and not just in molecular beams.

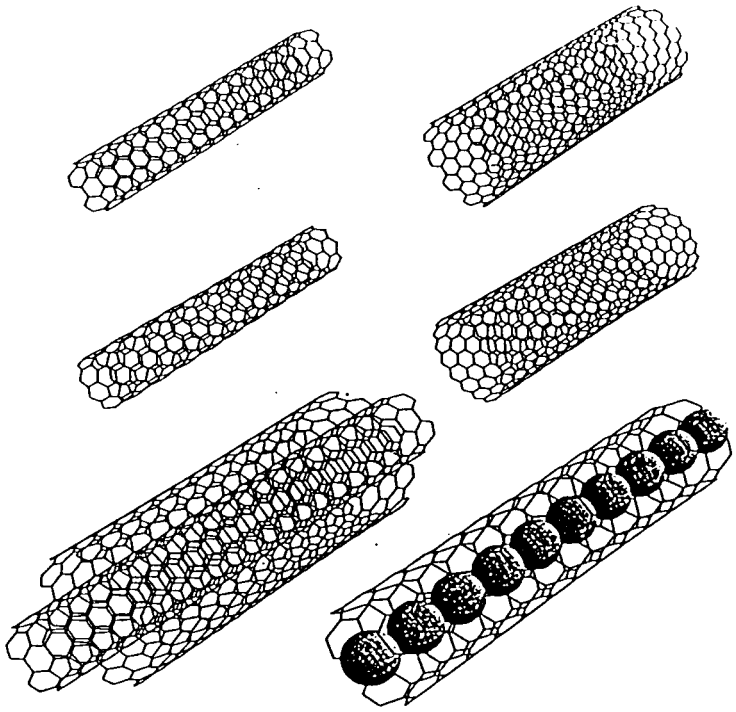

Figure 4.6. Examples of carbon nanotube structures, including multiwalled and metal-atom-filled nanotubes.

Carbon nanotubes have the interesting property that they are predicted to be either semiconducting or conducting (metallic), depending on the chirality and diameter of the nanotube. Such materials are being studied as conductive additives to plastics and for use in electrochemical applications where the uniformity of the nanotube diameter and length is not overly critical (Dresselhaus 1998). Another approach is to use the carbon nanotube as a template for a nanotube of an inorganic oxide. Hollow nanotubes of zirconia and yttria-stablilized zirconia have been prepared by coating treated carbon nanotubes with a zirconium compound and then burning out the carbon template (Rao et al. 1997). Finally, large scale production of single-walled nanotubes has recently been demonstrated, so one may anticipate a strong upsurge in the characterization and potential usage of single-walled carbon nanotubes in the future (Jounet et al. 1997).

Porous carbons are of interest as molecular sieve materials, both as sorbants and as membranes, or as nanostraws for filtration. One of the major research objectives is to develop materials or structures with exceedingly high storage capacity per unit volume and weight for gases such as H_2 or CH_4. H_2 or CH_4 could become an economic source of combustion fuel or a

means to power fuel cells for ultralow-emission vehicles or for electric power generation. Microporous hollow carbon fibers have exhibited high permeance and high selectivity as hydrogen selective membranes, and development is now underway to scale up these membranes to commercial levels (Soffer et al. 1987; Jones and Koros 1994; Rao and Sircar 1993). Carbon fiber materials produced via catalytic decomposition of hydrocarbon vapors have also recently been reported to exhibit exceptionally high hydrogen adsorption capacity (Baker 1998). More mundane uses of nanotubes are as nanometer reinforcing rods in polymers or even in concrete. Incorporation of conducting carbon nanotubes in construction materials such as concrete or structural plastics opens opportunities for real time monitoring of material integrity and quality.

Microporous and Dense Ultrathin Films

Research and development of microporous thin films for use as molecular sieving membranes using inorganic crystalline materials such as zeolites or porous silica is another area of active research around the world. For molecular sieving membranes, one critical challenge rests on discovering ways to create large scale, thin, nearly defect-free membranes. One recent example is the fabrication of mesoporous conducting thin films grown from liquid crystal mixtures (Attard et al. 1997). Transmission electron microscopy (TEM) reveals an ordered array of 2.5 nm diameter cylindrical holes in a 300 nm thick Pt film. The hole diameter can be varied either by changing the chain length of the surfactant molecule or by adding an alkane to the plating solution. It is interesting that this technique produces a continuous thin film with nanoscale porosity in an electrically conducting material.

Dense ultrathin films such as single monolayer films would be of significant importance in the semiconductor industry (see Chapter 3). Thin films of specialized coatings for corrosion, thermal, and/or chemical stability should be valuable for the chemical and aerospace industries. Novel chemical sensors may be anticipated through use of ultrathin films composed of specialized clusters. Typical techniques for production of thin films are physical vapor deposition, chemical vapor deposition, and Langmuir-Blodgett processes.

OPPORTUNITIES IN CHARACTERIZATION AND MANIPULATION AT THE NANOSCALE

Over the last two decades, the development and improvement of new techniques to fabricate and characterize nanoscale materials have fueled

much of the enormous growth in nanoscale science and technology, not only by making nanoscale materials relatively easily available for scientific study and characterization, but also in some instances, opening the door for large scale industrial use. For example, atomic force microscopy and scanning tunneling microscopy are two techniques that have become major workhorses for characterization of nanoscale materials. The strong upsurge in interest and funding in nanoscale materials must to some (large) degree be credited to the recent development of these two techniques. Combining X-ray structure, high resolution TEM and low energy, high resolution scanning electron microscopy (SEM), researchers now have the means to physically characterize even the smallest structures in ways impossible just a few years ago. Not only can a nanostructure be precisely examined, but its electronic character can also be mapped out.

Using the scanning probe devices, scientists can both image individual atoms and molecules and also manipulate and arrange them one at a time. This atomic manipulation to build structures is just in its infancy, but it does allow one to imagine a route to the ultimate goal of atomically tailored materials, built up atom-by-atom by a robotic synthesizer. The "abacus" of C_{60} molecules produced at the IBM laboratories in 1997 is an excellent example of possibilities that may lie ahead for manipulation at the atomic scale. The Atom Technology project in Japan is now in its second five-year program to push the frontiers of atom manipulation closer to the commercial sector (see NAIR site report in Appendix D).

Of all fundamental properties controlling the stability of atoms, clusters, and particles on a surface or support, knowledge of the adsorption and adhesive energies of the metal atom or particle on the solid metal or oxide surface is critical to fundamental understanding of the stability of high surface area materials for materials applications that include oxide-supported metal catalysts, bimetallic catalysts, and metal-ceramic interfaces used in microelectronics. Knowledge of such parameters allows researchers to predict the relative strengths of the metal-metal and metal atom-support interaction energies, and to infer relative stabilities as a function of the composition and size of the metal cluster. Recently it has become possible to experimentally measure the metal atom-surface bond strength on a per-atom basis using adsorption micro-calorimetry on ultrathin single crystal metal or metal oxide surfaces (Stuckless et al. 1997). The direct calorimetric measurement of metal adsorption energies developed at the University of Washington is based in part on earlier work first developed by D.A. King and colleagues at Cambridge University (Yeo et al. 1995). A technique such as this capable of probing interactions on an atom-by-atom or molecule-by-molecule basis can be thought of as another "atomic probe" that can be expected to substantially advance our database and understanding at the ultimate nanoscale for materials, that is, single atom binding energies to surfaces.

Similarly, new techniques are being developed to allow chemical and catalytic reactions to be followed in situ in real time. As an example, an infrared and nuclear magnetic resonance spectroscopic technique is being developed at the Max Planck Institute in Mülheim (see the MPI Mülheim site report in Appendix B) to monitor kinetics of CO adsorption on 1-3 nm diameter metal colloid particles (typically Pt, Rh, or Pd) in liquids and to follow in real time the way CO organizes itself on the particles while in liquid suspension. Such techniques will allow one to begin to understand the metal particle properties in solution and thus infer what might occur in real reaction mixtures. Extension of such techniques to real catalytic reactions in solution for catalyst particles of various sizes and composition is likely in the not too distant future.

SUMMARY

The areas where nanoscale high surface area materials may have the greatest future impact are difficult to predict, but some signs point to the possibility of substantial advancement in the areas of adsorption/separations, particularly in gas sorption and separations and in novel chemical catalysis using nanoscale catalyst particles.

At least two major challenges must be faced before utilization and generation of high surface area nanoscale materials becomes a commonplace reality. First is critical dimensional control of the nanoscale structure over long times and varying conditions. In nanoscale catalyst materials the critical chemical selectivity is likely to be intimately associated with the local environment around what is termed the “active” site. This suggests that the size, type, and geometry of the atoms making up the active site will play a critical role in defining the conditions under which this active site will be able to carry out its designed function. Ability to fabricate materials with “exactly” the same structure and composition at each active site has been and will continue to be a major challenge to materials and catalytic scientists.

A second challenge involves thermal and chemical stability control of the fabricated nanostructure. It is generally accepted that the smaller the nanostructure (active site) the more likely it is that the structure may move, aggregate, be poisoned, decompose, or change its shape, composition or morphology upon exposure to thermal and/or chemical cycling. Identifying windows of stable operation in which the specific structure or material will be able to retain the desired (and designed) behavior is critical for commercial applications. On the other hand, the driving force is the fact that nanostructured materials typically exhibit unique properties that are expected to open windows of opportunity previously inaccessible with existing materials.

It is important to recognize that nanoscale science and technology is not a "stand alone" field of endeavor, but rather is more of a "generic" area that is expected to have a critical impact and overlap in many areas of science and technology. The breadth of issues covered in this report can be taken as proof of this principle. The fields that fall under the "nanoscale" umbrella are many and diverse, illustrating that nanoscale science and technology is a collection of many different disciplines and areas of expertise. Such science and technology offers both an opportunity and a challenge to the scientific and technological community. Researchers in some areas of science included under the broad umbrella of nanoscale science and technology in this report do not normally consider (or in some cases, want) their scientific efforts to be labeled as "nanoscale." For this chapter, nanoscale science and technology broadly encompasses the science and technology that falls between that involving individual atoms or molecules at the one extreme and that involving "bulk" materials at the other extreme.

In summary, it is important to recognize that the use of nanostructuring or nanostructures to generate, fabricate or assemble high surface area materials is at an embryonic stage. The effect of the nanostructure and our ability to measure it will be increasingly important for future progress and development of materials for the marketplace. That said, it is apparent that so-called "mature" technologies such as catalysis, coatings, separations, etc., are already being impacted. Thus, one may eagerly anticipate exciting new advances in many diverse technological areas growing from our increasing understanding of nanostructuring and nanostructured materials.

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Chapter 5

Functional Nanoscale Devices

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Motorola

INTRODUCTION

The recent emergence of fabrication tools and techniques capable of constructing structures with dimensions ranging from 0.1 to 50 nm (see Fig. 5.1) has opened up numerous possibilities for investigating new devices in a size domain heretofore inaccessible to experimental researchers. The WTEC nanotechnology panel reviewed research in the United States, Japan, Taiwan, and Europe to find that there is considerable nanoscience and technology activity in university, industrial, and government laboratories around the world. The insight gained from this survey suggests areas of strength and areas of possible improvement in the field.

There is intense study around the world to determine the exact point in dimensional scaling where it becomes either physically unfeasible or financially impractical to continue the trend towards reducing the size while increasing the complexity of silicon chips. In some of the same laboratories where research activities on Si are decreasing, research activities on single-electron devices (SEDs) are increasing. Although there are myriad questions involving electrical contacts, interconnections, reliability, and the like, one of the fundamental issues in the miniaturization/complexity debate concerns the Si MOSFET itself when the gate length is reduced to less than 50 nm. Does it behave like a long gate device or does the output conductance increase to impractical levels due to short-channel effects? Based on the WTEC panel's survey, most of the activities examining these questions are taking place in Japanese industrial laboratories.

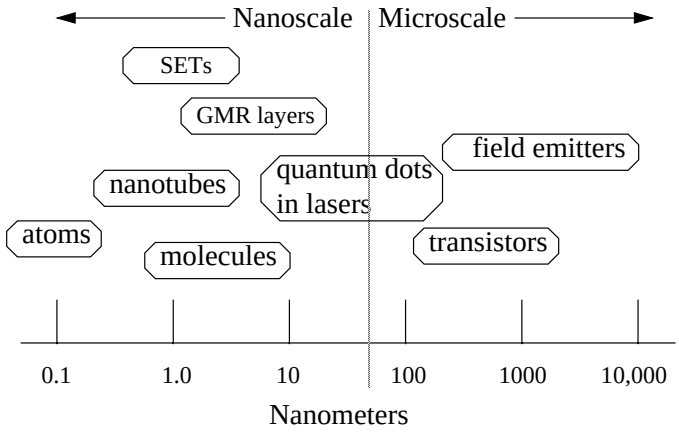

Figure 5.1. Functional device scales.

While the signature current-voltage (I-V) characteristics provide a common basis for comparison of device performance, there are significant variations in the fabrication methods and device structures being considered by the different labs in the countries the panel surveyed that have significant SED activity. The range of research in the surveyed laboratories spans electrical measurements from millikelvin to room temperature and from discrete electronic elements to integrated single-electron transistors (SETs). Materials that are used to form the active single-electron element range from charge clusters that are shaped by electric fields in a two-dimensional electron gas to metallic colloids to single oligomers. Progress in the field is hindered by architectures based on conventional circuit approaches that fail to take sufficient advantage of the unique properties of single-charge electronics to achieve significant impact in future high density applications. Most research in SED technology is fundamental and is distributed among universities funded by government agencies. A smaller body of application-directed research exists in industrial laboratories; these are mostly in Japan.

The field of magnetics has experienced increasing attention since giant magnetoresistance (GMR) in multilayered structures was discovered in 1988. In these structures ferromagnetic layers are quantum mechanically coupled across a 1-3 nm nonmagnetic metallic layer. GMR structures are under intense study for applications in hard disk heads, random access memory (RAM), and sensors. Several laboratories are investigating the physics of the transition of these layers, which are quantum mechanically confined in one dimension, to layered filaments in which there are one- and two-dimensional confinements. There are numerous experimental process approaches under consideration in fabricating GMR structures, including the following:

- magnetron or ion beam sputter deposition
- epitaxy for layered structures
- rubber stamping of nanoscale wire-like patterns
- electroplating into nanoscale pores in polymer membranes

In RAM applications, a high ratio of magnetoresistance combined with a small coercive switching field is key to density, speed, and low power. These features are also achieved in magnetic tunnel junctions in which the ferromagnetic layers are quantum mechanically coupled through a thin dielectric layer. Although research in nanoscale magnetics is underway internationally, most of the activities on the practical applications mentioned above are in the United States.

Optical devices have already benefited from incorporation of nanostructured materials: commercially available semiconductor lasers incorporate active regions comprised of quantum wells, the presence of which modifies the electronic density of states and the localization of electrons and holes, resulting in more efficient laser operation. Extrapolating from those results, even greater improvements are predicted for lasers utilizing either quantum wire or quantum dot active layers. Recent advances in the "self-assembled" formation of quantum dot structures have stimulated progress in the fabrication and characterization of quantum dot lasers in Japan, Europe, and the United States.

In late 1991, the first synthesis and characterization of carbon nanotubes were reported. The novel material contained a wide variety of multiwalled nanotubes (MWNT) containing 2 to 50 concentric cylindrical graphene sheets with a diameter of a few nm and a length of up to 1 μm. The material was produced at the negative electrode of an arc discharge and appeared to be mixed with a large amount of other forms of carbon. This initial work led many groups throughout the world to produce and purify nanotubes. The theoretical study of their electronic structure followed in the next year. Soon it became clear that nanotubes have unique electronic and mechanical properties that are expected to lead to ground-breaking industrial applications. Some of the progress made in this respect over recent years is summarized later in this chapter.

SINGLE-CHARGE ELECTRONICS

Even though the study of single-electron charging effects with granular metallic systems dates back to the 1950s, it was the research of Likharev and coworkers almost 10 years ago that laid much of the groundwork for understanding single-charge transport in nanoscale tunnel junctions (Likharev 1988; Averin and Likharev 1991, Chap. 6). The concept was developed of a Coulomb gap that can be exploited to control the transfer of

single charges. Since then, many research groups have made use of the Coulomb blockade effect to develop SED technology. Figures 5.2 through 5.11 show some of the myriad approaches to developing SEDs and representative laboratories pursuing the various SED concepts. Some of the more recent results are discussed below.

The group at Hitachi Europe uses a side-gated constriction in a delta-doped GaAs structure to fabricate a magnetic tunnel junction device in which a series of small islands separated by tunnel barriers are formed (Nakazato et al. 1992) (see, for example, Fig. 5.2). At ~ 2 K, the Coulomb gap voltage oscillates as a function of the side-gate voltage. Using the MTJ device as a building block, both memory and logic (inverter, NOR) functions have been demonstrated (Nakazato 1996, 65). The fabrication procedure makes use of standard semiconductor processing techniques and does not rely on lithography to define the nanoscale islands, since these are created by disorder in the delta-doped layer.

Other groups have utilized fine-line lithography to fabricate SEDs. At IBM, a flash memory SED was demonstrated by fabricating a sub-50 nm Si quantum dot (QD) on top of a MOSFET channel using a silicon-on-insulator (SOI) substrate, with the QD acting as a floating gate (Wesler et al. 1997). Single-electron charging was observed up to 90 K, while large threshold voltage shifts of up to 0.75 V were measured at 290 K. The University of Minnesota and Fujitsu have also reported similar structures (Guo et al. 1977; Nakajima et al. 1997). To overcome the lithography limitation on the QD size, the Toshiba group used a Si edge quantum wire approach (Ohata and Toriumi 1996). An inversion layer was formed at the 15 nm high Si sidewall of a SOI structure by growing a gate oxide and depositing a poly-Si gate there. Conductance oscillations were clearly seen at 4.2 K in this edge-channel MOSFET (Fig. 5.3). More recently, the Toshiba group has reverted back to a more planar device configuration, with a 50 nm wide Si quantum wire defined by e-beam lithography and oxidation of the surrounding SiO_2 (Koga et al. 1997, 79).

One method to form semiconductor QDs without depending on fine-line lithography is to make use of the self-organizing nature inherent in the Stranski-Krastanow thin film growth mode. In the initial stages of the heteroepitaxial growth of lattice-mismatched materials, strain-induced coherent relaxation occurs and dislocation-free islands are formed that are in the tens of nanometers range in size. There has been considerable research in these self-organized quantum dots (SOQDs) in the past few years, though much of the work has been of a fundamental nature (see, for example, Petroff and Demmester 1995; Nötzel 1996). More recently, the University of Tokyo has proposed the embedding of InAs SOQDs in AlGaAs/GaAs heterojunction field effect transistors (HFETs) to form a flash-memory SED (Sakaki et al. 1995).

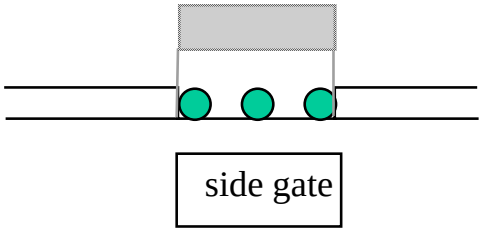

Figure 5.2. Metal colloids, self-assembled monolayer (SAM) coatings, polysilicon, quantum dots embedded in SiO_2 (Hitachi, IBM, RIKEN, NTT, ETL, University of Lund).

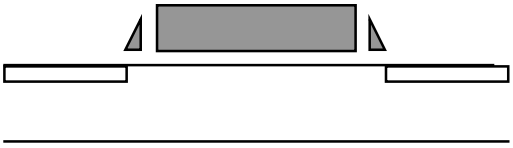

Figure 5.3. Sidewall extensions of MOSFET gate (Toshiba).

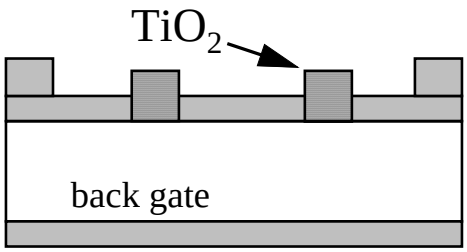

Figure 5.4. Oxidation of metal or semiconductor with scanning tunneling microscope (STM) tip (ETL).

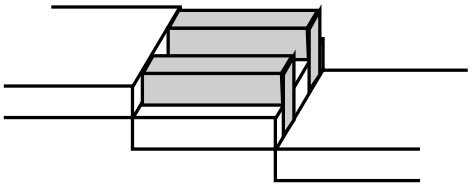

Figure 5.5. STM probe oxidation of metal on vicinal substrate steps (ETL).

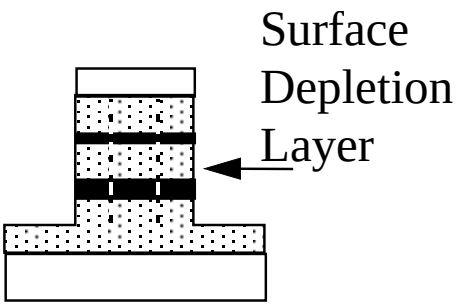

Figure 5.6. Double barrier tunnel diode structure (Max-Planck-Institut, Stuttgart; NTT).

