Introduction to Nanoscience

Study Guide

Study Guide Overview

Not all the chapters in the text are ubiquitously suitable for all students. Some are basic in nature (provide background material to bring students up to speed); some are more complex. Some emphasize biological phenomena, others chemical or physical. It is up to you the professor to pick and chose.

We also recommend that the professor of the class provide information in the form of presentations, articles, special lectures etc. to supplement material provided for by the text. Student presentations should be encouraged. Some guidelines are listed below:

- Preparing the student to give presentations, a necessity of any professional group whether business, academic or government related, is an oft overlooked aspect of professional development. Due to time constraints and the size of the class, presentations should not exceed 20 minutes with a 10 minute Q&A session.

- Students giving presentations should be able to answer any question about a topic or fact that he or she brings up in the presentation (within reason of course!). You brought it up– you answer it!

- Students in the audience should be required to ask at least one question each. Although this sounds somewhat authoritative, this minor exercise we believe will help the student develop the ability to question what is presented (a very important characteristic of scientists) as well as the opportunity to embellish the state of the art if asking a particularly brilliant question. No one will know unless the student is "brave enough" to ask.

- Questions come in many forms: a simple clarification of a procedure; a clarification of a concept; a question that ask "why" was something done or why the procedure occurred in a certain order; suggestions to improve the process or suggestions that elaborate upon its interpretation. And, last but not least, suggestions concerning how to proceed further can be brought to the forefront of the presentation Q&A session. The last three of course require more depth and insight than the former kinds.

We feel that decision-making following advanced discussion and preparation are viable means of charting the career path of willing students, hopefully as some form of nanoscience, nanotechnology or a societal inspired related field. Therefore, we recommend that, if at all possible, students form small groups that are willing to discuss aspects of NS and NT. Discussion topics are provided at the end of specific sections in the study guide.

Purpose of the Study Guide

Overall themes of the book include diametrically opposed concepts of continuum and boundaries, historical and modern perspectives, and the relationship of nano with nature and of nature with nano.

The purpose of the text is to provide a background, a baseline for expanded discussions between and among students and their professor. The purpose of this study guide is to help students navigate through the text and provide insight that is otherwise not explicitly provided by the text. This is accomplished by summarizing conceptual overviews, study objectives, explanatory text, references (with web links) and a summary after each chapter. The guide is intended to supplement concepts and themes presented in the text without becoming overtly burdensome.

PERSPECTIVES

Chapter 1 - Introduction

Chapter 1, Introduction, provides a broad perspective of nanoscience and nanotechnology– across temporal boundaries, historical aspects, technologies and people. We feel that this chapter, although not scientifically intensive, is valuable in the sense that is provides the perspective for what is to follow.

Chapter Objectives:

- Understand the distinction between science and technology
- Understand the definitions of the nanoscale, nanoscience and nanotechnology
- Delve into the impacts of nanoscience and nanotechnology from a scientific perspective– e.g. how are they changing science?
- Delve into the impacts of nanoscience and nanotechnology from the societal implications point of view– e.g. how are they changing our society?
- Comprehend the impact of a "disruptive technology"
- Comprehend the impact of an "enabling and convergent technology"
- Illustrate the convergence of academic disciplines on a piece of paper
- Illustrate the divergence of academic disciplines on a piece of paper
- Get a feel for the concept of the "integration of everything". Is it, in all actuality, a "continuum of continua"?

- Accumulate a working knowledge of the historical significance of NT
- Delve into the phrase "Nanotechnology, the next industrial revolution"! True, untrue or is the phrase an insignificant catchphrase?
- Introduction of basic nanotools such as the SEM, AFM, STM and SERS and some of the first true microscopic miniaturization techniques that made integrated circuits and MEMS possible
- Bring attention to the role of nature in nanotechnology and our NS– from macroscopic expressions of nanomaterials, cellular structure and functions to the molecular level of biochemistry and genetics
- Acquire a feel for the "scale of things", from the macroscopic to the subatomic and where nanoscale materials fit in
- Assimilate some of the grand challenges facing NS and NT

Section Overviews

1.0 The distinction between science and technology is part of the foundation of this text– e.g. we only focus on the science. Science is not technology and technology is not science. Science focuses on understanding properties and phenomena while technology is the application of science.

