

Chapter 1

Introduction and Overview

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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, overlaid 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.

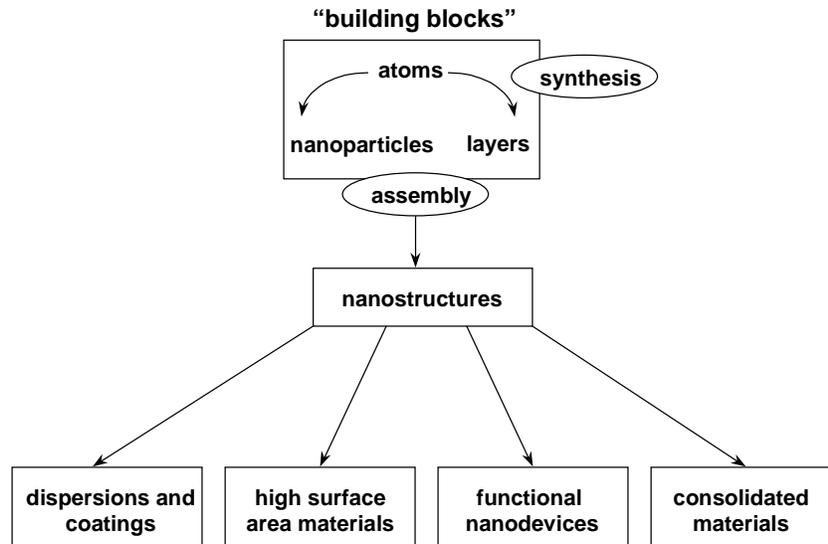


Figure 1.1. Organization of nanostructure science and technology and the WTEC study.

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 Recherche 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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