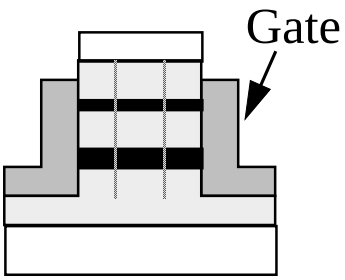

Figure 5.7. Gated double barrier tunnel diode structure (Max-Planck-Institut, Stuttgart; NTT; Purdue University).

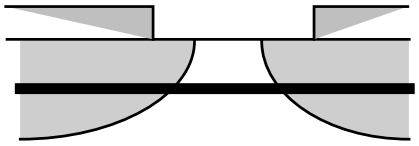

Figure 5.8. Depletion layer control of 2DEG area (Hitachi, University of Glasgow, University of Tokyo).

This concept was further demonstrated by the Sony group, which reported observing threshold voltage shifts at 300 K (Taira et al. 1997, 53). Fujitsu has also proposed the use of InGaAs QDs in a similar manner (Futatsugi et al. 1997, 46). The one difference in this case is that the QDs are formed at the bottom of tetrahedral-shaped recesses formed by substrate patterning. Since SOQDs form in a somewhat random manner on a planar surface, this approach provides positioning control.

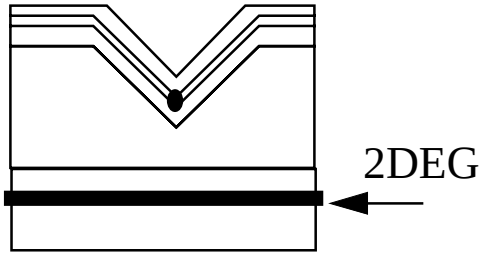

Figure 5.9. Tetrahedral shaped recess, TSR (Fujitsu).

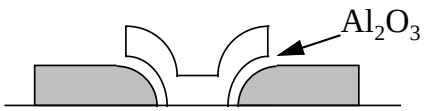

Figure 5.10. Double barrier metallic SET patterned by e-beam (NEC).

Of course, QDs can be formed with materials other than semiconductors. In fact, some of the earliest work in single-electron charging was done with metallic tunnel junctions. With modern fabrication tools and techniques, some groups have investigated the formation of nanoscale Au particles between metallic contacts. The University of Cambridge group used focused ion beam deposition to place Au dots between electrodes spaced 30 - 40 nm apart (Woodham and Ahmed 1997, 73). At Lund University in Sweden, atomic force microscopy (AFM) is utilized to move a 50 nm Au particle in between contacts formed by e-beam lithography (Carlsson et al. 1997, 128). Researchers observed conductance plateaus stable for several minutes at 300 K. The group at Cambridge University/Hitachi Europe used a colloidal process to form a chain of insulated Au particles between source, drain, and gate electrodes (Tsukagoshi et al. 1997, 67). At 4.2 K, the chain exhibited a Coulomb staircase and periodic conduction oscillations in I-V measurements.

For a very different approach, a molecular embodiment of a QD-based system can be realized by connecting a single molecule between metallic contacts. At Yale University a single molecule of benzene-1,4-dithiol was self-assembled from solution onto two electrodes of a mechanically controllable break junction (Fig. 5.11, left) (Reed et al. 1997). The spacing between the electrodes is ~ 0.8 nm, and I-V measurements at room temperature showed a gap ~ 0.7 V wide, which is attributed to a Coulomb gap. The Delft University of Technology in the Netherlands is also working on transport through oligomers (Fig. 5.11, right).

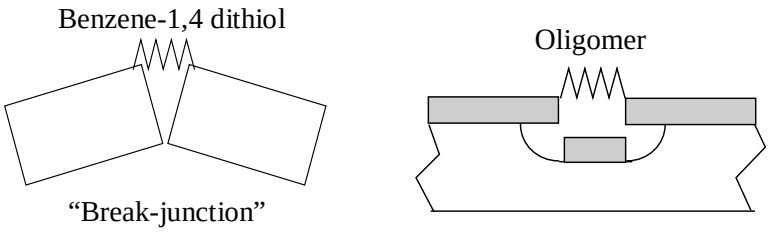

Figure 5.11. A single molecule connecting metallic contacts (Yale University, University of South Carolina, Delft University, Karlsruhe University).

Concerning the architecture in which SEDs are utilized, a number of approaches have been proposed. One of the more novel ideas is that of quantum cellular automata (QCA), based on some earlier work at Texas Instruments and developed at the University of Notre Dame (Lent et al. 1993; Tougaw and Lent 1994). The basic QCA cell is made up of a group of capacitively coupled QDs. Each cell holds two electrons, resulting in two polarization configurations that can represent the logic "0" and "1" states, and each cell interacts via Coulombic forces with neighboring cells. An array of cells can then be used to transmit binary information, which eliminates the need for physical interconnects between devices and represents a paradigm shift for ultralarge-scale integration (ULSI). Basic Boolean operations (AND, OR, etc.) can be implemented using QCA, and more complex functions have been simulated. Most recently, the Notre Dame group has demonstrated a nonlinear, bistable response of a QCA cell, albeit at a very low temperature of less than 20 mK (Snider et al. 1997, 233).

The QCA approach is not without its challenges (and critics). Circuit fabrication will be difficult because stringent control in QD positioning is required. Others have pointed out that bistability is only a necessary but not sufficient condition for the operation of Boolean logic circuits, because isolation is needed between the input and output, while background charge fluctuations will hamper logic implementation (Roychowdhury et al. 1966; Barker et al. 1997, 233). Thus, there is also considerable research in the use of SEDs with more conventional architectures. The group at Hitachi Europe uses its MTJ devices in binary decision diagram logic that is commonly used in large-scale integrated (LSI) circuits (Tsukagoshi et al. 1997, 67). The Toshiba group is combining its SED with a MOSFET to compensate for the lack of gain in the former, as are, presumably, other groups working on QD-based flash memory SEDs (Koga et al. 1997, 79). Tables 5.1 and 5.2 summarize some of these approaches.

TABLE 5.1. SET Architectures

Flash Memory	Digital Logic	Cellular Automata	Neural Networks
Hitachi	Hitachi (binary decision diagram logic)	Notre Dame Hitachi	Delft U. Technology
IBM	Hokkaido University		
Toshiba			

TABLE 5.2. Quantum Dot Flash Memory

	Hitachi	Minnesota	Fujitsu	IBM	Sony
Material	Poly-Si	SOI	SOI	SOI	GaAs
QD Material	Poly-Si	Poly-Si	Poly-Si	Poly-Si	InAs
QD Fab Method	E-beam / etch	E-beam / etch	E-beam / etch	E-beam / etch	Epitaxial self-assembly
QD Size (nm)	10 (estim.)	7 x 7 x 2 h	30 x 20 x 25 h	30 x 20 x 8 h	25 x 4 h
$2V_{th}$ (V)	0.5 - 1.0	0.055	0.1	0.75	0.45
Write/ Erase	15 V / 10 V	> 4 V	4 V	3 V	> 1 V
Retention	1 - 24 h	10 sec.		> 1 wk	10 sec.
Circuits	128 Mb LSI				

In summary, while significant progress has been made in nanofabrication techniques, the field of single-charge electronics is still limited in scope by the lack of a suitable architecture that fully utilizes the unique aspects of single-electron charging. Current approaches require many SED elements to achieve conventional functions such as adders, exclusive NORs, etc. Simulations of such circuits predict slow operating speed. The field seems to be stuck on applying conventional electronics to SEDs. Either a new architecture will be discovered or SEDs may find a niche home in those applications where measurements of single charges are needed.

For the fabrication of nanoscale electronic devices, the self-organizing technique appears to be the most promising. The field of self-organized semiconductor QDs is quite active, but aside from optical emitters, very few practical electronic functions have been proposed. Of those, the single-electron flash memory is attracting attention, but there has been no serious proposal as to how the device could operate under normal integrated circuit performance conditions and reliability specifications. Using the SED as a floating gate to a MOSFET has the same kinds of problems as applying conventional approaches to SED architectures; until someone comes up with a better idea, the future of these approaches remains to be determined.

NANOMAGNETICS

The discovery in 1988 of GMR in structures of alternating magnetic and nonmagnetic thin layers (Baibich et al. 1988) was the accumulation of several decades of intensive research in thin film magnetism (Shinjo and Takada 1987) and improvements in epitaxial growth techniques developed mainly in semiconductor materials. Not surprisingly, the first GMR structure was fabricated using molecular beam epitaxy (Baibich et al. 1988). The high quality magnetic and nonmagnetic metallic films provide electrons with a mean free path exceeding 100 Å; on the other hand, the epitaxial growth allows for each constituent layer of the structure to be as thin as a few atomic layers. The greatly enhanced spin-dependent scattering in these multilayered structures provides magnetoresistance changes as high as 50%. Table 5.3 shows some of the institutions involved in GMR research and development, based on various publications, patents, and WTEC visits.

Two subsequent major developments from IBM enabled the application of GMR materials to hard disk heads, RAM, and sensors. The first development was the demonstration of equally good or better GMR materials using high throughput and production-worthy magnetron sputtering systems (Parkin et al. 1990). The other development was the invention of magnetically soft spin-valve structures, which allow low field and low power operation (Dieny et al. 1991a; Dieny et al. 1991b).

TABLE 5.3. Giant Magnetoresistance Activities

Memory:	MRAM	HD Heads	Structures / Physics / Materials
• Fujitsu	■	■	• IMEC
• Hitachi	■	■	• L'Ecole Polytechnique Lausanne
• Honeywell	■		• IBM Zurich
• IBM	■	■	• Tohoku University
• Motorola	■		• Nagoya University
• Matsushita	■	■	• NIST
• Mitsubishi	■	■	• UC Santa Barbara
• Philips		■	• UC San Diego
• Samsung	■		• Carnegie Mellon
• Toshiba	■	■	• Princeton
• Seagate		■	
• Siemens	■		
• Sony		■	*Based on publications, patents or visits

Industrial R&D efforts on GMR materials initially focused on high density read heads. The major U.S. players are IBM, Seagate, Quantum, ReadRite, and Applied Magnetics. In Japan, all the semiconductor companies are involved, in addition to strong magnetic media powerhouses such as TDK and Yamaha. Korea's Samsung is also actively involved in the GMR race. In Europe, Thomson CSF, Philips, and Siemens seem to have fallen behind. All in all, IBM is in a commanding position to reap the benefits of the GMR phenomenon. In November 1997, it announced the volume production of the first generation of GMR read heads.

In 1995, a different class of high magnetoresistive materials was discovered in which the nonmagnetic layer separating the two ferromagnetic layers is made with an ultrathin insulating material, such as an aluminum oxide layer < 20 Å thick (Miyazaki and Tezuka 1995; Moodera et al. 1995). With the switching of magnetization of the two magnetic layers between parallel and antiparallel states, the differences in the tunneling coefficient of the junction and thus the magnetoresistance ratio have been demonstrated to be more than 25%. A distinctive feature of this MTJ class of materials is its high impedance (> 100 $k\Omega$-μm^2), which allows for large signal outputs.

The gradual improvement of GMR and MTJ materials have made them attractive for nonvolatile magnetic random access memory (MRAM) applications. The potential to make MRAM a high density, high speed, and low power, general purpose memory prompted the Defense Advanced Reseat Projects Agency to fund three MRAM consortia beginning in 1995, led by IBM, Motorola, and Honeywell, respectively. Other companies engaged in MRAM research are Hewlett-Packard, Matsushita, NEC, Fujitsu, Toshiba, Hitachi, and Siemens.

The key for a competitive MRAM technology is the fabrication of deep submicron-dimension magnetic cells. The further development of lithography tools utilizing e-beam and deep ultraviolet radiation is essential. Magnetic storage elements as small as 0.25 μm have been demonstrated by both Motorola and IBM (Tehrani et al. 1996; Chen et al. 1997; Gallagher et al. 1997). Among the steps of MRAM fabrication that are not yet compatible with semiconductor processing is the ion milling of the magnetic cells. The possibility of dry etching the magnetic materials has, nevertheless, been demonstrated (Jung et al. 1997). Figures 5.12 through 5.15 summarize the major directions in memory R&D. Arrows denote ferromagnetic layers.

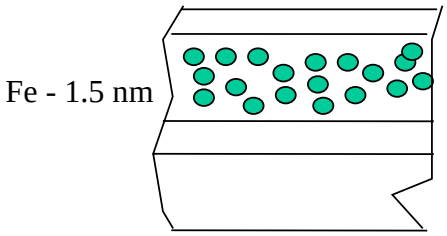

Figure 5.12. Granular GMR—Co, Fe (Nagoya University, Tohoku University, CNRS-Thomson, UCSB, UCSD).

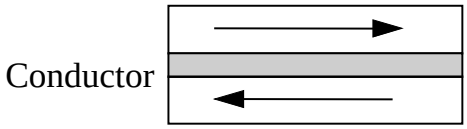

Figure 5.13. Current in plane (Matsushita, Fujitsu, Mitsubishi, Toshiba, Hitachi, Thomson, Philips, Siemens, IBM, Univ. Regensburg, IMEC, Nagoya University, Tohoku University, NIST).

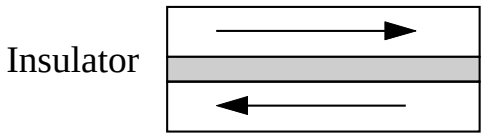

Figure 5.14. Magnetic tunnel junction (IBM, MIT, HP, Tohoku University).

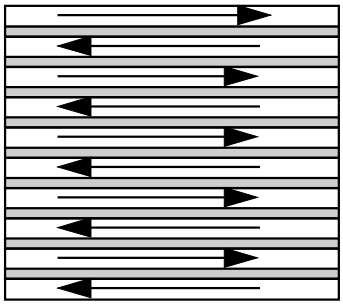

Figure 5.15. Ferromagnetic/metal/ferromagnetic: 3 - 60 periods free-standing (NRL, CNRS-Thomson, Philips, Michigan State, Lawrence Livermore Labs); plated into pores (L'École Polytechnique Fédérale de Lausanne, Johns Hopkins University, Université Catholique Louven).

The ability to fabricate submicron magnetic elements has opened a very rich and fascinating area of micromagnetics research. Characterization techniques having nanoscale resolution have been utilized and improved to measure and image the complex magnetization patterns in order to understand the magnetization switching characteristics. Examples of such techniques include the following:

- superconducting quantum interference device (SQUID) magnetometry (Zhu et al. 1997)
- magnetic force microscopy (MFM) (Ohkubo et al. 1991)
- scanning electron microscopy with polarization analysis (SEMPA) (Scheinfein et al. 1990)
- magnetic near-field microscopy (Betzig and Trautmann 1992)
- electron holography (Mankos et al. 1995)

Another essential tool is micromagnetics modeling, which is used to predict complex magnetic domain configurations in patterned magnetic elements and to generate transient pictures that demonstrate the process of forming complex domain configurations (Zheng and Zhu 1997).

By combining MFM, SQUID magnetometry, SEMPA, and micromagnetics modeling, researchers at Motorola have conducted a systematic study of the switching characteristics of single-layer and multilayer submicron magnetic structures. Three different phases of the magnetization phase diagram have been identified with regards to material composition, dimension, shape, thickness, and other structural parameters: (1) the quasi-single domain phase can be well described by the coherent rotation model (Sakaki et al. 1995); (2) the end-domain phase is dominated by the nonuniform regions of magnetization at the two ends of the element—the magnetization switching process can either be rotational or through domain wall nucleation and propagation (Shi et al. 1998); and (3) the trapped magnetization vortice (TMV) phase, which is characterized by the presence

of magnetization vortices. Nucleation from TMV sites requires lower reversal fields than coherent rotation, but a high field is needed to drive out TMVs in the element. When the driving field is not high enough, TMVs can cause unusually large fluctuations in the switching field (Shi et al. n.d.).

As the size of magnetic elements scales below 20 nm, a superparamagnetic phase emerges in which the room temperature thermal energy overcomes the magnetostatic energy well of the element, resulting in zero hysteresis (Hylton 1993). In other words, although the element itself is a single-domain ferromagnet, the ability of an individual magnetic "dot" to store magnetization orientation information is lost when its dimension is below a threshold. On the other hand, suitably prepared alloys of immiscible ferromagnetic and nonmagnetic metals that contain single-domain ferromagnetic grains in a nonmagnetic matrix have been shown to exhibit GMR characteristics. The moments of the magnetic grains are aligned at high fields and random at the coercive field, leading to GMR characteristics. In such "granular" metals, GMR has been reported for sputtered alloy films of CoCu (Berkowitz et al. 1992; Xiao et al. 1992), FeCu (Xiao et al. 1992), NiFe/Ag (Jiang et al. 1992), and CoAg (Carey et al. 1992; Tsoukatos et al. 1992). GMR values as high as 55% at 4.2 K and 20% at room temperature have been observed. The granular films require magnetic fields of the order of 10 kOe to achieve such a change in electrical resistance.

A very exciting consequence of ultrascaled magnetic particles is quantum tunneling of the magnetization direction of a collection of spins. There is no simple Schrödinger equation that describes this process, since it is not an elementary particle that is tunneling but a collective coordinate. Below its "blocking temperature," at which thermally assisted hopping between magnetic orientations becomes frozen out, magnetic particles of TbCeFe at sizes around 15 nm have been observed to behave independent of temperature and with no freeze-out magnetic relaxation (Barbara et al. 1993). Because of the coherent tunneling of the magnetization orientation between the symmetric double-well potential, a resonance line in the magnetic susceptibility and noise spectra has been observed at temperatures below 200 mK in zero applied magnetic field (Awschalom et al. 1992). This work has stimulated a number of theoretical investigations into the effects of dissipation and the feasibility of producing quantum effects in larger magnetic structures (Prokofev and Stamp 1993; Gaarg 1994; Braun and Loss 1994).

Another interesting type of nanomagnetic structure is nanometer ferromagnetic wires fabricated using conventional nanolithography (Adeyeye et al. 1997; Chou 1997), nanoimprint lithography (Chou et al. 1995), AFM/MFM direct writing (Kong et al. 1997), groove deposition (Hong and Giordano 1995), and electrodeposition into pores of template polymer membranes (Piraux et al. 1994; Blondel et al. 1994). Such nanowires of either single layer or multilayers may provide new approaches

to very small magnetoresistive sensors, ultrahigh-density hard disks (Chou et al. 1994), and other extensions of conventional applications. Another intriguing possibility is the suggestion to use heterostructure nanowires to investigate single electron tunneling (Cavicchi and Silsbee 1984; Kumzerov and Poborchii 1994).

Recently, molecular magnetism has received much attention with the development of a variety of synthesis techniques largely adapted from biology and chemistry (Kahn 1993). Natural and artificial ferritin proteins are examples of systems obtained using these methods (Gatteschi et al. 1994). The ability to add one magnetic ion at a time has resulted in nanoscale magnets precisely defined by atomic weight. Ferritin consists of a segmented protein shell in the shape of a hollow sphere, with an outer diameter of 12.5 nm and an inner diameter of 7.5 nm. In vivo, the inner space is normally filled with a crystal of an iron oxide that is antiferromagnetic below 240 K. The empty protein shells can also serve as vessels for the synthesis of ferrimagnetic magnetite and maghemite. Thus, there exists a system in which its size as well as the nature of its magnetic interactions can be varied.

Another example of molecular magnetism is a cobalt-iron-cyanide-based Prussian blue analog (Sato et al. 1996a). In the ground state the Fe^{+2} and Co^{+3} ions are low-spin and diamagnetic, and there is no interaction between them. Red light excitation transfers one electron from an iron site to a cobalt site, resulting in high-spin Fe^{+3} and Co^{+2} ions and magnetic interactions between them. The application of a blue light causes a transition back to the initial state and switches off the Fe^{+3}-Co^{+2} interactions. In addition to this kind of photochemically controllable magnets, electrochemically controllable magnets have also been reported (Sato et al. 1996b).

QUANTUM DOT LASERS

Semiconductor lasers are key components in a host of widely used technological products, including compact disk players and laser printers, and they will play critical roles in optical communication schemes. The basis of laser operation depends on the creation of nonequilibrium populations of electrons and holes, and coupling of electrons and holes to an optical field, which will stimulate radiative emission. Calculations carried out in the early 1970s by C. Henry (Dingle and Henry 1976) predicted the advantages of using quantum wells as the active layer in such lasers: the carrier confinement and nature of the electronic density of states should result in more efficient devices operating at lower threshold currents than lasers with “bulk” active layers. In addition, the use of a quantum well, with discrete transition energy levels dependent on the quantum well dimensions

(thickness), provides a means of "tuning" the resulting wavelength of the material. The critical feature size—in this case, the thickness of the quantum well—depends on the desired spacing between energy levels. For energy levels of greater than a few tens of millielectron volts (meV, to be compared with room temperature thermal energy of 25 meV), the critical dimension is approximately a few hundred angstroms. Although the first quantum well laser, demonstrated in 1975, was many times less efficient than a conventional laser (van der Ziel et al. 1975), the situation was reversed by 1981 through the use of new materials growth capabilities (molecular beam epitaxy), and optimization of the heterostructure laser design (Tsang 1982).