Discussion Topics: Discuss the relationship between science and technology in nature. Is it science? Is it technology? Is it just "there"? Or do both require a human perspective?

1.01 Definitions are always required. The definitions of nanoscience and nanotechnology are not particularly clear. The federal government defines nanotechnology as existing between 1 and 100-nm. What about 150-nm particles or those that are less than 1-nm (such as large biomolecules)?

Nano is the next step in the natural progression of miniaturization of materials from the micron size domain. Most micron-sized objects do not explicitly exhibit properties that are clearly distinct from bulk material counterparts. Many web-based and other definitions of nanotechnology emphasize that nanomaterials possess remarkable properties that are clearly distinct from the macroscopic rendition of the material. For example, the optical properties of a 100-nm particle may be described by optical constants derived from bulk materials. Is this material then a true nanomaterial?

Many definitions imply the need for "control" of nanomaterials. The term control connotes many things depending on your level of certain hormones. Without control, what do we have (with regard to nanomaterials and devices)? Does nature exert control over processes, especially those of the biological realm?

Figure 1.5 displays several continua in the graph: a continuum of linear size (macro → micro → nano), an academic one (chemistry, biology and physics, although the order is in actuality multi-dimensional); a temporal continuum (1960 → 2040) and one between science and technology. Are there more?

Discussion Topics: Form a group a small group and discuss the relative merits of the definitions provided in the chapter. Are there means of improving them? Of reducing them? Of adding new ones?

1.1 ***Historical Perspectives*** are vitally important– e.g. standing on the shoulders of giants", etc. Without such we would never realize the links between what we do now with what has already been accomplished. It is remarkable, from our perspective, that the ancients were able to delve into the atomic realm, albeit in a non-experimental fashion, and predict accurately the existence of substances that were not visible to the naked eye– hence the beginnings of nanotechnology (and nanoscience).

From the historical perspective, was the contribution of nanotechnology based more so on nanotechnology rather than nanoscience? Although the Greeks (and other ancient cultures) discussed the atom (science), most of the examples of historical nanomaterials are based in nanotechnology.

The purpose of this section is to demonstrate (vividly) the contribution to technology by nanomaterials (not necessarily devices). ***Colored glasses*** in particular have existed since antiquity– pigments as well. Why would colored materials be some of the first to be nanosized? How would an ancient craftsman make colored glass?

Why do colored glasses filled with nanometals exhibit such remarkable colors? There are two fundamental reasons. First, as materials assume smaller dimensions, other factors become involved in the expression of physical properties. The most obvious one is that a boundary starts assuming more importance. The boundary (the surface, for example) of a bulk material does not influence its physical properties. Why is this? Bulk gold looks like bulk gold when in the form of an ingot at Fort Knox or a gold ring. Both are bulk forms of gold although their mass is radically different. If I make the gold even smaller, say for example into a tiny link in a chain, it still looks gold although it is several hundred times less in mass than a ring– or even into gold dust (large to micron-sized particulates) extracted from a stream near Sutter's Mill in California.

The ancients were also quite efficient at beating gold into thin foils– some on the order of hundreds of nanometers in thickness. What does it look like? It still looks like gold!! at least in 2-dimensions. But what if I were to shine a light through the film? The color is most likely different than that of the bulk. Why is that? Why doesn't it look like gold anymore? By making it extremely thin, the boundaries on either side now play a role. For example, if thin enough, light can be transmitted through the film. There are fewer gold atoms along the thickness. Therefore, along one dimension at least, the gold is no longer like bulk gold– e.g. differences in reflection and transmission properties.

Sputtered films differ more radically from the bulk. Sputtered films are often an agglomeration of particles, adding another variable into the equation. Single particles, like those found in gold colloidal solutions can be extremely colored.