Even greater benefits have been predicted for lasers with quantum dot active layers. Arakawa and Sakaki (1982) predicted in the early 1980s that quantum dot lasers should exhibit performance that is less temperature-dependent than existing semiconductor lasers, and that will in particular not degrade at elevated temperatures. Other benefits of quantum dot active layers include further reduction in threshold currents and an increase in differential gain—that is, more efficient laser operation (Asada et al. 1986). Figures 5.16 and 5.17 illustrate some of the key concepts in the laser operation. Stimulated recombination of electron-hole pairs takes place in the GaAs quantum well region, where the confinement of carriers and of the optical mode enhance the interaction between carriers and radiation (Fig. 5.16). In particular, note the change in the electronic density of states, as a function of the "dimensionality" of the active layer, shown in Figure 5.17. The population inversion (creation of electrons and holes) necessary for lasing occurs more efficiently as the active layer material is scaled down from bulk (3-dimensional) to quantum dots (0-dimensional). However, the advantages in operation depend not only on the absolute size of the nanostructures in the active region, but also on the uniformity of size. A broad distribution of sizes "smears" the density of states, producing behavior similar to that of bulk material.

Thus, the challenge in realizing quantum dot lasers with operation superior to that shown by quantum well lasers is that of forming high quality, uniform quantum dots in the active layer. Initially, the most widely followed approach to forming quantum dots was through electron beam lithography of suitably small featured patterns (~300 Å) and subsequent dry-etch transfer of dots into the substrate material. The problem that plagued these quantum dot arrays was their exceedingly low optical efficiency: high surface-to-volume ratios of these nanostructures and associated high surface recombination rates, together with damage introduced during the fabrication itself, precluded the successful formation of a quantum dot laser.

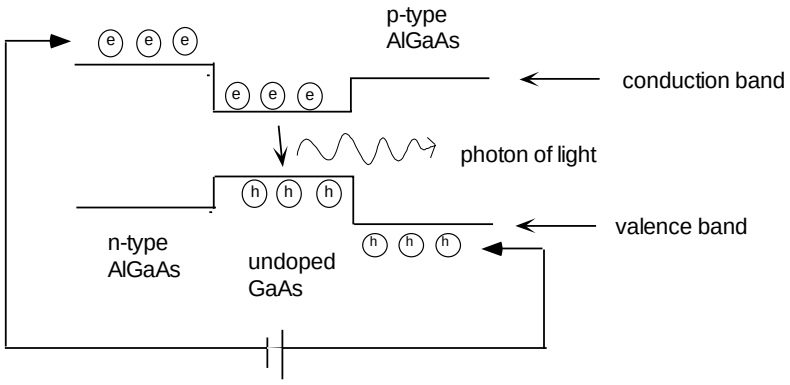

Figure 5.16. Schematic of a semiconductor laser.

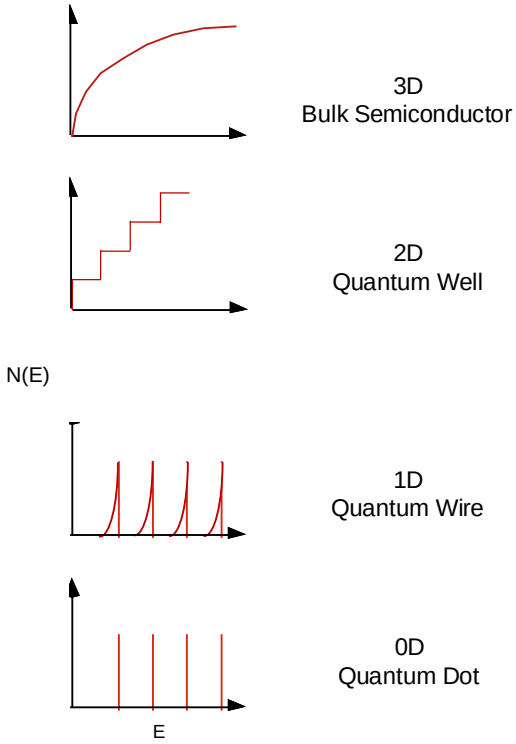

Figure 5.17. Density of electronic states as a function of structure size.

With the demonstration of the high optical efficiency self-assembled formation of quantum dots (see Chapter 2), formed without need of external processing and having the natural overgrowth of cladding material (which addressed issues of surface recombination), there ensued a marked increase

in quantum dot laser research. The first demonstration of a quantum dot laser with high threshold density was reported by Ledentsov and colleagues in 1994. Bimberg et al. (1996) achieved improved operation by increasing the density of the quantum dot structures, stacking successive, strain-aligned rows of quantum dots and therefore achieving vertical as well as lateral coupling of the quantum dots. In addition to utilizing their quantum size effects in edge-emitting lasers, self-assembled quantum dots have also been incorporated within vertical cavity surface-emitting lasers. Table 5.4 gives a partial summary of the work and achievements in quantum dot lasers.

As with the demonstration of the advantages of the quantum well laser that preceded it, the full promise of the quantum dot laser must await advances in the understanding of the materials growth and optimization of the laser structure. Although the self-assembled dots have provided an enormous stimulus to work in this field, there remain a number of critical issues involving their growth and formation: greater uniformity of size, controllable achievement of higher quantum dot density, and closer dot-to-dot interaction range will further improve laser performance. Better understanding of carrier confinement dynamics and capture times, and better evaluation of loss mechanisms, will further improve device characteristics. It should be noted that the spatial localization of carriers brought about by the quantum dot confinement may play a role in the "anomalous" optical efficiency of the GaN-based materials, which is exceptional in light of the high concentration of threading dislocations ($\sim 10^8$ - 10^{10} cm^{-2}) that currently plague this material system. The localization imposed by the perhaps natural nanostructure of the GaN materials may make the dislocation largely irrelevant to the purely optical (but not to the electrical) behavior of the material.

CARBON NANOTUBES

The first synthesis and characterization of carbon nanotubes were reported by Iijima from NEC in late 1991. The initial theoretical study of their electronic structure was soon followed with the work by Dresselhaus and coworkers at MIT (Dresselhaus et al. 1992; Saito et al. 1992a; Saito et al. 1992b). Since then, the fabrication of nanotubes has been improved by several groups, and methods other than arc discharge have been explored. The main issues are to separate the nanotubes from other forms of carbon also produced in the fabrication process and to increase the yield of single-walled nanotubes (SWNT) for potential applications. Following Iijima's work, macroscopic quantities of MWNT were produced with an improved arc discharge method by Ebbesen and coworkers at NEC (Tsukuba) (Ebbesen and Ajayan 1992).

TABLE 5.4. Summary of Quantum Dot Laser Results

Year	QD composition & size	Threshold (kA/cm^2)	Operating T (K)	Wavelength (μm)	Reference
1994	InAs 7 nm	1 0.1	300 77	0.9 0.95	(Kirstaedter et al. 1994) Europe/Russia
1994	InGaAs 30 nm	7.6	77	1.26	(Hirayama et al. 1994) Japan
1995	$In_{0.5}Ga_{0.5}As$ 20 nm	0.8	85	0.92	(Shoji et al. 1995) Japan
1996	InP 25 nm	25	300	0.7	(Moritz et al. 1996) Europe
1996	$In_{0.3}Ga_{0.7}As$	0.5 1.2	300	1.2 1	(Mirin et al. 1996) United States
1996	$In_{0.4}Ga_{0.6}As$ 12 nm	0.65	300	1	(Kamath et al. 1996) United States
1996	$In_{0.5}Ga_{0.5}As$ 10 layers	0.06	300	1	(Ledentsov et al. 1996) Russia/Europe

Source: Bimberg et al. 1997

It was not until 1995 that Smalley and colleagues at Rice University showed that SWNT can be efficiently produced by laser ablation of a graphite rod (Guo et al. 1995). In the following year, that same group produced what is considered to be among the best SWNT material generated so far; over 70% of the volume of material was nanotubes bundled together into crystalline ropes of metallic character (Thess et al. 1996). Also in 1996, a group from the Chinese Academy of Science used chemical vapor deposition to produce a 50 mm thick film of nanotubes that were highly aligned perpendicular to the surface (Li et al. 1996). Progress in recent years leads one to predict that it will indeed be possible to produce high quality carbon nanotubes in macroscopic quantities needed for many of the applications outlined below.

Nanotube bundles form a low density material and are expected to have high stiffness and axial strength as a result of their seamless cylindrical graphitic structure. It is therefore predicted that they can be used to fabricate a material with better mechanical properties than the present carbon fiber materials. Information about the mechanical properties of nanotubes has been gathered recently by a study of the thermal vibrations of a single

SWNT attached to a substrate (Treacy et al. 1996). Ebbesen's group at the Princeton NEC Research Institute found that nanotubes have an exceptionally high Young's modulus (~ 2 x 10^9 Pa) (Treacy et al. 1996). In order to reach a better understanding of the mechanical properties and intrinsic limitations of nanotubes, Bernholc's group from North Carolina State University theoretically studied the behavior of nanotubes beyond the linear Hooke's law and the nature of the defects leading to dislocations and fractures (Yakobson et al. 1996; Nardelli et al. 1998).

Nanotubes are highly polarizable nanoscale straws, a property that confers on them the capacity to ingest inorganic elements by nanocapillarity (Pederson and Broughton 1992). As a result, it has been conjectured that they could be used as minute molds to shape nanometer-sized quantum wires and as miniature test tubes. Ajayan and coworkers at NEC (Tsukuba) have first shown that lead can be introduced into carbon nanotubes (Ajayan and Iijima 1993). The efficiency of their process is low, and prior removal of the caps from the ends of the nanotubes is expected to improve the situation (Tsang et al. 1993). More information about the mechanism of NT filling was obtained by Pascard and coworkers from the École Polytechnique in France by studying the propensity to form nanowires for 15 encapsulated metal elements (Guerret-Plécourt et al. 1994). Finally, external decoration of nanotubes with metal atoms has been demonstrated and is predicted to have applications in catalysis (Satishkumar et al. 1996). Table 5.5 summarizes the primary methods of nanotube fabrication and the institutions engaged in specific methods of nanotube fabrication.

Early theoretical studies already showed that the electronic properties of nanotubes strongly depend on their diameter and their chirality leading to metallic or semiconducting structures (Saito et al. 1992c). It was conjectured that these properties can be used to construct nanoscale electronic devices. While theoretical studies were promptly published, it was only in 1996 that Ebbesen and coworkers (1996) at the Princeton NEC Research Institute presented reliable four-point probe conductivity measurements on MWNT, confirming the theoretical predictions. In 1997, two groups, one at Lawrence Berkeley National Laboratory (Bockrath et al. 1997) and the second at Delft University (Tans et al. 1997) in the Netherlands showed that conductivity through nanotubes is controlled by low dimensional effects such as resonant tunneling and single-electron charging effects. Hall effect measurements at the École Polytechnique Fédérale de Lausanne (EPFL) in Switzerland have shown that hole transport is predominant in electronic conductance (Baumgartner et al. 1997). Despite these and other very recent and encouraging efforts such as those studying the mean free path of carriers in nanotubes, the conduction mechanism is still only partially understood (Petit et al. 1997).

TABLE 5.5. Nanotube Fabrication Methods

Method	Institution
Laser ablation – SWNT	Rice University
Arc discharge – SWNT	University of Montpellier
	University of Kentucky
Arc discharge - MWNT	NEC
Chemical vapor deposition - aligned MWNT	Beijing

Metallic nanotubes are strongly polarizable in an electric field and thereby lead to field enhancement at their extremity, the strength of which depends on the ratio of the diameter to the length and can be extremely large for routinely produced nanotubes. For this reason and possibly others related to quantum confinement effects, nanotubes are expected to form outstanding field-emitting materials. In 1995, the Rice University group showed that nanotubes emit electrons very efficiently when immersed in an electric field and irradiated by a laser to remove their cap (Rinzler et al. 1995). They attribute their observation to the unraveling of an atomic wire of carbon atoms. Efficient field emission was also obtained from carefully aligned nanotubes by de Heer and coworkers (1995) at EPFL, whereas Collins and coworkers from the University of California at Berkeley (Collins and Zettl 1996, 1997), have used randomly oriented nanotubes with similar results. Efficient field-emitting material is highly desirable for the production of field-emission displays and microwave tubes.

Recently, a group from Mie University in Japan has built a cathode ray tube (CRT) using nanotube field emitters (Saito et al. n.d.). In this work, the layers of nanotubes were cut out from the soot produced in an arc discharge chamber. This fabrication method is presently not compatible with industrial production requirements, and more progress must be made before this effort can be translated into an industrial product. Table 5.6 summarizes the electrical and field emission properties of nanotubes, with the representative institutions pursuing these studies.

In summary, macroscopic amounts of good quality nanotubes can presently be fabricated by several groups around the world, and the theoretical understanding of the electronic structure and related properties of nanotubes has reached a very good level. However, despite the fact that many potential applications are mentioned in the literature over and over again, only the outstanding field emission properties of nanotubes have achieved realization in practical devices. One of the main obstacles simply remains the controlled manipulation of nanoscale objects. In this respect it seems that the generation of self-aligned structures is a path to explore further, especially after the encouraging successes reported in the literature in 1997-98.

TABLE 5.6. Electrical and Field Emission Properties of Nanotubes

Results	Institution
Theory and experiment: nanotubes can be metallic or semiconducting	MIT, NEC
Conductivity shows low dimensional signature	LBNL
	Delft University
Field emission from unraveled carbon chains at the end of nanotubes	Rice University
Field emission from aligned nanotubes attached to scanning probe tip	EPFL
CRTs fabricated with nanotubes as field emitters	Mie University

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Chapter 6

Bulk Behavior of Nanostructured Materials

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INTRODUCTION

Bulk nanostructured materials are defined as bulk solids with nanoscale or partly nanoscale microstructures. This category of nanostructured materials has historical roots going back many decades but has a relatively recent focus due to new discoveries of unique properties of some nanoscale materials.

Early in the century, when "microstructures" were revealed primarily with the optical microscope, it was recognized that refined microstructures, for example, small grain sizes, often provided attractive properties such as increased strength and toughness in structural materials. A classic example of property enhancement due to a refined microstructure—with features too small to resolve with the optical microscope—was age hardening of aluminum alloys. The phenomenon, discovered by Alfred Wilm in 1906, was essentially explained by Merica, Waltenberg, and Scott in 1919 (Mehl and Cahn 1983, 18), and the microstructural features responsible were first inferred by the X-ray studies of Guinier and Preston in 1938. With the advent of transmission electron microscopy (TEM) and sophisticated X-ray diffraction methods it is now known that the fine precipitates responsible for age hardening, in Al-4% Cu alloys, for example, are clusters of Cu atoms—Guinier-Preston (GP) zones—and the metastable partially coherent θ' precipitate (Silcock et al. 1953-54; Cohen 1992). Maximum hardness is observed with a mixture of GPII (or θ") (coarsened GP zones) and θ' with the dimensions of the θ' plates, typically about 10 nm in thickness by 100 nm in diameter. Therefore, the important microstructural feature of age-

hardened aluminum alloys is nanoscale. There are a number of other examples of nanoscale microstructures providing optimized properties. The critical current density J_C of commercial superconducting Nb_3Sn is controlled by grain size and is inversely proportional to grain size, with grain sizes of 50-80 nm providing high values of J_C (Scanlan et al. 1975).

The field of nanocrystalline (or nanostructured, or nanophase) materials as a major identifiable activity in modern materials science results to a large degree from the work in the 1980s of Gleiter and coworkers (Gleiter 1990), who synthesized ultrafine-grained materials by the in situ consolidation of nanoscale atomic clusters. The ultrasmall size (< 100 nm) of the grains in these nanocrystalline materials can result in dramatically improved—or different—properties from conventional grain-size (> 1 μm) polycrystalline or single crystal materials of the same chemical composition. This is the stimulus for the tremendous appeal of these materials.

While there are a number of bulk properties that may be dramatically changed when the microstructure is nanoscale, this chapter focuses on those for which the recent work with nanostructured materials has been most extensive. These are (1) the mechanical properties of nanostructured materials for a variety of potential structural applications, and (2) ferromagnetic materials with nanoscale microstructures for potential applications as soft magnetic materials and permanent magnet materials, and for other special applications such as information storage, magnetoresistance spin valves, and magnetic nanocomposite refrigerants. Other bulk applications such as hydrogen storage are discussed briefly.

MECHANICAL BEHAVIOR: STRUCTURAL NANOSTRUCTURED MATERIALS

The great interest in the mechanical behavior of nanostructured materials originates from the unique mechanical properties first observed and/or predicted for the materials prepared by the gas condensation method. Among these early observations/predictions were the following:

- lower elastic moduli than for conventional grain size materials—by as much as 30 - 50%
- very high hardness and strength—hardness values for nanocrystalline pure metals (~ 10 nm grain size) are 2 to 7 times higher than those of larger grained (>1 μm) metals
- a negative Hall-Petch slope, i.e., decreasing hardness with decreasing grain size in the nanoscale grain size regime
- ductility—perhaps superplastic behavior—at low homologous temperatures in brittle ceramics or intermetallics with nanoscale grain sizes, believed due to diffusional deformation mechanisms

While some of these early observations have been verified by subsequent studies, some have been found to be due to high porosity in the early bulk samples or to other artifacts introduced by the processing procedures. The following summarizes the author's understanding of the state of the art of the mechanical behavior of nanostructured materials, as determined from the literature, presentations at the U.S. workshop (Siegel et al. 1998), and the WTEC panel's site visits in Japan and Europe.

Elastic Properties

Early measurements of the elastic constants on nanocrystalline (nc) materials prepared by the inert gas condensation method gave values, for example for Young's Modulus, *E*, that were significantly lower than values for conventional grain size materials. While various reasons were given for the lower values of *E*, it was suggested by Krstic and coworkers (1993) that the presence of extrinsic defects—pores and cracks, for example—was responsible for the low values of *E* in nc materials compacted from powders. This conclusion was based on the observation that nc NiP produced by electroplating with negligible porosity levels had an *E* value comparable to fully dense conventional grain size Ni (Wong et al. 1994, 85). Subsequent work on porosity-free materials has supported these conclusions, and it is now believed that the intrinsic elastic moduli of nanostructured materials are essentially the same as those for conventional grain size materials until the grain size becomes very small, e.g., < 5 nm, such that the number of atoms associated with the grain boundaries and triple junctions becomes very large. This is illustrated in Figure 6.1 for nanocrystalline Fe prepared by mechanical attrition and measured by a nano-indentation technique. Thus, for most nanostructured materials (grain size > 10 nm), the elastic moduli are not unique properties and not a "negative."

Hardness and Strength

Hardness and strength of conventional grain size materials (grain diameter, $d > 1\ \mu m$) is a function of grain size. For ductile polycrystalline materials the empirical Hall-Petch equation has been found to express the grain-size dependence of flow stress at any plastic strain out to ductile fracture. In terms of yield stress, this expression is $\sigma_o = \sigma_i + kd^{-1/2}$, where σ_o = yield stress, σ_i = friction stress opposing dislocation motion, k = constant, and d = grain diameter. Similar results are obtained for hardness, with $H_o = H_i + kd^{-1/2}$. To explain these empirical observations, several models have been proposed, which involve either dislocation pileups at grain boundaries or grain boundary dislocation networks as dislocation sources. In

all cases the Hall-Petch effect is due to dislocation motion/generation in materials that exhibit plastic deformation.

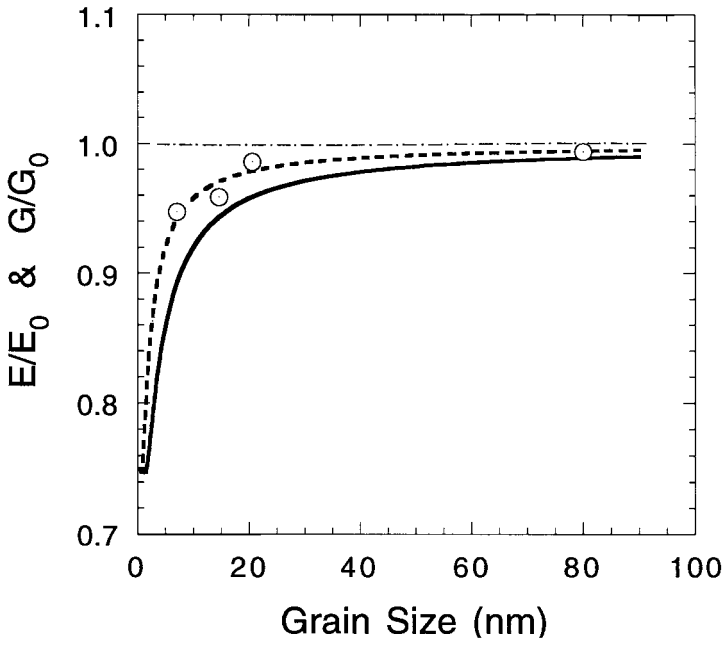


Figure 6.1. Ratio of the Young's (*E*) and shear (G) moduli of nanocrystalline materials to those of conventional grain size materials as a function of grain size. The dashed and solid curves correspond to a grain boundary thickness of 0.5 and 1 nm, respectively (Shen et al. 1995).

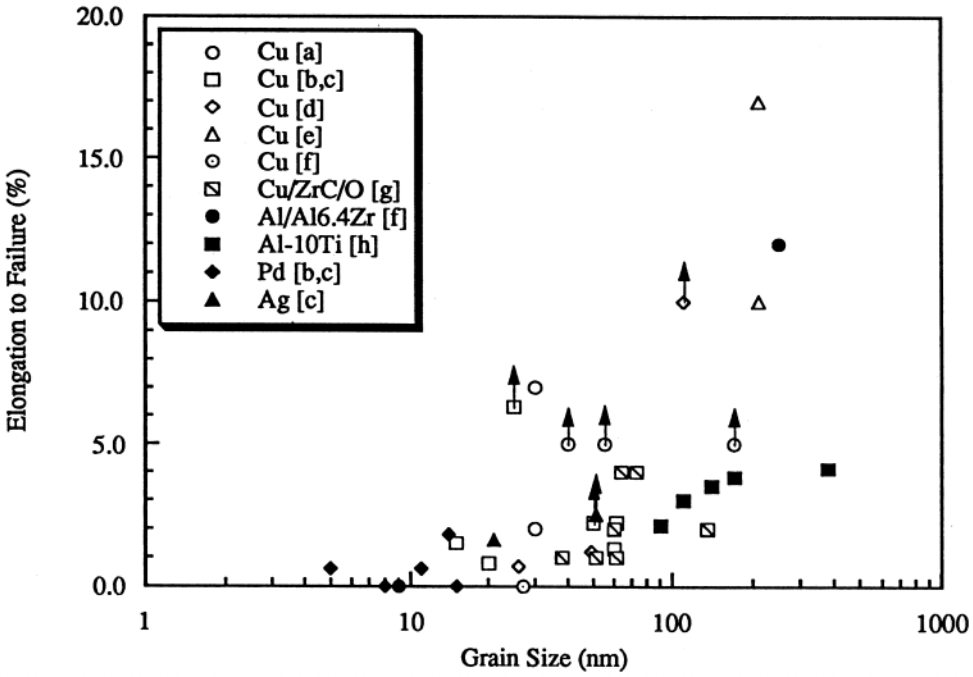
Most of the mechanical property data on nc materials have pertained to hardness, although some tensile test data are becoming available. Several recent reviews have summarized the mechanical behavior of these materials (Siegel and Fougere 1994, 233–261; Siegel 1997; Morris and Morris 1997; Weertman and Averback 1996, 323–345). It is clear that as grain size is reduced through the nanoscale regime (< 100 nm), hardness typically increases with decreasing grain size and can be factors of 2 to 7 times harder for pure nc metals (10 nm grain size) than for large-grained (> 1 μm) metals.

The experimental results of hardness measurements, summarized previously, show different behavior for dependence on grain size at the smallest nc grains (< 20 nm), including (a) a positive slope ("normal" Hall-Petch behavior), (b) essentially no dependence (~ zero slope), and (c) in some cases, a negative slope (Siegel and Fougere 1994, 233–261; Siegel 1997; Morris and Morris 1997; Weertman and Averback 1996, 323–345). Most data that exhibit the negative Hall-Petch effect at the smallest grain sizes have resulted from nc samples that have been annealed to increase their

grain size. It is suggested that thermally treating nanophase samples in the as-produced condition may result in such changes in structure as densification, stress relief, phase transformations, or grain boundary structure, all of which may lead to the observed negative Hall-Petch behavior (Siegel and Fougere 1994, 233–261). Only a few cases of negative Hall-Petch behavior have been reported for as-produced nanocrystalline samples with a range of grain sizes. These include electrodeposited nc alloys and devitrified nc alloys (Erb et al 1996, 93-110; Alves et al. 1996). Nanocrystalline thin films with grain sizes ≤ 6 nm are also observed to exhibit a negative Hall-Petch effect (Veprek 1998). While it seems likely that in many cases the observed negative Hall-Petch slopes are due to artifacts of the specimen preparation methods, it is also likely that conventional dislocation-based deformation is not operable in nanocrystalline materials at the smallest grain sizes (< ~30 nm). At these grain sizes, theoretically, mobile dislocations are unlikely to occur; nor have they been observed in *in situ* TEM deformation experiments (Siegel and Fougere 1994, 233–261; Milligan et al 1993; Ke et al. 1995). Thus, the hardness, strength, and deformation behavior of nanocrystalline materials is unique and not yet well understood.

Ductility and Toughness

It is well known that grain size has a strong effect on the ductility and toughness of conventional grain size (> 1 μm) materials. For example, the ductile/brittle transition temperature in mild steel can be lowered about 40°C by reducing the grain size by a factor of 5. On a very basic level, mechanical failure, which limits ductility, is an interplay or competition between dislocations and cracks (Thomson 1996, 2208–2291). Nucleation and propagation of cracks can be used as the explanation for the fracture stress dependence on grain size (Nagpal and Baker 1990). Grain size refinement can make crack propagation more difficult and therefore, in conventional grain size materials, increase the apparent fracture toughness. However, the large increases in yield stress (hardness) observed in nc materials suggest that fracture stress can be lower than yield stress and therefore result in reduced ductility. The results of ductility measurements on nc metals are mixed and are sensitive to flaws and porosity, surface finish, and method of testing (e.g., tension or compression testing). In tension, for grain sizes < 30 nm, essentially brittle behavior has been observed for pure nanocrystalline metals that exhibit significant ductility when the grain size is conventional. This is illustrated in Figure 6.2.



Key to Sources

a. Gunther et al. 1990	e. Gertsman et al. 1994
b. Nieman et al. 1991a	f. Eastman et al. 1997, 173-182
c. Nieman et al. 1991b	g. Morris and Morris 1991
d. Sanders et al. 1996, 379-386	h. Liang et al. 1996

Figure 6.2. Elongation to failure in tension vs. grain size for some nanocrystalline metals and alloys.

In some metals, Cu for example, ductile behavior is observed in compression, along with yield strengths about twice those observed in tension. While it is likely that the flaws and porosity present in many nc samples seriously affect the results of mechanical tests and may be partly responsible for the asymmetry of results in compression compared to tension tests, the nature of the deformation process in terms of shear banding (see below) may also be important. The above behavior is presumably due to the inability of usual dislocation generation and motion to occur at these smallest nc grain sizes.

An intriguing suggestion based on early observations of ductile behavior of brittle nc ceramics at low temperatures is that brittle ceramics or intermetallics might exhibit ductility with nc grain structures (Karch et al. 1987; Bohn et al. 1991). Karch and colleagues (1987) observed apparent

plastic behavior in compression in nc CaF_2 at 80°C and nc TiO_2 at 180°C. These observations were attributed to enhanced diffusional creep providing the plasticity at these temperatures, where conventional grain-size materials would fail in the elastic regime. It was assumed that diffusional creep was responsible for the plasticity; observations were rationalized, with boundary diffusion dominating the behavior such that the strain (creep) rate is defined as

$$\frac{d\varepsilon}{dt} = \frac{B\sigma\Omega\Delta D_b}{d^3 kT} \qquad \text{(Equation 1)}$$

where σ is the applied stress, Ω the atomic volume, d the grain size, k the Boltzmann constant, T the temperature, B a constant, and D_b the grain boundary diffusion coefficients. Going from a grain size of 1 µm to 10 nm should increase $d\varepsilon/dt$ by 10^6 or more if D_b is significantly larger for nc materials. However, these results on nc CaF_2 and nc TiO_2 have not been reproduced, and it is believed that the porous nature of these samples was responsible for the apparent ductile behavior. In addition, the idea of unusually high creep rates at low temperatures has been refuted. Recent creep measurements of nc Cu, Pd, and Al-Zr at moderate temperatures by Sanders et al. (1997) find creep rates comparable to or lower than corresponding coarse-grain rates. The creep curves at low and moderate homologous temperatures (.24 – .48 T_M) could be fit by the equation for exhaustion (logarithmic) creep. One explanation is that the observed low creep rates are caused by the high fraction of low energy grain boundaries in conjunction with the limitation on dislocation activity by the small grain sizes.

In sum, the predicted ductility due to diffusional creep in nc brittle ceramics or intermetallics at temperatures significantly less than 0.5 T_M has not been realized.

Superplastic Behavior

Superplasticity is the capability of some polycrystalline materials to exhibit very large tensile deformations without necking or fracture. Typically, elongations of 100% to > 1000% are considered the defining features of this phenomenon. As grain size is decreased it is found that the temperature is lowered at which superplasticity occurs, and the strain rate for its occurrence is increased. As discussed previously, Equation 1 suggests that creep rates might be enhanced by many orders of magnitude and superplastic behavior might be observed in nc materials at temperatures much lower than 0.5 T_M. As mentioned above, actual creep experiments have not borne out this prediction, but instead have shown creep rates

comparable to or lower than those in coarse-grained samples of the same material. This is presumably why little enhancement in ductility or superplastic behavior has been observed for nc materials at temperatures $< 0.5\ T_M$. However, there is evidence of enhancement of superplastic behavior in nc materials at temperatures $> 0.5\ T_M$. Superplasticity has been observed at somewhat lower temperatures and at higher strain rates in nc materials. The evidence for tensile superplasticity is limited and observed typically at temperatures greater than $0.5\ T_M$ and in materials that exhibit superplasticity in coarser grain sizes (1–10 µm). For example, Mishra et al. (1997) observed superplastic behavior in nc Pb-62%Sn at $0.64\ T_M$ and nc Zn–22%Al at 0.52 to $0.60\ T_M$. However, Salishekev et al (1994) observed superplastic behavior in submicron—200 nm—Ti and several Ti and Ni base alloys. Here, superplasticity (190% elongation, m = 0.32) was observed in Ti at $0.42\ T_M$. This was at a temperature 50°C lower than for 10 µm grain size Ti. The flow stress for the 200 nm Ti at 550°C was 90 MPa, compared to 120 MPa for 10 µm Ti at 600°C.

Very recently, Mishra and Mukherjee (1997) have observed superplastic behavior in Ni_3Al with a 50 nm grain size at temperatures of 0.56 to $0.60\ T_M$ to strains of 300 - 600%, but with unusual stress-strain behavior and significant apparent strain-hardening. These new results suggest very different mechanisms may be causing superplastic behavior in these nc materials.

Unique Mechanical Properties of Nanocrystalline Materials

While there are still only limited data on the mechanical behavior—especially tensile properties—of nc materials, some generalizations may be made regarding the deformation mechanisms. It is likely that for the larger end of the nanoscale grain sizes, about 50 - 100 nm, dislocation activity dominates for test temperatures $< 0.5\ T_M$. As grain size decreases, dislocation activity apparently decreases. The essential lack of dislocations at grain sizes below 50 nm is presumably the result of the image forces that act on dislocations near surfaces or interfaces. The lack of dislocations in small, confined spaces such as single-crystal whiskers has been known for many years (Darken 1961). Creation of new dislocations is also made difficult as the grain size reaches the lower end of the nanoscale (< 10 nm). Stresses needed to activate dislocation sources, such as the Frank-Read source, are inversely proportional to the distance between dislocation pinning points. Since nanoscale grains will limit the distance between such pinning points, the stresses to activate dislocation sources can reach the theoretical shear stress of a dislocation-free crystal at the smallest grain sizes (~ 2 nm). Thus, at the smallest grain sizes we may have new phenomena controlling deformation behavior. It has been suggested that such

phenomena may involve grain boundary sliding and/or grain rotation accompanied by short-range diffusion-assisted healing events (Siegel 1997).

Several examples of deformation by shear banding have been reported for nc materials. Carsley et al (1997, 183-192) have studied nc Fe–10% Cu alloys with grain sizes ranging from 45 to 1,680 nm. In all cases, deformation in compression proceeds by intense localized shear banding. The stress-strain curves exhibited essentially elastic, perfectly plastic behavior; that is, no measurable strain hardening was observed. Shear banding is also the deformation mode observed in amorphous metallic alloys and amorphous polymers. The deformation shear banding in nc Fe–10% Cu was compared to that for metallic glasses, amorphous polymers, and coarse-grained polycrystalline metals after significant plasticity and work hardening had taken place. While this suggests a close similarity between deformation in nc materials and amorphous materials, not all tensile data on nc materials exhibit a lack of strain hardening. The Fe–10% Cu samples of Carsley et al. (1997, 183-192) showed shear bands even in their larger grained specimens (i.e., about 1,000 nm).

Theoretical Needs

Central to all of the above discussion is the lack of understanding of the microscopic deformation and fracture mechanisms in nc materials. Clearly, a stronger theoretical effort is needed to guide critical experiments and point the direction for optimizing properties. There has been limited work in this area, especially in Russia, in applying disclination theory to grain rotation (Romanov and Vladimirov 1992, 191), for example. However, a much larger theoretical effort is required. Another alternate deformation mechanism that may be important in nc materials is mechanical twinning (Huang et al. 1996). Little theoretical work has been carried out to address this possibility. Another important potential approach to understanding the deformation mechanisms in nc materials is to explore the rich older literature on shear banding—mechanical instabilities that have been observed in, for example, mild steels as grain size decreases; the approach to very low strain hardening (perfectly plastic behavior) is observed. Amorphous materials exhibit many of the phenomenological characteristics of deformation in nc materials, that is, shear banding, asymmetry between tensile and compressive behavior, and perfectly plastic behavior. However, deformation mechanisms are not well understood in amorphous materials either. Recent work on bulk metallic glasses may help clarify this.

Applications

Of the present or near-term applications for nc materials, the hard material WC/Co is an example of several important trends. Nanostructured WC/Co composites have been prepared that can have the following characteristics:

- nanoscale grain sizes after consolidation of powder
- hardness values about twice that of conventional micrograined WC/Co
- enhanced wear resistance and cutting performance

While this material has increased hardness and strength, preliminary reports from Stevens Institute of Technology in Hoboken, NJ, and the Royal Institute of Technology in Stockholm, Sweden, point to similar or increased fracture toughness values for nanostructured WC/Co. As noted earlier, single-phase nanostructured materials studied to date have exhibited high strength and hardness but brittle behavior at low homologous temperatures ($< 0.5\ T_M$). The results of these studies of WC/Co two-phase nanostructured materials suggest that the combination of high hardness/strength and toughness/ductility may be possible in multiphase nanostructured materials.

Other examples that point to this possibility come from the work of Professor A. Inoue at Tohoku University in Japan, whose lab the WTEC panel visited (see Appendix D). Inoue and coworkers have synthesized a variety of multiphase Al, Mg, and Ni-base alloys with nanoscale microstructures. Many of these alloys consist of nanocrystallites in an amorphous matrix. Some Al-rich alloys contain nanoscale quasi-crystalline particles surrounded by crystalline face-centered cubic Al. The fascinating properties of these multiphase nanostructured alloys include extremely high strength coupled with some ductility. Ductility is high in compression, but uniform elongation in tension is limited. Again, this behavior is analogous to that exhibited by ductile amorphous alloys. These results again suggest the possibility for development of nanostructured multiphase composites that combine extremely high hardness and strength with toughness and ductility. Such materials could have many applications as unique structural materials.

Multiphase ceramic nanocomposites are the focus of several efforts. One significant effort is underway at the Research Center for Intermaterials of the Institute of Scientific and Industrial Research at Osaka University in Japan (see site report, Appendix D). Professor Koichi Niihara has a large effort studying micro-nano composites such as Al_2O_3/SiC that have enhanced toughness and also a variety of hard matrix/soft dispersion or soft matrix/hard dispersion nanocomposites. The enhanced toughness in some ceramic nanocomposites observed by Prof. Niihara has been verified by parallel studies of Dr. Steve Roberts at University of Oxford in England (see site report, Appendix B).

While "low temperature" superplasticity has not been realized in nanostructured materials, enhanced superplastic behavior has been observed at elevated temperatures in terms of a somewhat lower temperature range for superplasticity and, perhaps more significant, a higher strain rate regime. While much needs to be understood about superplastic behavior of nanostructured materials, the possibility for using more conventional strain rates for forming has major industrial implications. This is of particular interest for near net shape forming of ceramics.

Outstanding Issues: Opportunities and Challenges

Perhaps the overriding issue for defining the mechanical behavior of nanostructured materials is the lack of understanding of the mechanisms for plastic deformation and fracture in these materials. An extensive experimental and theoretical research effort should be applied to solve these questions. Only with such understanding can the intelligent design of nanostructured materials with optimum mechanical properties be realized.

Since many of the synthesis routes for nanostructured materials involve using powder or particulate products, compaction of such powders is needed to form bulk parts without coarsening the nanoscale microstructure. While there has been ongoing work on compaction and the thermal stability of nanocrystalline microstructures, more basic work is needed in this critical area. If some unique properties are limited to the finest grain sizes, methods must be found to stabilize the grain size while attaining theoretical density and complete particulate bonding. Furthermore, conventional processing methods are desirable if realistic scaleup and economy are to be realized.

Near-term opportunities for structural applications of nanostructured materials are in the form of coatings prepared by, for example, thermal spray deposition or electrodeposition. There is a significant effort in the United States on thermal spray deposition of nc materials. Several groups in Canada lead in deposition of nc materials by electrodeposition methods. A spin-off company, Nanometals, formed under the auspices of Parteq Research and Development Innovations, has adopted a commercial electrodeposition method to produce nanostructured metals.

Structural applications of nanostructured materials may be viewed as a focused approach to a long standing, well known design of materials with optimum mechanical properties. Use of nanoscale precipitates or dispersoids has been known for decades to improve mechanical behavior. The "new" emphasis on using nanostructured materials comes from 2 significant factors:

1. the special processing methods to push microstructures to the limits of the nanoscale
2. the unique properties and phenomena—as yet not well understood—when this limit is approached

FERROMAGNETIC NANOSTRUCTURED MATERIALS

Soft Magnetic Nanocrystalline Alloys

The discovery of nanocrystalline Fe-based soft magnetic materials is less than ten years old. The first class of such materials was the melt-spun Fe-Si-B alloys containing small amounts of Nb and Cu (Yoshizawa et al. 1988). The Fe-Si-B-Nb-Cu amorphous phase transforms to a body-centered cubic (bcc) Fe-Si solid solution with grain sizes of about 10 nm during annealing at temperatures above the crystallization temperature. The presence of small amounts of Cu helps increase the nucleation rate of the bcc phase while Nb retards the grain growth. These "Finemet" alloys provide low core losses (even lower than amorphous soft magnetic alloys such as Co-Fe-Si-B), exhibit saturation induction of about 1.2 T, and exhibit very good properties at high frequencies, comparable to the best Co-based amorphous alloys. These were first developed in Japan and have stimulated a large amount of research and development worldwide to optimize the magnetic properties. There has been relatively little work in the United States in this area, however.

While many of the soft magnetic properties of Finemet-type nanocrystalline alloys are superior, they exhibit lower saturation inductions than Fe-metalloid amorphous alloys, mainly because of the lower Fe content to attain amorphization and because of the addition of Nb and Cu (or other elements to control the nucleation and growth kinetics). In order to remedy this problem, another class of Fe-based nanocrystalline alloys was developed by Inoue and coworkers at Tohoku University (Makino et al. 1997), which is commercialized by Alps Electric Co., Ltd., of Nagaoka, Japan (see also the Tohoku University site report, Appendix D). These "Nanoperm" alloys are based on the Fe-Zr-B system; they contain larger concentrations of Fe (83-89 at.%) compared to the Finemet alloys (~ 74 at.% Fe) and have higher values of saturation induction (~ 1.6-1.7 T). The Nanoperm nc alloys have very low energy losses at power frequencies (60 Hz), making them potentially interesting for electrical power distribution transformers. The issues of composition modification, processing, and the brittle mechanical behavior of these nanocrystalline/amorphous alloys are discussed by V.R. Ramanan in the first volume of this WTEC study, the proceedings of the May 8-9, 1997 panel workshop on the status of nanostructure science and technology in the United States (Ramanan 1998, 113-116). Figure 6.3 compares the soft magnetic properties of Finemet, Nanoperm, and other materials.

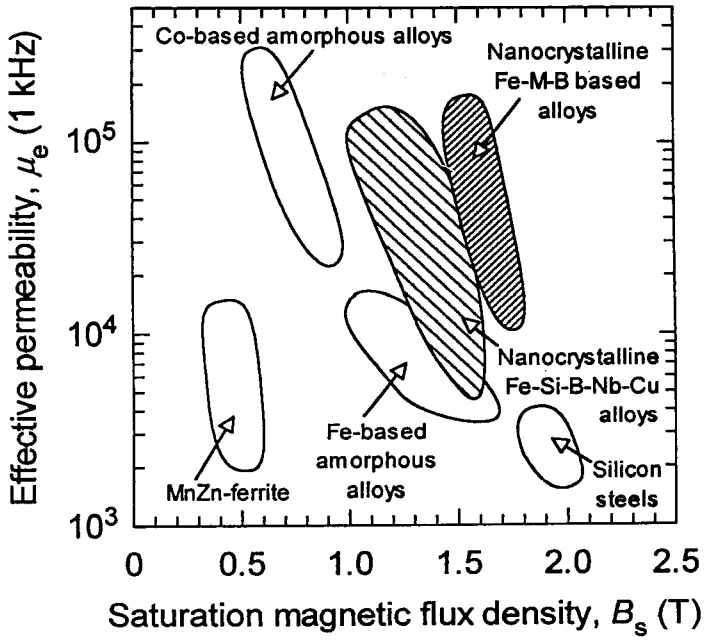


Figure 6.3. Effective permeability, μ_e, vs. saturation magnetic flux density, B_s, for soft ferromagnetic materials (after A. Inoue 1997).

While there has been extensive research on these alloys, particularly in Japan and Europe, most of the development has been carried out in Japan. The Finemet family of alloys is marketed by Hitachi Special Metals. Vacuumschmelze GmbH (Germany) and Impky (France) also market similar alloys. The Nanoperm alloys are being commercialized by Alps Electric Co. (Japan). No extensive research nor any commercialization of these materials has been carried out in the United States.

The small single-domain nanocrystalline Fe particles in the amorphous matrix gives these alloys their unique magnetic behavior, the most dramatic being the lowest energy losses (narrowest B/H hysteresis loop) of any known materials, along with very high permeabilities. These alloys can also exhibit nearly or exactly zero magnetostriction. To date, these materials have been made by crystallization of rapidly solidified amorphous ribbons. Other methods that might provide geometrically desirable products should be explored or developed. Electrodeposition is one such method that requires further work. Electrodeposited nc Fe-Ni soft magnetic alloys are being developed in Canada.

The brittle nature of these materials is a problem for scaleup and transformer manufacture. The brittleness problem must be solved by finding less brittle materials or applying the handling and processing knowledge that exists for embrittled (after annealing) metallic glasses.

Permanent Magnet Materials

The first attempts to produce nanoscale microstructures to enhance the magnetic properties of the Nb-Fe-B permanent magnetic materials used mechanical alloying of blended elemental powders followed by heat treatment (Schultz et al. 1987). Since the grain structure so obtained does not exhibit any crystallographic texture—and limits the energy product—special processing methods such as die-upsetting were used by Schultz and coworkers (1989) to provide the crystallographic anisotropy. While the coercivities of these nanocrystalline alloys are high, the remanent magnetization is decreased.

Recent approaches to increasing the magnetic induction have utilized exchange coupling in magnetically hard and soft phases. The Fe-rich compositions (e.g., $Fe_{90}Nd_7B_3$) result in a mixture of the hard $Fe_{14}Nd_2B$ phase and soft αFe phase. The nanoscale two-phase mixtures of a hard magnetic phase and a soft magnetic phase can exhibit values of remanent magnetization, M_r, significantly greater than the isotropic value of 0.5 M_s. This "remanence enhancement" is associated with exchange coupling between the hard and soft phases, which forces the magnetization vector of the soft phase to be rotated to that of the hard phase (Smith et al. 1996). Two important requirements for alloys to exhibit remanence enhancement are a nanocrystalline grain size and a degree of coherence across interphase boundaries sufficient to enable adjacent phases to be exchange-coupled. The significant feature of the exchange coupling is that it allows crystallographically isotropic materials to exhibit remanence values approaching those achieved after full alignment. Such two-phase nanoscale ferromagnetic alloys have been prepared by nonequilibrium methods such as melt-spinning, mechanical alloying, and sputter deposition. Besides the high reduced remanence, the material cost is reduced by reduction in the content of the expensive hard rare earth-containing magnetic phase.

The theoretical understanding of remanence enhancement appears to be developed to a degree enabling prediction of magnet performance; however, this performance, while a significant improvement over single-phase isotropic magnets, does not reach predicted values. Work is required on optimizing the orientation relationships between the hard and soft phases and the interphase properties (coherency) between them.

Research on nanocrystalline hard magnetic alloys has received attention worldwide. The U.S. efforts are summarized in the article by G.C. Hadjipanayis (1998, 107-112). While less research seems to be carried out in the world on these materials compared to the nanocrystalline soft magnetic alloys, some efforts exist in most countries. Notable programs are those of L. Schultz and coworkers at the Institut für Festköper und Werkstofforschung (IFW) in Dresden (see site report in Appendix B) and P.G. McCormick and coworkers at the University of Western Australia.

While the very low losses of the nc soft magnetic materials (Finemet or Nanoperm) are dependent on grain size for their properties, the hard magnetic nc alloys with remanence enhancement provide flexibility in processing, especially with powder materials. These remanence-enhanced nc hard magnetic alloys may find many applications as permanent magnet components.

Giant Magnetoresistance (GMR)

The phenomenon of giant magnetoresistance (GMR)—the decrease of electrical resistance of materials when exposed to a magnetic field—was first reported in a number of multilayer ferromagnetic/nonferromagnetic thin film systems (Baibich et al. 1988). More recently, GMR was observed in equiaxed granular nanocrystalline materials (Berkowitz et al. 1992). In particular, GMR systems with low saturation fields offer a wide area for application in magnetoresistive devices. GMR sensors have a higher output than conventional anisotropic magnetoresistive sensors or Hall effect sensors. They can operate at higher magnetic fields than conventional magnetoresistive sensors. In multilayer systems the antiferromagnetic alignment of the ferromagnetic layers in zero field becomes ferromagnetic as the field is applied and causes a decrease in resistance. Granular materials that show GMR consist of small ferromagnetic single-domain particles with randomly oriented magnetic axes in a nonmagnetic matrix. An external field rotates the magnetic axes of all magnetic particles. The rotation towards complete alignment of all magnetic axes again reduces the resistance in a similar way as for multilayers. The GMR in granular systems is isotropic. The explanation for the GMR is spin-dependent scattering of the conduction electrons at the ferromagnetic/nonmagnetic interfaces and, to a lesser extent, within the magnetic grains. The GMR scales inversely with the average particle diameter.

There is worldwide research on the GMR effect. U.S. programs are reviewed by R. Shull and G.C. Hadjipanayis in the proceedings of the WTEC U.S. nanotechnologies workshop (Shull 1998, 43-58; Hadjipanayis 1998, 107-112). The NIST work described by Shull has provided material with the largest GMR values for the smallest switching fields. Japanese research on GMR includes studies in Prof. Fujimori's group at Tohoku University (see site report in Appendix D).

While the theory for GMR of spin-dependent scattering referred to above has been used as an explanation, other explanations taking into account interaction between magnetic regions have been proposed (El-Hilo et al. 1994). Combined theoretical and experimental studies should help to clarify the mechanism for this effect.

Other Ferromagnetic Nanocrystalline Materials

Magnetic nanocomposite refrigerants, which have four times the magnetocaloric effects of the best low temperature magnetic refrigerant, were developed by NIST and described by R. Shull (1998, 43-58). The entropy change at a given (low) temperature for a system of magnetic spins is enhanced when the isolated spins are clustered. Shull et al. (1993) have shown that the nanocomposite $Gd_3Ga_{5-x}Fe_xO_{12}$ gives superior magnetocaloric effects, which increase with x up to $x = 2.5$ and can be extended to higher temperatures than conventional materials.

Magnetostrictive materials such as Terfonol-D ($Tb_{0.3}Dy_{0.7}Fe_2$) have been of scientific and technological interest in recent years. It is suggested by G.C. Hadjipanayis (1998, 107-112) that nanostructured magnetostrictive materials can have improved properties, such as lower saturation fields, with reduced anisotropy and in multilayers with alternate layers of magnetostrictive and soft magnetic materials that are exchange-coupled. Hadjipanayis states that most of the research in this area is carried out in Japan and Europe.

Opportunities and Challenges

Nanocrystalline magnetic materials offer perhaps the nearest-term prospect of significant applications of bulk nanostructured materials. The remanence enhancement in two-phase hard/soft magnetic materials can result in excellent energy products—comparable to those from rapid solidification processing routes—in powder composites. The flexibility in manufacturing this allows should provide many possible permanent magnet applications.

Nanocrystalline soft magnetic materials have the lowest energy losses of any material. While problems such as mechanical brittleness remain, these materials promise to replace existing transformer core materials for power applications. The U.S. research and industrial effort in these materials lags the efforts in Japan.

OTHER BULK APPLICATIONS OF NANOSTRUCTURED MATERIALS

Nanocrystalline Hydrogen Storage Materials

R.B. Schwarz (1998, 93-95) has pointed out that nanostructured materials offer several potential advantages for hydrogen storage materials. Rapid kinetics of absorption/desorption can be aided by refining the microstructure

to the nanoscale. For example, nanoscale inclusions of Mg_2Ni in Mg catalyze the decomposition of the molecular hydrogen, increasing the hydrogen absorption/desorption kinetics. Another advantage of the nanoscale microstructure is that the alloy powder does not comminute on repeated charging/discharging with hydrogen. This is not strictly a bulk material, since powder agglomerates or green compacts can be used, thus obviating the need for compaction to theoretical density.

Nanocrystalline Corrosion-Resistant Materials

The limited work to date on corrosion resistance of nanocrystalline materials indicates that no generalizations can be made. Superior localized corrosion resistance in HCl was observed for nanocrystalline 304 stainless steel (Fe–18%Cr–8%Ni) prepared by sputter deposition (Inturi and Szklavska-Smialowska 1991 and 1992). This was attributed to the fine grain size and homogeneity of the nc material. However, the average dissolution rate of nc Ni was found to be higher than that for coarse-grained material (Rofagha et al. 1991).

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Chapter 7

Biologically Related Aspects of Nanoparticles, Nanostructured Materials, and Nanodevices

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INTRODUCTION

Biological molecules and systems have a number of attributes that make them highly suitable for nanotechnology applications. For example, proteins fold into precisely defined three-dimensional shapes, and nucleic acids assemble according to well-understood rules. Antibodies are highly specific in recognizing and binding their ligands, and biological assemblies such as molecular motors can perform transport operations. Because of these and other favorable properties, biomolecules, biophysics, and biology are themes that run through all of the topics of this report.

Although very promising, the bio-related aspects of nanoparticles, nanostructured materials, and nanodevices, are, for the most part, not as well developed as the nonbiological ones. However, a number of recent workshops (e.g., the U.S./EC Workshop on Nanobiotechnology), symposia (e.g., the Conference on Molecular Nanotechnology, and the Symposium on Bio-Nano Electronics), and books (e.g., *Nanofabrication and Biosystem,s* Hoch et al. 1996) attest to the fact that many of the novel developments in this field are poised for rapid expansion.

This chapter is organized along the lines of the main report (Figure 7.1). It first puts into perspective current research directed toward biological synthesis and assembly as it pertains to the building blocks of nano-technology. It then focuses on the current state of the art in biological aspects of dispersions and coatings, high surface area materials, and functional

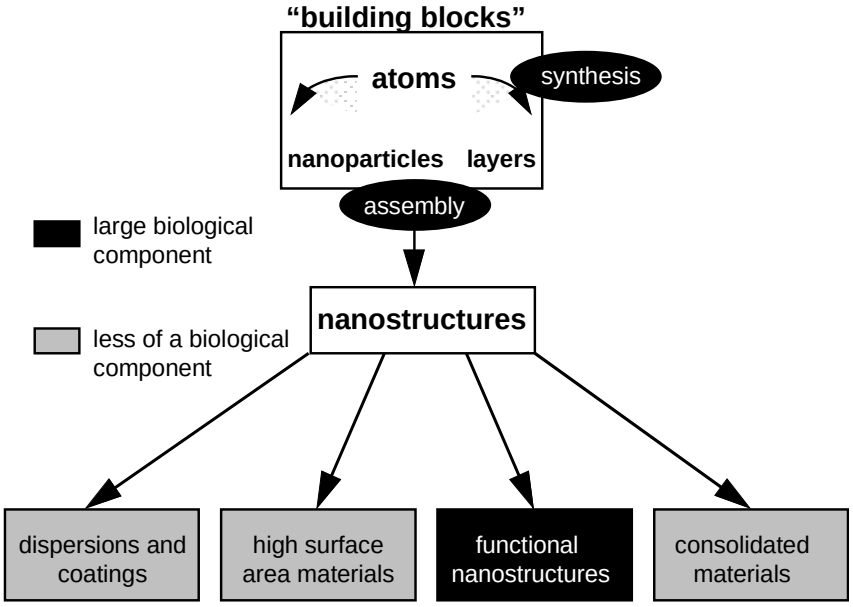


Figure 7.1. Organization of the WTEC study; sections with large biological content are indicated.

nanostructures. Finally, it ends with a section on the challenges and opportunities for the biological aspects of nanotechnology.

NANOTECHNOLOGY BUILDING BLOCKS

Synthesis

Although it seems at first that Nature has provided a limited number of basic building blocks—amino acids, lipids, and nucleic acids—the chemical diversity of these molecules and the different ways they can be polymerized or assembled provide an enormous range of possible structures. Furthermore, advances in chemical synthesis and biotechnology enable one to combine these building blocks, almost at will, to produce new materials and structures that have not yet been made in Nature. These self-assembled materials often have enhanced properties as well as unique applications.

The selected examples below show ways in which clever synthetic methodologies are being harnessed to provide novel biological building blocks for nanotechnology.

The protein polymers produced by Tirrell and coworkers (1994) are examples of this new methodology. In one set of experiments, proteins were

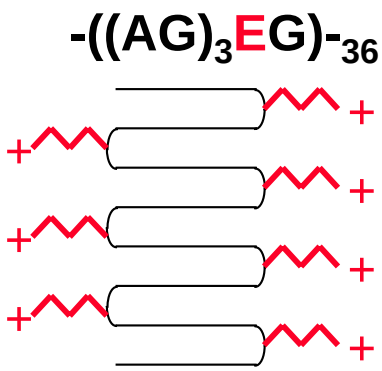


Figure 7.2. Top: a 36-mer protein polymer with the repeat sequence (ulanine-glycine)$_3$ – glutamic acid – glycine. Bottom: idealized folding of this protein polymer, where the glutamic acid sidechains (+) are on the surface of the folds.

designed from first principles to have folds in specific locations and surface-reactive groups in other places (Figure 7.2) (Krejchi et al. 1994; 1997). One of the target sequences was -((AG)$_3$EG)$_{-36}$. The hypothesis was that the AG regions would form hydrogen-bonded networks of beta sheets and that the glutamic acid would provide a functional group for surface modification. Synthetic DNAs coding for these proteins were produced, inserted into an *E. coli* expression system, and the desired proteins were produced and harvested. These biopolymers formed chain-folded lamellar crystals with the anticipated folds. In addition to serving as a source of totally new materials, this type of research also enables us to test our understanding of amino acid interactions and our ability to predict chain folding.

Biopolymers produced via biotechnology are monodisperse; that is, they have precisely defined and controlled chain lengths; on the other hand, it is virtually impossible to produce a monodisperse synthetic polymer. It has recently been shown that polymers with well-defined chain lengths can have unusual liquid crystalline properties. For example, Yu et al. (1997) have shown that bacterial methods for polymer synthesis can be used to produce poly(gamma-benzyl alpha L-glutamate) that exhibits smectic ordering in solution and in films. The distribution in chain length normally found for synthetic polymers makes it unusual to find them in smectic phases. This work is important in that it suggests that we now have a route to new smectic phases whose layer spacings can be controlled on the scale of tens of nanometers.

The biotechnology-based synthetic approaches described above generally require that the final product be made from the natural, or L-amino acids. Progress is now being made so that biological machinery (e.g., *E. coli*), can be co-opted to incorporate non-natural amino acids such as β-alanine or

dehydroproline or fluorotyrosine, or ones with alkene or alkyne functionality (Deming et al. 1997). Research along these lines opens new avenues for producing controlled-length polymers with controllable surface properties, as well as biosynthetic polymers that demonstrate electrical phenomena like conductivity. Such molecules could be used in nanotechnology applications.

Novel chemical synthesis methods are also being developed to produce "chimeric" molecules that contain organic turn units and hydrogen-bonding networks of amino acids (Winningham and Sogah 1997). Another approach includes incorporating all tools of chemistry into the synthesis of proteins, making it possible to produce, for example, mirror-image proteins. These proteins, by virtue of their D-amino acid composition, resist biodegradation and could have important pharmaceutical applications (Muir et al. 1997).

Arnold and coworkers are using a totally different approach to produce proteins with enhanced properties such as catalytic activity or binding affinity. Called "directed evolution," this method uses random mutagenesis and multiple generations to produce new proteins with enhanced properties. Directed evolution, which involves DNA shuffling, has been used to obtain esterases with five- to six-fold enhanced activity against *p*-nitrobenzyl esters (Moore et al. 1997).

Assembly

The ability of biological molecules to undergo highly controlled and hierarchical assembly makes them ideal for applications in nanotechnology. The self-assembly hierarchy of biological materials begins with monomer molecules (e.g., nucleotides and nucleosides, amino acids, lipids), which form polymers (e.g., DNA, RNA, proteins, polysaccharides), then assemblies (e.g., membranes, organelles), and finally cells, organs, organisms, and even populations (Rousseau and Jelinski 1991, 571-608). Consequently, biological materials assembly on a very broad range of organizational length scales, and in both hierarchical and nested manners (Aksay et al. 1996; Aksay 1998). Research frontiers that exploit the capacity of biomolecules and cellular systems to undergo self-assembly have been identified in two recent National Research Council reports (NRC 1994 and 1996). Examples of self-assembled systems include monolayers and multilayers, biocompatible layers, decorated membranes, organized structures such as microtubules and biomineralization, and the intracellular assembly of CdSe semiconductors and chains of magnetite.

A number of researchers have been exploiting the predictable base-pairing of DNA to build molecular-sized, complex, three-dimensional objects. For example, Seeman and coworkers (Seeman 1998) have been investigating these properties of DNA molecules with the goal of forming complex 2-D and 3-D periodic structures with defined topologies. DNA is

ideal for building molecular nanotechnology objects, as it offers synthetic control, predictability of interactions, and well-controlled "sticky ends" that assemble in highly specific fashion. Furthermore, the existence of stable branched DNA molecules permits complex and interlocking shapes to be formed. Using such technology, a number of topologies have been prepared, including cubes (Chen and Seeman 1991), truncated octahedra (Figure 7.3) (Zhang and Seeman 1994), and Borromean rings (Mao et al. 1997).

Other researchers are using the capacity of DNA to self-organize to develop photonic array devices and other molecular photonic components (Sosnowski et al. 1997). This approach uses DNA-derived structures and a microelectronic template device that produces controlled electric fields. The electric fields regulate transport, hybridization, and denaturation of oligonucleotides. Because these electric fields direct the assembly and transport of the devices on the template surface, this method offers a versatile way to control assembly.

There is a large body of literature on the self-assembly on monolayers of lipid and lipid-like molecules (Allara 1996, 97-102; Bishop and Nuzzo 1996). Devices using self-assembled monolayers are now available for analyzing the binding of biological molecules, as well as for spatially tailoring the

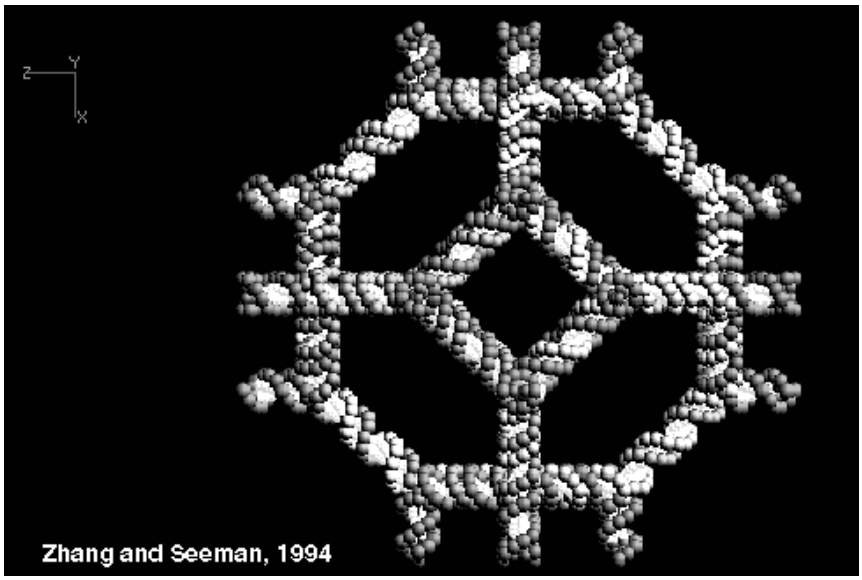


Figure 7.3. Idealized truncated octahedron assembled from DNA. This view is down the four-fold axis of the squares. Each edge of the octahedron contains two double-helical turns of DNA.

surface activity. The technology to make self-assembled monolayers (SAMs) is now so well developed that it should be possible to use them for complex electronic structures and molecular-scale devices.

Research stemming from the study of SAMs (e.g., alkylthiols and other biomembrane mimics on gold) led to the discovery of "stamping" (Figure 7.4) (Kumar and Whitesides 1993). This method, in which an elastomeric stamp is used for rapid pattern transfer, has now been driven to < 50 nanometer scales and extended to nonflat surfaces. It is also called "soft lithography" and offers exciting possibilities for producing devices with unusual shapes or geometries.

Self-assembled organic materials such as proteins and/or lipids can be used to form the scaffolding for the deposition of inorganic material to form ceramics such as hydroxyapatite, calcium carbonate, silicon dioxide, and iron oxide. Although the formation of special ceramics is bio-inspired, the organic material need not be of biological origin. An example is production of template-assisted nanostructured ceramic thin films (Aksay et al. 1996).

A particularly interesting example of bio-inspired self-assembly has been described in a recent article by Stupp and coworkers (Stupp et al. 1997). This work, in which organic "rod-coil" molecules were induced to self-assemble, is significant in that the molecules orient themselves and self-assemble over a wide range of length scales, including mushroom-shaped clusters (Figure 7.5); sheets of the clusters packed side-by-side; and thick films, where the sheets pack in a head-to-tail fashion. The interplay between hydrophobic and hydrophilic forces is thought to be partially responsible for the controlled assembly.

DISPERSIONS AND COATINGS

Drug Delivery Systems

Nanoparticles and nanospheres have considerable utility as controlled drug delivery systems (Hanes et al. 1997). When suitably encapsulated, a pharmaceutical can be delivered to the appropriate site, its concentration can be maintained at proper levels for long periods of time, and it can be prevented from undergoing premature degradation (see Chapter 3). Nanoparticles (as opposed to micron-sized particles) have the advantage that they are small enough that they can be injected into the circulatory system.

Highly porous materials are also ideal candidates for controlled drug delivery (Schnur et al. 1994) and for tissue engineering (Hubbell and Langer 1995). An example of a controlled drug delivery system comes from the area of microtubules. Phospholipid bilayers can self-assemble into long cylindrical tubes with diameters usually below a micron and lengths up to hundreds of microns (Schnur 1993). During synthesis, drugs can be entrained

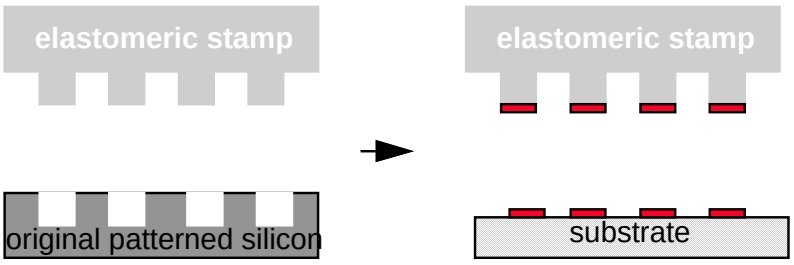


Figure 7.4. An elastomeric stamp (top left) is made from an original master (bottom left). The stamp is dipped into the biological material (top right) and the pattern is transferred to the substrate (bottom right).

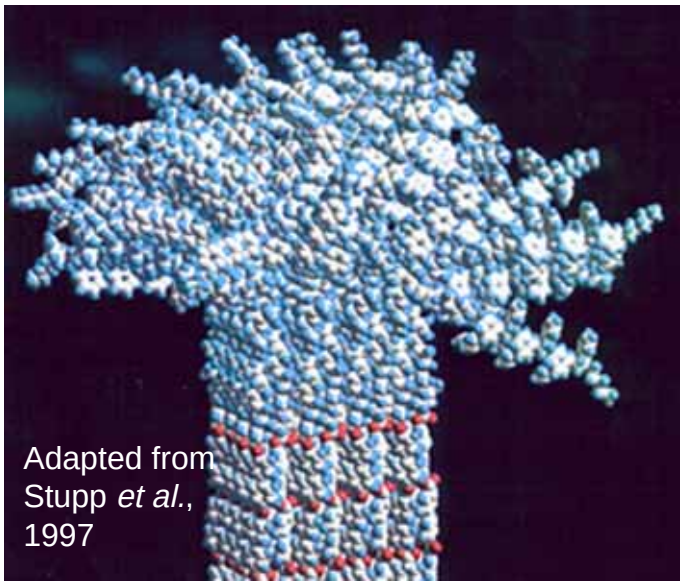


Figure 7.5. Mushroom-shaped clusters formed from self-assembly of rod-coil molecules; these clusters can undergo further packing to form sheets.

in these nanotubes, and the final product can be used as a controlled delivery system. Tubules prepared from phospholipid bilayers are ideal for such applications because they are biocompatible.

Dendrimers can be prepared so they are of discrete size and contain specific functional groups (Karak and Maiti 1997). They can be functionalized and used in biomedicine. Examples include gene transfer agents for gene therapy, made to carry and control the relaxivity of paramagnetic MRI (magnetic resonance imaging) contrast agents (Toth et al. 1996), and to deliver drugs on a controlled release basis.

Role of Nanoparticles in Health and Pollution

Although beyond the scope of this review, it is important to keep in mind the potential role of atmospheric nanoparticles in photocatalytic and thermal production of atmospheric pollutants. Atmospheric aerosols in heavily polluted areas have the potential to accelerate ozone formation reactions. Furthermore, because they are respirable, they could represent a health hazard. Two controversial studies (the Harvard University six-city study and the American Cancer Society study) have linked the presence of fine particular matter to premature mortality (*Chemical and Engineering News* 1997).

Atmospheric aerosols generally contain two major components: one is composed of amorphous carbon that has fullerene-like particles dispersed in it; the second is inorganic and consists of oxides and sulfides supported on clay minerals. In particular, the iron oxide, manganese oxide, and iron sulfide nanoparticles have band-gaps that could enhance the photocatalytic adsorption of solar radiation. In addition, these materials are acidic and may be coated with water, which would enhance their catalytic ability to crack hydrocarbons and create free radicals (Chianelli 1998). At present this is an underexplored area of research that bears scrutiny.

It is interesting to note that some microorganisms produce and sequester CdSe and CdS nanoparticles in response to high levels of toxic Cd^{++} in their environment (Brus 1996). A large number of organisms also have the ability to precipitate ferrimagnetic minerals Fe_3O_4 and Fe_3S_4 (see Consolidated Materials, below).

HIGH SURFACE AREA MATERIALS

Membranes for Biological Separations

Supported polymeric membranes can be used to remove low molecular weight organics from aqueous solution (Ho et al. 1996). They work by filling the pores of microfiltration or ultrafiltration membranes with functional, polymeric, or oligomeric liquids that have an affinity for the compound of interest. These ideas can be extended to microemulsions and used for separations of large biological molecules. For example, non-ionic microemulsions (i.e., oil-water systems) have been used for hemoglobin extraction. These results augur well for the separation of other biological materials (Qutubuddin et al. 1994). Molecular imprinting can also be used to produce high surface area adsorbents that are enantioselective for amino acids and other biological molecules (Vidyasankar et al. 1997).

Bacterial Cell Surface Layers as Patterning Elements

Crystalline bacterial cell surface layers (S-layers) are composed of repeating protein units. These layers self-assemble and have a high binding capacity. They have been explored as patterning elements for molecular nanotechnology. For example, they have been used to pattern cadmium sulfide superlattices (Shenton et al. 1997).

FUNCTIONAL NANOSTRUCTURES

Molecular Computation

The smallest possible computer would ideally be able to perform computations on a molecular scale. Even though the computation may be carried out on that scale, the issue becomes one of having enough molecules to obtain sufficient signal-to-noise ratio to read out the answer. Consequently, at least at present, these computations must be carried out in bulk or with extremes in temperature. There has been a recent development along this line. Adleman (1994) has shown how the rules of DNA self-assembly, coupled with polymerase chain reaction (PCR) amplification of DNA, can lead to a molecular computer of sorts. The system was used to solve the Hamiltonian path problem, a classic and difficult (NP complete) mathematical problem that involves finding a path between vertices of a graph. The starting and ending vertices of each edge of the graph were encoded as the first and second halves of a strand of DNA. A solution to the problem (what is the path between two specific vertices?) was obtained by using PCR primers for the two vertices. Others have extended these ideas and shown that it is possible to make DNA add (Guarnieri et al. 1996). Although these are exciting demonstrations, at present this technology has a number of drawbacks, including the labor and time it takes to analyze the results of the computation, and the uncertainties associated with wet chemistry.

Optoelectronic Devices

Biological molecules and assemblies, such as the photochemical reaction center, are capable of capturing light with good quantum efficiency and transforming it into chemical energy. If properly exploited, such assemblies have potential applications as biomolecule information processing units.

Bacteriorhodopsin, from the purple membrane bacterium *Halobacterium halobium*, is one such system that has been studied extensively and has been

commercialized into optical holographic memories (Birge 1995). In the bacterium, the protein bacteriorhodopsin self-assembles into ordered lipid patches. The protein absorbs light and undergoes a cycle involving a complex series of intermediates, resulting in a proton being pumped across the membrane. It was information developed from understanding the basic science behind the way that bacteriorhodopsin works that led to the use of bacteriorhodopsin as a biomolecule information processing unit. To be used for information storage, the protein is placed under nonbiological conditions. It is dispersed and immobilized into a matrix (e.g., collagen or another polymeric substance) and held at liquid nitrogen temperatures. At this low temperature, the protein acts as an optically-driven bistable switch. One form, the light-adapted form of bacteriorhodopsin, absorbs light at 570 nm. When irradiated with green light at 77 K, it switches to a different stable form that absorbs at 630 nm. Using light of different colors enables one to read and write images onto these memories. By subtracting one memory from the other, these memories are especially useful for realtime, rapid comparison of images.

Molecular Motors

The molecular motors found in biology provide for bacterial locomotion, as well as for the active transport and delivery of molecules. For example, the bacterial flagellar motor is about 20 nm in diameter, and is comprised of a complex assembly of more than 10 different proteins (Imae and Atsumi 1989). The role of the motor is to rotate the helical flagella of the bacterium so that it is able to swim. Chemical energy (in this case protons or sodium) is transduced into mechanical energy.

Other examples of molecular motors include RNA polymerase (Yin et al. 1995), F_1-ATPase (Noji et al. 1997), myosin, and kinesin (Seventh Biophysical Discussions 1995). The fuel that powers these motors is ATP (adenosine triphosphate). A number of researchers have proposed schemes by which such motors could be used to deliver molecules, one at a time, for the purpose of the ground-up assembly of nanoscale devices (NRC 1996). It is envisioned that the highways could be actin or tubulin, which would need to be immobilized onto a surface. Myosin or kinesin, which naturally travel along these highways, could be used to deliver molecular “packages” to a specific assembly site.

Other Forms of Biological Transport Using Nanoparticles

In the human body, the function of the high density lipoproteins is to transport cholesterol. The ~ 7.5 nm discoidal lipoprotein assemblies are sandwiched between discs of phospholipids and stacked, poker-chip style.

The lipoproteins stabilize the cholesterol particles and assist in their transport. Current research involves manipulating and fusing the assemblies and particles with an atomic force microscope (ATM) tip (Sligar 1998).

Bioelectronics

There has been considerable research activity in molecular electronics and bioelectronics, particularly in Japan (Aizawa 1994). Although this area of nanotechnology is still not as well developed as others in this report, it bears watching. For example, Shionoya and coworkers at the Institute for Molecular Science of the Okazaki National Research Institutes in Japan (see site report, Appendix D) have proposed that novel combinations of DNA, metal ligands, DNA templating, and proteins could produce molecular wires; molecular hoops through which DNA could be threaded; and double-stranded peptides whose helix pitch could be controlled by an entrained metal (Figure 7.6). The active site containing the metal could be induced to go from $Cu(I)_{tetrahedral}$ to $CU(II)_{square\ planar}$, perhaps by electrons delivered by a scanning tunneling microscope (STM) tip.

CONSOLIDATED MATERIALS

Ceramics

Biomolecule/inorganic interactions can be used to produce ceramics with increased toughness. Fundamental studies of biomineralization, in which an organic substance (usually protein or peptide or lipid) interacts with an inorganic phase (e.g., calcium carbonate or hydroxyapatite) have led to the bioinspired synthesis of composite materials.

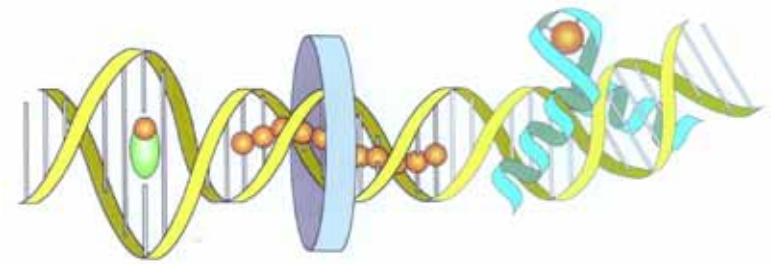


Figure 7.6. Novel combinations of DNA, metal ligands, DNA templating, and proteins are being investigated for molecular wires, inductors, and switches (photo courtesy of Shionoya and coworkers, Inst. for Molecular Science).

The structure and porosity of the inorganic phase can be controlled by templating with an organic surfactant, vesicular arrays, or liquid crystalline materials. Micelle-templated synthesis can produce ceramics with 20-100 Å pore dimensions (Ying 1998). These tailored pores can be used as catalysts and absorbents, and for gas/liquid separations and thermal and acoustic insulation. Their selectivity makes them very useful for biochemical and pharmaceutical separations. Bioceramics can also be made that are more compatible with teeth and bone.

An interesting example of an organic/inorganic composite is the new packaging material that has been developed to replace the polystyrene "clam-shell" for fast food products. Composed of potato starch and calcium carbonate, this foam combines the advantages of good thermal insulation properties and light weight with biodegradability (Stucky 1978).

Biological Bar Magnets

It has been well documented that a very large number of organisms have the ability to precipitate ferrimagnetic minerals such as Fe_3O_4 and Fe_3S_4. In addition, linear chains of membrane-bound crystals of magnetite, called magnetosomes, have been found in microorganisms and fish (Kirschvink et al. 1992). For example, the Fe_3O_4 domain size in the organism *A. magnetotactum* is about 500 Å, and a chain of 22 of those domains has a magnetic moment of 1.3×10^{-15}. It is not immediately clear how these particles could be exploited for nonbiological applications.

OPPORTUNITIES AND CHALLENGES

This section of the review describes current limits on the biological aspects of nanotechnology. It outlines selected broad areas of research opportunity, and it sets forth challenges for the intermediate and long-term future.

Enabling Technologies

We owe much of the recent progress in the biological aspects of nanotechnology and nanoparticles to important enabling technologies. Many of these enabling technologies are described in other parts of this report. Those that have had a significant impact on biological measurements include techniques and instrumentation such as optical traps, laser tweezers, and "nano-pokers" to measure femtoNewton forces (Svoboda and Block 1994), and AFM and STM (Wildoer et al. 1998).

There is also a need to move detection away from the ensemble, to the single molecule scale. This includes driving instrumentation toward single-molecule spectroscopy; single-spin detection (Rugar et al. 1994); chemical analysis of nanoliter volumes (Hietpas et al. 1996, 139-158); nuclear magnetic resonance microcoils; nanoscale electrode arrays and chemical sensing and detecting technology (McConnell 1996, 97-102); separations technology; chemical analysis of single cells (Hietpas et al. 1996); new biological transformations; and chemical probes of nanostructures.

Enhanced computational infrastructure, both hardware and algorithm development, will also be required to investigate supramolecular assemblies and to understand interactions that occur over a wide variety of time and length scales. At present, we are fairly well equipped to handle quantum mechanical calculations. At the next level of computational complexity, the molecular dynamics force fields and atomic charges can presently handle up to about a million particles and still retain their accuracy. The next scale of complexity, mesoscale modeling, currently requires the use of pseudo atoms. Much more research is required to improve the accuracy of finite element calculations and the modeling of materials applications (Goddard 1998).

Surface Interactions and the Interface Between Biomolecules and Substrates

Much of the progress in the biological aspects of nanotechnology has come from research on surface interactions. It will be important to continue to develop a better understanding of the interface between biomolecules and surfaces. Of particular interest are questions about whether surfaces cause biomolecules to denature, the optimum length of linker groups, and ways to communicate from the biomolecule, through the linker, to the substrate. Another challenge is to produce nanometer ultrathin films that have stable order (Jaworek et al. 1998).

Robustness of Biomolecules and Their Interactions in Aqueous Solution

Although much progress has been made on ways to confer additional robustness on biomolecules, it will be necessary to continue to improve the stability and reliability of biomolecular assemblies. Such research may be along the lines of understanding the thermal stability of biomolecules, perhaps by examining extremophiles and molecules produced by directed evolution. It will also be necessary to produce molecules that can work in the absence of water, or to devise ways in which aqueous solutions can be used reliably.

Assemblers or Templating

The hierarchical self-assembly of biomolecules is often touted as one of their key attributes for nanotechnology applications. However, there remains much to be learned about how to make periodic arrays of biomolecular assemblies, how to use biological templating in an efficient manner, how to mimic biological self-assembly with nonbiological molecules, and how to exploit differences between biological and nonbiological self-assembly.

Combinatorial Approaches to Nanotechnology

Combinatorial chemistry has had an enormous impact on drug discovery and development in the past several years. Ability to develop molecularly sensitive screening techniques is one of the limiting factors of combinatorial chemistry. It would be intriguing to discover screening methods that are particularly sensitive for picking up new phenomena exhibited by biological nanoparticles.

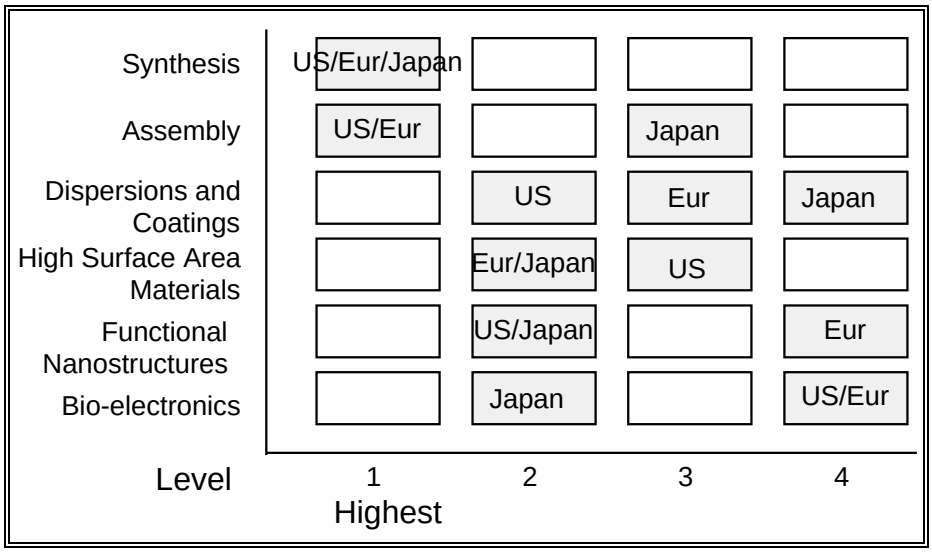
Biomimetics and Polymer-Biopolymer Chimeras

The largest impact of biological sciences on nanotechnology may prove to be through the lessons one can learn from biology, rather than from directly employing the biological molecules themselves. To this end, it is important to support research on various aspects of biomimetics, including activities in which synthetic and biologically-based molecules are combined in chimeric fashion.

TECHNOLOGICAL COMPARISONS

Table 7.1 makes subjective comparisons, weighted by level of effort, impact of research, etc., between the state of biology-related nanotechnology work in Japan, Europe, and the United States.

TABLE 7.1. Comparisons Between Japan, Europe, and the United States in Biologically Related Aspects of Nanotechnology



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Chapter 8

Research Programs on Nanotechnology in the World
(Americas, Asia/Pacific, and Europe)

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INTRODUCTION

Scientific breakthroughs combined with recent research programs in the United States, Japan, and Europe, and various initiatives in Australia, Canada, China, Korea, Singapore, and Taiwan highlight the international interest in nanoscale science and technology. Definitions of nanotechnology vary somewhat from country to country. Nanotechnology as defined for the projects reviewed in this chapter arises from the exploitation of the novel and improved physical, chemical, mechanical, and biological properties, phenomena, and processes of systems that are intermediate in size between isolated atoms/molecules and bulk materials, where phenomena length and time scales become comparable to those of the structure. It implies the ability to generate and utilize structures, components, and devices with a size range from about 0.1 nm (atomic and molecular scale) to about 100 nm (or larger in some situations) by control at atomic, molecular, and macromolecular levels. Novel properties occur compared to bulk behavior because of the small structure size and short time scale of various processes. Nanotechnology's size range and particularly its new phenomena set it apart from the technologies referred to as microelectromechanical systems (MEMS) in the United States or microsystems technologies (MST) in Europe.

[1] Opinions expressed here are those of the author and do not necessarily reflect the position of the National Science Foundation.

It is estimated that nanotechnology is presently at a level of development similar to that of computer/information technology in the 1950s. As indicated in the preceding chapters and as evidenced by the WTEC panel's research and observations during the course of this study, the development of nanoscale science and technology is expected by most scientists working in the field to have a broad and fundamental effect on many other technologies. This helps to explain the phenomenal levels of R&D activity worldwide. This chapter presents an overview of most of the significant nanotechnology research programs in the world. Where possible, a general picture is given of the funding levels of the programs, based on site interviews and publications.

AMERICAS

Aspects of nanoscience are taught and researched in the physics, chemistry, and biology departments of research universities throughout the American continents. However, significant activities in nanotechnology, including production and application of nanostructures, have been limited essentially to the United States and Canada.

The United States[2]

Various U.S. public and private funding agencies; large companies in chemical, computer, pharmaceutical, and other areas; as well as small and medium-size enterprises provide support for precompetitive research programs on nanotechnology. Most of the supported programs are evolving out of disciplinary research programs, and only some are identified as primarily dealing with nanotechnology. U.S. government agencies sponsored basic research in this area at a level estimated at about $116 million in 1997 (Siegel et al. 1998), as shown in Table 8.1. The National Science Foundation (NSF) has the largest share of the U.S. government investment, with an expenditure of about $65 million per year, or about 2.4% of its overall research investment in 1997. In 1998 it expanded its research support to functional nanostructures with an initiative in excess of $13 million.

[2] For a more in-depth look at the state of nanoscale science and engineering R&D in the United States, see Siegel et al. 1998.

TABLE 8.1. Support for Nanotechnology Research from U.S. Federal Agencies in 1997

Agency	Nanotechnology Research ($M)
National Science Foundation (NSF)	65
Defense Advanced Research Projects Agency (DARPA)	10
Army Research Office (ARO)	15
Office of Naval Research (ONR)	3
Air Force Office of Scientific Research (AFOSR)	4
Department of Energy (DOE)	7
National Institutes of Health (NIH)	5
National Institute of Standards and Technology (NIST)	4
National Aeronautics and Space Administration (NASA)	3
Total	116

NSF activities in nanotechnology include research supported by the Advanced Materials and Processing Program; the Ultrafine Particle Engineering initiative dedicated to new concepts and fundamental research to generate nanoparticles at high rates; the National Nanofabrication User Network (NNUN); and Instrument Development for Nano-Science and Engineering (NANO-95) to advance atomic-scale measurements of molecules, clusters, nanoparticles, and nanostructured materials. A current activity is the initiative, Synthesis, Processing, and Utilization of Functional Nanostructures (NSF 98-20 1997).

In the United States, a number of large multinational corporations, small enterprises, and consortia are pursuing nanotechnology-related research and development activities. Dow, DuPont, Eastman Kodak, Hewlett-Packard (HP), Hughes Electronics, Lucent, Motorola, Texas Instruments, Xerox, and other multinationals have established specialized groups in their long-term research laboratories, where the total research expenditure for nanotechnology research is estimated to be comparable to the U.S. government funding. Computer and electronics companies allocate up to half of their long-term research resources to nanotechnology programs. HP spends 50% of long-term (over 5 years) research on nanotechnology (Williams 1998). Small business enterprises, such as Aerochem Research Laboratory, Nanodyne, Michigan Molecular Institute, and Particle Technology, Inc., have generated an innovative competitive environment in various technological areas, including dispersions, coatings, structural materials, filtration, nanoparticle manufacturing processes, and functional nanostructures (sensors, electronic devices, etc.). Small niches in the market as well as support from several U.S. government agencies through the Small Business for Innovative Research (SBIR) program have provided the nuclei

for high-tech enterprises. The university-small business technology transfer (STTR) program at NSF is dedicated to nanotechnology in fiscal year 1999. Two semiconductor processing consortia, the Semiconductor Manufacturing and Technology Institute (Sematech) and the Semiconductor Research Corporation (SRC), are developing significant research activities on functional nanostructures on inorganic surfaces.

A series of interdisciplinary centers with nanotechnology activities has been established in the last few years at many U.S. universities, creating a growing public research and education infrastructure for this field. Examples of such centers are

- Brown University, Material Research Science and Engineering Center
- Rice University, Richard Smalley's Center for Nanoscale Science and Technology (CNST)
- University of California–Berkeley, nanoelectronics facilities
- University of Illinois at Urbana, the Engineering Research Center on Microelectronics in collaboration with the Beckman Institute, a private foundation
- University of North Carolina
- University of Texas–Austin
- Rensselaer Polytechnic Institute
- University of Washington (focus on nanobiotechnology)
- University of Wisconsin at Madison (focus on nanostructured materials)

NNUN, mentioned above, is an interuniversity effort supported by NSF at five universities: Cornell, Stanford, University of California–Santa Barbara (UCSB), Penn State, and Howard. It has focused on nanoelectronics, optoelectronics, electromechanical systems, and biotechnology. The Center for Quantized Electronic Structures (QUEST) at UCSB is a national facility developing expertise on underlying physics and chemistry aspects. Hundreds of graduate students have completed their education in connection with these centers in the last few years.

Current interest in nanotechnology in the United States is broad-based and generally spread into small groups. The research themes receiving the most attention include

1. metallic and ceramic nanostructured materials with engineered properties
2. molecular manipulation of polymeric macromolecules
3. chemistry self-assembling techniques of "soft" nanostructures
4. thermal spray processing and chemistry-based techniques for nanostructured coatings
5. nanofabrication of electronic products and sensors
6. nanostructured materials for energy-related processes such as catalysts and soft magnets

7. nanomachining
8. miniaturization of spacecraft systems

In addition, neural communication and chip technologies are being investigated for biochemical applications; metrology has been developed for thermal and mechanical properties, magnetism, micromagnetic modeling, and thermodynamics of nanostructures; modeling at the atomistic level has been established as a computational tool; and nanoprobes have been constructed to study material structures and devices with nanometer length scale accuracy and picosecond time resolution. While generation of nanostructures under controlled conditions by building up from atoms and molecules is the most promising approach, materials restructuring and scaling-down approaches will continue. Exploratory research includes tools of quantum control and atom manipulation, computer design of hierarchically structured materials (e.g., Olson 1997), artificially structured molecules, combination of organic and inorganic nanostructures, biomimetics, nanoscale robotics, encoding and utilization of information by biological structures, DNA computing, interacting textiles, and chemical and bioagent detectors.

Commercially viable technologies are already in place in the United States for some ceramic, metallic, and polymeric nanoparticles, nanostructured alloys, colorants and cosmetics, electronic components such as those for media recording, and hard-disk reading, to name a few. The time interval from discovery to technological application varies greatly. For instance, it took several years from the basic research discovery of the giant magnetoresistance (GMR) phenomenon in nanocrystalline materials (Berkowitz et al. 1992) to industry domination by the corresponding technology by 1997. GMR technology has now completely replaced the old technologies for computer disk heads, the critical components in hard disk drives, for which there is a $20+ billion market (Williams 1998). All disk heads currently manufactured by IBM and HP are based on this discovery. In another example, nanolayers with selective optical barriers are used at Kodak in more than 90% of graphics black and white film (Mendel 1997) and for various optical and infrared filters, which constitute a multibillion-dollar business. Other current applications of nanotechnology are hard coatings, chemical and biodetectors, drug delivery systems via nanoparticles, chemical-mechanical polishing with nanoparticle slurries in the electronics industry, and advanced laser technology. Several nanoparticle synthesis processes developed their scientific bases decades ago, but most processes are still developing their scientific bases (Roco 1998). Most of the technology base development for nanoparticle work is in an embryonic phase, and industry alone cannot sustain the research effort required for establishing the scientific and technological infrastructure. This is the role

of government (e.g., NSF and NIH) and private agency (e.g., Beckman Institute) support for fundamental research.

Nanotechnology research in the United States has been developed in open competition with other research topics within various disciplines. This is one of the reasons that the U.S. research efforts in nanotechnology are relatively fragmented and partially overlapping among disciplines, areas of relevance, and sources of funding. This situation has advantages in establishing competitive paths in the emerging nanotechnology field and in promoting innovative ideas; it also has some disadvantages for developing system applications. An interagency coordinating "Group on Nanotechnology" targets some improvement of the current situation. The group was established in 1997 with participants from twelve government funding/research agencies to enhance communication and develop partnerships among practicing nanoscience professionals.

Canada

Canada's National Research Council supports nanotechnology through the Institute for Microstructural Science, which has the mission to interact with industry and universities to develop the infrastructure for information technology. The main project, the Semiconductor Nanostructure Project, was initiated in 1990. It provides support for fundamental research at a series of universities, including Queen's, Carleton, and Ottawa Universities.

ASIA/PACIFIC

There are significant research programs on nanotechnology in Japan, as well as in China, Taiwan, South Korea, and Singapore.

Japan

The term "nanotechnology" is frequently used in Japan specifically to describe the construction of nanostructures on semiconductors/inorganic substrates for future electronic and computer technologies, and to describe the development of equipment for measurement at nanometer level (Sienko 1998). There are, however, Japanese programs in a number of other areas related to nanotechnology in the broader definition used in this report.

Government agencies and large corporations are the main sources of funding for nanotechnology in Japan; small and medium-size companies play only a minor role. Research activities are generally grouped in relatively large industrial, government, and academic laboratories. The three

main government organizations sponsoring nanotechnology in Japan are the Ministry of International Trade and Industry (MITI), the Science and Technology Agency (STA), and Monbusho (the Ministry of Education, Science, Sports, and Culture). Funding for nanotechnology research should be viewed in the context of an overall increased level of support for basic research in Japan since 1995 as a result of Japan's Science and Technology Basic Law No. 130 (effective November 15, 1995), even if the law has not been fully implemented. The data presented below are based on information received from Japanese colleagues during the WTEC visit in July 1997 (see site reports in Appendix D). All budgets are for the fiscal year 1996 (1 April 1996 to 31 March 1997) and assume an exchange rate of ¥115 = $1, unless otherwise stated. The first five-year program on ultrafine particles started in 1981 under the Exploratory Research for Advanced Technologies (ERATO) program; an overview of the results of that program was published in 1991 (Uyeda 1991).

It is estimated that the Agency of Industrial Science and Technology (AIST) within MITI had a budget of approximately $60 million per year for nanotechnology in 1996/97 (roughly 2.2% of the AIST budget). The National Institute for Advancement of Interdisciplinary Research (NAIR) hosts three AIST projects:

1. Joint Research Center for Atom Technology (JRCAT), with a ten-year budget of about $220 million for 1992-2001 ($25 million per year in 1996)
2. Research on Cluster Science program, with about $10 million for the interval 1992-1997
3. Research on Bionic Design program, with $10 million for 1992-1997, about half on nanotechnology

Other efforts supported to various degrees by MITI include the following:

- the Electrotechnical Laboratory in Tsukuba, which allocates about 17% (or $17 million per year) of its efforts on advanced nanotechnology projects
- the Quantum Functional Devices Program, funded at about $64 million for 1991-2001 (about $6.4 million in 1996)
- the Osaka National Research Institute and the National Industrial Research Institute of Nagoya, which each spend in the range of $2.5-3 million per year for nanotechnology
- the Association of Super-Advanced Electronics Technologies (ASET), a relatively new MITI-sponsored consortium with partial interest in nanotechnology; it has similarities with the U.S. Ultra Electronics program of DARPA

It is estimated that STA investment in nanotechnology research was about $35 million in 1996, mainly within five organizations:

1. Institute of Physical and Chemical Research (RIKEN), where nanotechnology is included in the Frontier Materials Research initiative
2. National Research Institute for Metals (NRIM)
3. National Institute for Research in Inorganic Materials (NIRIM)
4. Japan Science and Technology Corporation (JST—formerly called JRDC), which manages the ERATO program, including four nanotechnology-related projects, each with total budgets of $13-18 million for five years:
   - Quantum Wave Project (1988-1993)
   - Atomcraft Project (1989-1994)
   - Electron Wavefront Project (1989-1994)
   - Quantum Fluctuation Project (1993-1998)

Monbusho supports nanotechnology programs at universities and national research institutes, as well as via the Japan Society for Promotion of Science (JSPS). The most active programs are those at Tokyo University, Kyoto University, Tokyo Institute of Technology, Tohoku University, and Osaka University (see Appendix D). The Institute of Molecular Science and the Exploratory Research on Novel Artificial Materials and Substances program promote new research ideas for next-generation industries (5-year university-industry research projects). The "Research for the Future" initiative sponsored by JSPS has a program on "nanostructurally controlled spin-dependent quantum effects" (1996-2001) at Tohoku University. Monbusho's funding contribution to nanotechnology programs is estimated at ~ $25 million.

In total, MITI, STA, and Monbusho allocated ~ $120 million for nanotechnology in 1996.

Large companies also drive nanotechnology research in Japan. Important research efforts are at six institutions: Hitachi (Central R&D Laboratories, where nanotechnology is ~ 25% of long-term research)—Hitachi has ~ $70 billion per year in sales (see site report in Appendix D); NEC (Fundamental Research Laboratories, where nanotechnology is estimated to be ~ 50% of the precompetitive research)—NEC has ~ $40 billion per year in sales (see site report in Appendix D); NTT (Atsugi Lab); Fujitsu (Quantum Electron Devices Lab); Sony; and Fuji Photo Film Co.

An allocation of 10% of sales for research and development is customary in these companies, with ~ 10% of this for long-term research. Some Japanese nanostructured products already have considerable market impact. Nihon Shinku Gijutsu (ULVAC) produces over $4 million per year in sales of particles for electronics, optics, and arts. Also, there are in Japan, as in

the United States, private consortia making an increased contribution to nanotechnology R&D:

- The Semiconductor Industry Research Institute of Japan (SIRI), established in 1994, focuses on long-term research with partial government funding
- Semiconductor Leading Edge Technologies, Inc. (SELETE), established by ten large Japanese semiconductor companies in 1996, focuses on applied research and development with an estimated budget of $60 million in 1997
- Semiconductor Technology Academic Research Center (STARC) promotes industry-university interactions

Strengthening of the nanotechnology research infrastructure in the last years has been fueled by both the overall increase of government funding for basic research and by larger numbers of academic and industry researchers choosing nanotechnology as their primary field of research. Potential industrial applications provide a strong stimulus. A systems approach has been adopted in most laboratory projects, including multiple characterization methods and processing techniques. A special Japanese research strength is instrumentation development. The university-industry interaction is stimulated by the new MITI projects awarded to universities in the last few years that encourage temporary hiring of research personnel from industry. Other issues currently being addressed are more extensive use of peer review, promoting personnel mobility and intellectual independence, rewarding researchers for patents, promoting interdisciplinary and international interactions, and better use of the physical infrastructure.

China

Nanoscience and nanotechnology have received increased attention in China since the mid-1980s. Approximately 3,000 researchers there now contribute to this field (Bai 1996). The ten-year "Climbing Project on Nanometer Science" (1990-1999) and a series of advanced materials research projects are the core activities. The Chinese Academy of Sciences sponsors relatively large groups, while the China National Science Foundation (CNSF) provides support mainly for individual research projects. Areas of strength are development of nanoprobes and manufacturing processes using nanotubes. The Chinese Physics Society and the Chinese Society of Particuology are societies involved in the dissemination of nanotechnology research.

India

India's main research activities are on nanostructured materials and electronic devices (Sikka 1995). These involve a combination of research institutions (the Central Electronics Engineering Research Institute in Pilani, the Space Application Center in Ahmedabad, and others), funding organizations (the Centre for Development of Materials in Pune, the Indian Institute of Science in Bangalore, and others), and industry.

Taiwan

Taiwan's major nanotechnology research effort is conducted in the area of miniaturization of electronic circuits. The research is conducted in academic institutions and at the Industrial Technology Research Institute. Government funds for fundamental research are channeled via the National Science Council. (See site reports in Appendix E.)

South Korea

A national research focus on nanotechnology was established in Korea in 1995. The Electronics and Telecommunications Research Institute (ETRI) in Taejon, Korea's science city, targets advanced technologies for information and computer infrastructures, with a focus on nanotechnology (ATIP 1998). The emphasis is on nanoscale semiconductor devices and particularly on semiconductor quantum nanostructures and device applications (lasers, modulators, switches and logical devices, resonant tunneling devices, self-assembled nanosize dots, single-electron transistors, and quantum wires).

Singapore

Nanotechnology research received a considerable boost in Singapore by the initiation of a national program in this area in 1995.

Australia

The National Research Council (NRC) of Australia has sponsored R&D in nanotechnology since 1993 (ASTC 1993). Research groups work on synthesis of nanoparticles for membranes and catalysts (University of New South Wales), nanofiltration (UNESCO Center for Membrane Science and Technology), and use of nanoparticles in processing minerals for special products (the Advanced Mineral Products Research Center at the University

of Melbourne). AWA Electronics in Homebush has the largest industrial research facility for nanoelectronics in Australia.

EUROPE

European Community (EC)

The term "nanotechnology" is frequently defined in Europe as "the direct control of atoms and molecules" for materials and devices. A more specific definition from H. Rohrer (1997) is a "one-to-one relationship between a nano-object or nano-part of an object and another nano-, micro- or bulk object." The nanotechnology field as defined in this WTEC report includes these aspects, with the clarification that only the specific, distinctive properties and phenomena manifesting at length scales between individual atoms/molecules and bulk behavior are considered.

There are a combination of national programs, collaborative European (mostly EC) networks, and large corporations that fund nanotechnology research in Europe. Multinational European programs include the following:

1. The ESPRIT Advanced Research Initiative in Microelectronics and the BRITE/EURAM projects on materials science in the EC are partially dedicated to nanotechnology.
2. The PHANTOMS (Physics and Technology of Mesoscale Systems) program is a network created in 1992 with about 40 members to stimulate nanoelectronics, nanofabrication, optoelectronics, and electronic switching. Its coordinating center is at the IMEC Center for Microelectronics in Leuven, Belgium (see site report in Appendix B).
3. The European Science Foundation has sponsored a network since 1995 for Vapor-phase Synthesis and Processing of Nanoparticle Materials (NANO) in order to promote bridges between the aerosol and materials science communities working on nanoparticles. The NANO network includes 18 research centers and is codirected by Duisburg University and Delft University of Technology.
4. The European Consortium on NanoMaterials (ECNM) was formed in 1996, with its coordinating center in Lausanne, Switzerland. This group aims at fundamental research to solve technological problems for nanomaterials and at improved communication between researchers and industry.
5. NEOME (Network for Excellence on Organic Materials for Electronics) has had some programs related to nanotechnology since 1992.

6. The European Society for Precision Engineering and Nanotechnology (EUSPEN) was designed in 1997 with participation from industry and universities from six EC countries.
7. The Joint Research Center Nanostructured Materials Network, established in 1996, has its center in Ispra, Italy.

It is expected that the European Framework V will introduce additional programs on nanotechnology, particularly by adding a new dimension in nanobiology in the next four-year plan.

Germany

The Federal Ministry of Education, Science, Research, and Technology (BMBF) in Germany provides substantial national support for nanotechnology. The Fraunhofer Institutes, Max Planck Institutes, and several universities have formed centers of excellence in the field. It is estimated that in 1997 BMBF supported programs on nanotechnology with a budget of approximately $50 million per year. Two of the largest upcoming projects are "CESAR," a $50 million science center in Bonn equally sponsored by the state and federal governments with about one-third of its research dedicated to nanoscience, and a new institute for carbon-reinforced materials near Karlsruhe ($4 million over 3 years, 1998-2001). BMBF is establishing five "centers of competence in nanotechnology" in Germany starting in 1998, with topics ranging from molecular architecture to ultraprecision manufacturing.

U.K.

A network program (LINK Nanotechnology Programme) was launched in the United Kingdom in 1988 with an annual budget of about $2 million per year. The Engineering and Physical Sciences Research Council (EPSRC) is funding materials science projects related to nanotechnology with a total value of about $7 million for a five-year interval (1994-1999). About $1 million is specifically earmarked for nanoparticle research. The National Physical Laboratory established a forum called the National Initiative on Nanotechnology (NION) for promoting nanotechnology in universities, industry, and government laboratories.

France

The Centre National de la Récherche Scientifique (CNRS) has developed research programs on nanoparticles and nanostructured materials at about 40 physics laboratories and 20 chemistry laboratories in France. Synthesis

methods include molecular beam and cluster deposition, lithography, electrochemistry, soft chemistry, and biosynthesis. Nanotechnology activity has grown within a wide variety of research groups, including ones focused on molecular electronics, large gap semiconductors and nanomagnetism, catalysts, nanofilters, therapy problems, agrochemistry, and even cements for ductile nanoconcretes. It is estimated that CNRS spends about 2% of its budget and dedicates 500 researchers in 60 laboratories (or about $40 million per year) on projects related to nanoscience and nanotechnology. Companies collaborating to research and produce nanomaterials include Thompson, St. Gobain, Rhône Poulenc, Air Liquide, and IEMN. Also, there is the "French Club Nanotechnologie," aimed at promoting interactions in this field in France.

Sweden

The estimated total expenditure for research on nanotechnology in Sweden is ~ $10 million per year. There are four materials research consortia involved in this field:

1. Ångström Consortium in Uppsala, with a budget of ~ $0.8 million per year in 1998 for surface nanocoatings
2. Nanometer Structures Consortium in Lund with a budget of ~ $3.5 million per year partially supported by ESPRIT (~ $1 million per year)
3. Cluster-based and Ultrafine Particle Materials in the University of Uppsala and Royal Institute of Technology with a budget of ~ $0.4 million per year in 1998
4. Brinell Center at the Royal Institute of Technology

Switzerland

There is a Swiss national program on nanotechnology with a special strength in instrumentation. The most advanced research centers are focused on nanoprobes and molecule manipulation on surfaces (IBM Research Laboratory in Zürich), devices and sensors (Paul Scherrer Institute), nanoelectronics (ETH Zürich), and self-assembling on surfaces in patterns determined by the substrate or template (L'École Polytechnique Fédérale de Lausanne). See the site reports on all of these institutions in Appendix B.

The Netherlands

The most active research centers in the Netherlands are the DIMES institute at Delft University of Technology, which receives one-third support from industry, and the Philips Research Institute in Eindhoven, which

researches self-assembling monolayers and patterning on metallic and silicon surfaces. The SST Netherlands Study Center for Technology Trends is completing a study on nanotechnology and aims at promoting increased funding and research networking in the Netherlands (ten Wolte 1997).

Finland

The Academy of Finland and the Finnish Technology Development Center began a three-year nanotechnology program in 1997. The program involves sixteen projects with funding of $9 million for a three-year period (1997-1999) for nanobiology, functional nanostructures, nanoelectronics, and other areas. Research on actuators and sensors is the Finnish area of strength.

Belgium and Spain

Since about 1993 both Belgium and Spain have established nanotechnology programs, centers of excellence, and university-industry interactions.

Multinational Efforts

Large multinational companies with significant nanotechnology research activities in Europe include IBM (Zürich), Philips, Siemens, Bayer, and Hitachi. Degussa Co., with headquarters in Germany, is a commercial supplier since 1940 of microparticles and, now, nanoparticles.

Western Europe has a variety of approaches to funding research on nanotechnology. These are discussed in detail in other studies. IPTS (the Science and Technology Forecast Institute) has conducted a study on nanotechnology research in the EC (Malsh 1997). Other European studies published recently include those by VDI (1996), UNIDO (1997), the U.K. Parliamentary Office of Science and Technology (1997), and NANO network (Fissan and Schoonman 1997). The overall expenditure for nanotechnology research within the EC was estimated in 1997 to be over $128 million per year.

RUSSIA AND OTHER FSU COUNTRIES

Support for generation of nanoparticles and nanostructured materials has a tradition in Russia and other countries of the former Soviet Union (FSU) dating back to the mid-1970s; before 1990 an important part of this support

was connected to defense research. The first public paper concerning the special properties of nanostructures was published in Russia in 1976. In 1979 the Council of the Academy of Sciences created a section on "Ultra-Dispersed Systems." Research strengths are in the areas of preparation processes of nanostructured materials and in several basic scientific aspects. Metallurgical research for special metals, including those with nanocrystalline structures, has received particular attention; research for nanodevices has been relatively less developed. Due to funding limitations, characterization and utilization of nanoparticles and nanostructured materials requiring costly equipment are less advanced than processing.

Russian government funds are allocated mainly for research personnel and less for infrastructure (*Chem. Eng. News* 1997). Funding for nanotechnology is channeled via the Ministry of Science and Technology, the Russian Foundation for Fundamental Research, the Academy of Sciences, the Ministry of Higher Education, and other ministries with specific targets. The Ministry of Higher Education has relatively little research funding. Overall, 2.8% of the civilian budget in Russia in 1997 was planned for allocation to science. There is no centralized program on nanotechnology; however, there are components in specific institutional programs. Currently, about 20% of science research in Russia is funded via international organizations. The significant level of interest in the FSU can be identified by the relatively large participation at a series of Russian conferences on nanotechnology, the first in 1984 (First USSR Conference on Physics and Chemistry of Ultradispersed Systems), a second in 1989, and a third in 1993.

The Ministry of Science and Technology contributes to nanotechnology through several of its specific programs related to solid-state physics, surface science, fullerenes and nanostructures, and particularly "electronic and optical properties of nanostructures." This last program involves a network of scientific centers: the Ioffe Institute in St. Petersburg, Lebedev Institute in Moscow, Moscow State University, Novgograd Institute of Microstructures, Novosibirsk Institute of Semiconductor Physics, and others. This research network has an annual meeting on nanostructures, physics, and technology, and has developed interactions with the PHANTOMS network in the EC. The U.S. Civilian Research and Development Foundation has provided research funds in the FSU for several projects related to nanotechnology, including "Highly Non-Equilibrium States and Processes in Nanomaterials" at the Ioffe Institute (1996-1998).

Russian government and international organizations are the primary research sponsors for nanotechnology in Russia. However, laboratories and companies privatized in the last few years, such as the Delta Research Institute in Moscow, are under development. With a relatively lower base in

characterization and advanced computing, the research focus is on advanced processing and continuum modeling. Research strengths are in the fields of physico-chemistry, nanostructured materials, nanoparticle generation and processing methods, and applications for hard materials, purification, and the oil industry, and biologically active systems (Siegel et al. n.d.).

There are related programs in Ukraine, Belarus, and Georgia, mostly under the direction of the respective academies of sciences in these countries, that are dedicated to crystalline nanostructures and advanced structural and nanoelectronic materials. Several innovative processes, such as diamond powder production by detonation synthesis at SINTA in Belarus, are not well known abroad.

CLOSING REMARKS

Nanotechnology in the United States, Japan, and Western Europe is making progress in developing a suitable research infrastructure. The promise of nanotechnology is being realized through the confluence of advances in two fields: (1) scientific discovery that has enabled the atomic, molecular, and supramolecular control of material building blocks, and (2) manufacturing that provides the means to assemble and utilize these tailored building blocks for new processes and devices in a wide variety of applications. Technology programs cannot be developed without strong supporting science programs because of the scale and complexity of the nanosystems. The overlapping of discipline-oriented research with nanotechnology-targeted programs seems appropriate at this point in time. Highly interdisciplinary and multiapplication nanotechnology provides generic approaches that enable advances in other technologies, from dispersions, catalysts, and electronics to biomedicine. Essential trends include the following:

- learning from nature (including templating, self-assembly, multifunctionality)
- building up functional nanostructures from molecules
- convergence of miniaturization and assembly techniques
- novel materials by design
- use of hierarchical/adaptive simulations

A characteristic of discovery in nanotechnology is the potential for revolutionary steps. The question “what if?” is progressively replaced by “at what cost?” The road from basic research to applications may vary from a few months to decades. Research and development is expensive, and the field needs support from related areas. The R&D environment should favor multiapplication and international partnerships.

Based on the data for 1996 and 1997 collected during this WTEC study, 1997 government expenditures for nanotechnology research were at similar absolute levels in the United States, Japan, and Western Europe (Table 8.2). (Estimated OECD data for 1997 indicated GDPs of $4.49 billion for Japan, $7.76 billion for the United States, and $7.00 billion for Western Europe.)

The largest funding opportunities for nanotechnology are provided by NSF in the United States (approximately $65 million per year for fundamental research), by MITI in Japan (approximately $50 million per year for fundamental research and development), and by BMBF in Germany (approximately $50 million per year for fundamental and applied research).

Large companies in areas such as dispersions, electronics, multimedia, and bioengineering contribute to research to a larger extent in Japan and the United States than in Europe. While multinational companies are pursuing nanotechnology research activities in almost all developed countries, the presence of an active group of small and medium-size companies introducing new processes to the market is limited to the United States.

In the United States, individual and small-group researchers as well as industrial and national laboratories for specialized topics have established a strong position in synthesis and assembly of nanoscale building blocks and catalysts, and in polymeric and biological approaches to nanostructured materials. The Japanese large-group research institutes, and more recently academic laboratories, have made particular advances in nanodevices and nano-instrumentation. The European "mosaic" provides a diverse combination of university research, networks, and national laboratories with special performance in dispersion and coatings, nanobiotechnology, and nanoprobes. With a relatively lower base in characterization and computing infrastructure, the research focus in Russia is on physico-chemistry phenomena, advanced processing, and continuum modeling. Interest and economic support, particularly for device-related research, is growing in China, Australia, India, Taiwan, Korea, and Singapore.

TABLE 8.2. Government Expenditures on Nanotechnology Research in 1997, Based on the WTEC Site Interviews

Geographical Area	Annual Budget, NTR* ($ million)	Relative Annual Budget NTR/GDP* (ppm)
Japan	120	27
United States	116	15
Western Europe	128	18
Other countries (FSU, China, Canada, Australia, Korea, Taiwan, Singapore)	70	-
Total	432	-

* NTR – nanotechnology research; GDP – Gross Domestic Product

The pace of revolutionary discoveries that we are witnessing now in nanotechnology is expected to accelerate in the next decade worldwide. This will have a profound impact on existing and emerging technologies in almost all industry sectors, in conservation of materials and energy, in biomedicine, and in environmental sustainability.

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APPENDICES

Appendix A. Biographies of Panelists and Other Team Members

PANELISTS

Dr. Richard W. Siegel (Panel Chair)
Robert W. Hunt Professor and Head, Materials Science and Engineering Dept.
Rensselaer Polytechnic Institute

Dr. Siegel holds an AB degree (Physics) from Williams College and MS (Physics) and PhD (Metallurgy) degrees from the University of Illinois in Urbana. He is the past Chairman of the International Committee on Nanostructured Materials and earlier served on the U.S. National Materials Advisory Board Committee on Materials with Submicron-Sized Microstructures and was the co-chairman of the Study Panel on Clusters and Cluster-Assembled Materials for the U.S. Department of Energy. He was on the faculty of the State University of New York at Stony Brook from 1966 to 1976 and at Argonne National Laboratory from 1974 to 1995.

He has authored more than 180 publications in the areas of defects in metals; diffusion; and nanophase metal, ceramic, and composite materials. In addition, he has presented more than 300 invited lectures around the world and has edited 9 books on these subjects. He was listed by *Science Watch* as the fourth most highly cited author in materials science during 1990-1994. Dr. Siegel is an associate editor of *Materials Letters* and a founding principal editor of *Nanostructured Materials.* He is a founder and director of Nanophase Technologies Corporation, and was recognized for this effort by a 1991 U.S. Federal Laboratory Consortium Award for Excellence in Technology Transfer. He is an honorary member of the Materials Research Societies of India and Japan, a 1994 recipient of an Alexander von Humboldt Foundation Senior Research Award in Germany, and he presented the 1996 MacDonald Lecture in Canada.

Dr. Evelyn Hu (Panel Co-chair)
Professor of Electrical and Computer Engineering and Director, Center for Quantized Electronic Structures
University of California Santa Barbara

Dr. Hu's research focus as Director of QUEST, the NSF-funded Science and Technology Center focusing on Quantized Electronic Structures, is high-resolution, low-damage fabrication of electronic and optoelectronic devices. She is also the Director of the University's node of the NSF-sponsored National Nanofabrication Users Network. Prior to joining UCSB, Dr. Hu was a member of technical staff and subsequently a supervisor in the Department of VLSI Patterning Processes at AT&T Bell Laboratories.

She received her BA in Physics (summa cum laude) from Barnard College and her MA and PhD in Physics from Columbia University. She currently serves on the Defense Advanced Research Projects Agency Defense Research Science Council. She is a Fellow of the IEEE, a Fellow of the American Physical Society (APS), and holds an honorary doctorate of engineering from the University of Glasgow.

Dr. Donald M. Cox
Exxon Research and Engineering Company

Dr. Cox is a physicist in the Corporate Research Laboratories of Exxon Research and Engineering Company. He received a BA in Physics and Mathematics from Indiana State College and his PhD degree in Atomic and Molecular Physics from the Joint Institute for Laboratory Astrophysics (JILA) at the University of Colorado. After postdoctoral research at New York University where he studied properties of thermal equilibrium alkali plasmas, he joined Exxon Research and Engineering Company in 1973.

At Exxon, Dr. Cox's research interests have encompassed a variety of areas, including laser isotope separation of molecules using infrared multiphoton excitation and dissociation; optoacoustic spectroscopy; studies of the electronic, magnetic, and chemical properties of size-selected transition metal clusters both in the gas phase and deposited on substrates; investigations probing the properties and uses of carbon clusters, fullerenes and carbon nanotubes; and most recently, studies of microporous materials useful in gas separations via membranes and sorption. He is a member of the APS and ACS and has two patents and over 100 publications.

Dr. Herb Goronkin
Director, Physical Research Laboratory
Phoenix Corporate Research Laboratories, Motorola Corp.

Dr. Goronkin received his BA, MA, and PhD in Physics from Temple University and began work on high-speed devices and compound semiconductor materials in 1963. He joined Motorola in 1977 to start the GaAs electronics program. This program developed Motorola's early versions of MESFETs, MMICs, and HFETs for low-power, low-noise applications, and the high-efficiency 3-volt power HFET for wireless applications. The Physical Research Lab is engaged in quantum devices for future ULSICs, giant magnetoresistance for nonvolatile memory, molecular self-assembly for future electronic and bioelectronic applications, and data mining using neural networks. The lab is the only non-Japanese organization working on MITI's 10-year program on quantum functional devices.

Dr. Goronkin is a fellow of the IEEE and member of the American Physical Society and Sigma Xi. He has served on many conference committees and organizations and given several conference short courses on III-V device physics. He has over 40 patents and numerous publications. Motorola presented him with the Distinguished Innovator Award (1992) and the Master Innovator Award (1995), and he is a member of Motorola's Science Advisory Board Associates. Also, the Phoenix Section of the IEEE selected him as Senior Engineer of the Year (1993). He is currently director of the Physical Research Lab in the Phoenix Corporate Research Laboratories and a Motorola Dan Noble Fellow.

Dr. Lynn Jelinski
At time of this study: Professor of Engineering and Director, Center for Advanced Technology and Office of Economic Development, Biotechnology Program, Cornell University
Presently: Vice Chancellor for Research and Graduate Studies, Louisiana State University

Dr. Jelinski's research involves the use of magnetic resonance for studies of biomaterials, including spider silk. Prior to joining Cornell in 1991 and Louisiana State University in 1998, she was head of the Biophysics and Polymer Chemistry Departments at AT&T Bell Laboratories.

She graduated from Duke University (BS) and the University of Hawaii (PhD), both in chemistry. She is on a number of editorial boards and has served nationally in various capacities, including as a member of the Galvin Commission on the Future of the Department of Energy Laboratories. She currently serves on numerous panels and advisory boards, including the

Massachusetts Institute of Technology's Department of Nuclear Engineering and the National Science Foundation's Mathematics and Physical Sciences Division. She has published over 100 papers on her research.

Dr. Carl C. Koch
Professor, Associate Department Head, and Director of Graduate Programs
Materials Science and Engineering Department, North Carolina State Univ.

Dr. Koch's present research interests include non-equilibrium processing, metastable materials, and intermetallic compounds. Current projects are studies of ductility of nanocrystalline materials and metastable structures in polymer alloys.

Dr. Koch received his PhD in metallurgy from Case Western Reserve University (1964) and was an NSF postdoctoral fellow at Birmingham University, England (1964-65). In 1965 he joined Oak Ridge National Laboratory, where he became a group leader in 1970. In 1983 he was appointed professor at North Carolina State University. He is a fellow of the APS, ASM International, and AAAS. He is a member of TMS and MRS. He has received a Department of Energy Metallurgy and Ceramics Award. He was cited in Science Watch (October 1995) for the third highest number of citations per paper in the world for high impact papers in materials science for 1990-1994. Coholder of three U.S. patents, he has coedited four books and authored or coauthored over 170 papers. He is editor of *Material Science and Engineering A* and associate editor of *Nanostructured Materials*.

Mr. John Mendel
Senior Unit Director, Dispersion Technology
Emulsion Process Division, Eastman Kodak Co.

Mr. Mendel's unit is a particle technology center involved with process research and development, scale-up, technology transfer, and manufacturing support. The unit's scientists and engineers address issues in particle size reduction, dispersion stabilization, process scale-up, process verification, and characterization, as well as resolving day-to-day manufacturing issues. This work involves interaction with Kodak plants worldwide on a variety of nanoparticle systems, including organic dyes and pigments, and important inorganic materials.

Mr. Mendel received his BS degree in Physical Chemistry from the University of Washington in Seattle and his MS degree also in Physical Chemistry from Boston College prior to entering industry at Hercules Development Center. For three years he worked on pigmented polymer systems before joining Kodak in Rochester, New York. He has been with

Kodak for 26 years. For the past nine years he has been the Unit Director for the Dispersion Technology Unit in Kodak's Emulsion Process Division.

Dr. David T. Shaw
Professor, Electrical and Computer Engineering
Executive Director, New York State Institute of Superconductivity
Director, Integrated Nanostructure Characterization Laboratory, State University of New York, Buffalo

As founding president of the American Association for Aerosol Research (AAAR), Dr. Shaw has been actively involved with the development of nanoparticle technology. Together with Benjamin Liu and David Ensor, he was one of the founding editors-in-chief for the journal *Aerosol Science and Technology*, which is one of the major journals covering the generation, characterization, and applications of nanoparticles. He has published more than 230 journal papers and is the editor of seven monographs on aerosol science and technology. He has lectured extensively in Japan, Europe, and China and is well known for his work on the role of nanoparticles in the fundamental and the applied aspects of superconductivity, and for his work on magnetic and supermagnetic nanoparticles.

Dr. Shaw was a member of the US/USSR and US/OECD delegations on submicron particles, and led the U.S. delegation in a jointly sponsored effort to promote cooperation in the field of superconductivity between the United States and Japan. He is the recipient of the Association Award (1985) and the International Research Fellow Award (1994) from AAAR. Prof. Shaw received a bachelor's degree in Mechanical Engineering from the National Taiwan University and his MS and PhD degrees from Purdue University.

NSF COORDINATOR

Dr. M.C. Roco
Program Director, Directorate for Engineering
National Science Foundation (NSF)

Dr. Roco's area of responsibility at NSF includes chemical and mechanical engineering and the initiatives on functional nanostructures and nanoparticle manufacturing. He was a professor of mechanical engineering at the University of Kentucky (1981-1995) and has been a consultant to industry in the areas of two-phase flow equipment, surface phenomena, computer-aided design, toner-based copy machines, and chemical processing. Dr. Roco was honored as a recipient of the Carl Duisberg

Award in Germany, Gary Leach Award in the United States, special service awards from ASME and AICHE, the ASME Fluids Engineering Award, and as Outstanding Research Professor at the University of Kentucky. He served as associate technical editor for the *Journal of Fluids Engineering* and *Engineering Journal of Flow Visualization* and is currently editor of the *Journal of Nanoparticle Research.* He is credited with 13 inventions, has authored more than 100 archival articles, and has coauthored the books, *Slurry Flow: Theory and Practice* (1991) and *Particulate Two-Phase Flow* (1993). He is a fellow of ASME and is currently chair of the International Multiphase Award Committee (since 1995), chair of the Particle Technology Forum of AICHE (since 1996), and member of the executive committee of the Institute of Multiphase Science and Technology.

OTHER TEAM MEMBERS

Hiroshi Morishita
President, HMI Corporation

Mr. Morishita specializes in ultramicro manipulation technology for microelectromechanical systems. He founded HMI Corporation in 1991 to commercialize his ultramicro manipulator system. He extended his interest and business to the field of archaeological excavating machines and to the new robot manipulator system to help bed-ridden persons. In 1994, he became a consultant to WTEC panel members concerning their study tours in Japan. He graduated from the University of Tokyo (BA, MA in mechanical engineering) and is in the final stages of preparing his doctoral thesis. He was a visiting researcher in the Mechanical Engineering Department (1992 and 1993) and in the Research Center for Advanced Science and Technology (in 1994 and 1995) of the University of Tokyo.

Cecil H. Uyehara
Senior Advisor to WTEC for Japan Operations
President, Uyehara International Associates

Cecil H. Uyehara, president of Uyehara International Associates, is a consultant on U.S.-Japanese relations in the fields of science and technology. He served in the U.S. government for almost 25 years, with the U.S. Air Force (weapons systems planning), the Office of Management and Budget (military assistance), and the Agency for International Development (AID). He has published on Japanese politics, scientific advice and public policy, and Japanese calligraphy. He organized the first U.S. Congressional

hearings on Japanese science and technology, lectures at the U.S. Foreign Service Institute on Japanese science and technology, and has served as a consultant to the *Yomiuri Shimbun* and the Library of Congress on Japanese calligraphy. He received a BA from Keio University and an MA from the University of Minnesota, both in Political Economy. He has received awards and grants from the Ford Foundation, American Philosophical Society, University of Minnesota (Shevlin Fellowship), and the National Institute of Public Affairs.

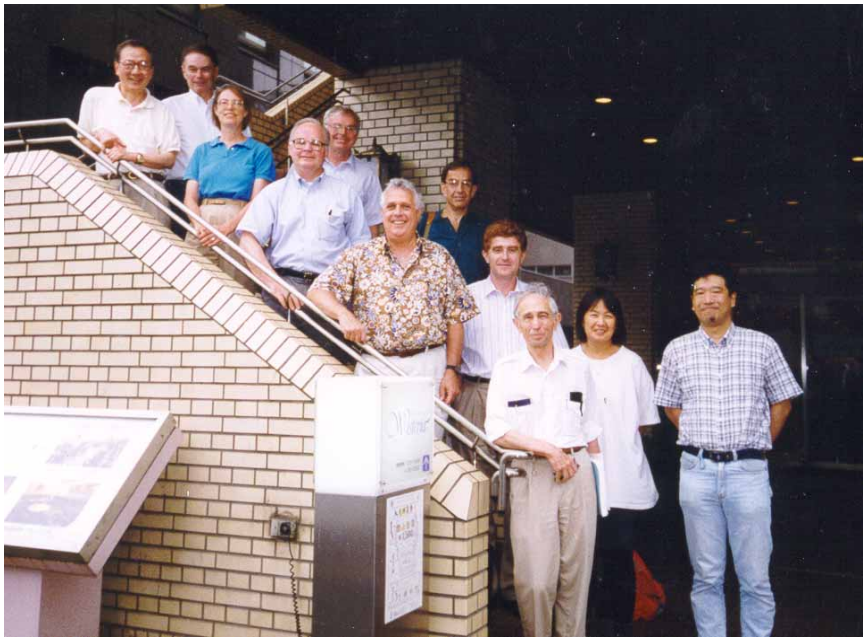

Figure A.1. Panelists and other team members at the Yaesu Fujiya Hotel in Tokyo, July 1997. From left: David Shaw, John Mendel, Lynn Jelinski, Donald Cox, Carl Koch, Richard Siegel, Herb Goronkin, Mike Roco, Cecil Uyehara, Evelyn Hu, Hiroshi Morishita.