Back to our first factor, the boundary plays a role by restricting the freedom of the surface electrons of gold. Think of it as swimming in a smaller and smaller pool. After a certain number of reductions, down to the size of a bathtub for example, your motion becomes severely restricted and so is the motion of the electron– e.g. it collides more so with the boundary. Restricting the space of an electron increases its energy so to speak and its interaction of light is also altered accordingly– e.g. it absorbs shorter wavelengths. Note that the optical constants of such remain the same, only the observable manifestation of physical properties become altered. Please refer to:

Professor Faraday on the relations of gold to light, in *The Mechanics Magazine*, R.A. Brooman and E.J. Reed, Eds., 67, pp. 2-4, Robertson, Brooman & Co., London (1857)

The article can be found online at

http://books.google.com/books?id=ZLAAAAAAMAAJ&pg=PR11&lpg=PR11&dq=beaten+gold+films&source=web&ots=0Jh4VIylmW&sig=LpPifyl6dOa0je-ec4pxBexf4Xg&hl=en

In the second case, as the particle becomes even smaller, the surface plays an even larger role but also does the structure of the material itself. In this case, the particle has shrunk to the domain of the quantum dimension and a concomitant loss of available energy levels is the result. Fewer available energy levels implies limited options for electrons.

Photography emerged a few hundred years ago– due to nanometer and micrometer scale materials. Think for a minute about what goes into a photographic print. What substance is exposed to light that results in an image? What substance would impart the resolution required to create an image? The answer is of course micron to nanosized photosensitive particulates.

Catalysts are another nanomaterial (for the most part) that has been around quite some time. The formation of soap in particular was quite a revolutionary breakthrough. How many nanomaterials are involved in soap production by the ancients? What about the action of soap itself? What branches of chemistry were foreshadowed by such action?

Integrated Circuits and Chips Microtechnology is mature and well-developed for over forty years. The integrated circuit has revolutionized our lives and how we interact with others on a global scale. MEMS devices (microelectromechanical machines) in particular have been installed in common devices that regulate a variety of finctions.

A MEMS device is simply a mechanical device containing electronic components that are on the order of hundreds of microns to a few microns in size. MEMS devices are fabricated via lithography or other means to etch away bulk materials, sometimes with the assistance of a maskant material.

Discussion Topics: Refer to **Figures 1.9** and **1.10**, those centered on Michael Faraday. Pretend that you are Faraday presenting his research to the Royal Society in 1856– no electron microscopes, no spectrometers, no atomic force microscopes. How would you present his results and explain the phenomenon of colored fluids?

1.2 ***Advanced materials*** that are considered to be nanomaterials have made the scene in a big way over the past 20 years or so and incipiently over the past 100 years or so. Thin films, observed by Benjamin Franklin, were known to possess special properties– e.g. the calming effect on water. Langmuir and Blodgett developed their special technique of forming thin organic layers on water and the invention of invisible glass in the 1940s. This led to the development of more sophisticated techniques involving molecular self-assembly. Fullerenes and carbon nanotubes, quantum dots and ferrofluids etc. all have made contributions to nanoscience and technology. The significance of each are summarized below:

Thin films: Coating a substrate material with a thin film can change the chemical nature of the surface from hydrophilic to hydrophobic and vice versa or for render it for further chemical modification. A thin film can impart special electronic properties to a bulk material surface by adding an insulator layer, a semiconducting layer or a conducting layer– or, if thin enough, can create a tunneling junction. The properties of the layer are directly related to its thickness, structure and/or chemical nature.

Porous layers: Porous anodic alumina forms as a template consisting of hexagonally-packed pore channels available for further functionality.

Fullerenes and Carbon Nanotubes: These are allomorphs of carbon that offer a unique set of properties to scientists and engineers. Fullerenes are some of the smallest nanomaterials but are also the most uniform (monodisperse), stable (in the kinetic sense) and versatile (chemically modifiable). The basic C_{60} is an assembly of 60 carbon atoms in the structure of a soccer ball that contains hexagons and pentagons. Single-walled carbon nanotubes are basically extensions of hemifullerenes along one of its symmetry axes. SWNTs are the strongest materials known to science. Why? When conducting a tensile test on a metal, the limiting factor is usually the strength between grains of the metal, grains that are often micron-sized. In the case of the SWNT, the tensile strength limit is determined by the C–C bond, one of the strongest in nature.

Quantum Dots: One of the most magnificent achievements of nanoscience and technology is the quantum dot– a material in which electrons are confined in all three spatially defined directions. The QD is the manifestation of bulk-quantum boundary, the point at which physical properties are radically altered from that of the macroscopic material. The QD is known as a zero-dimensional material and its properties vary according to size. CdSe QDs, for example, fluoresce at different wavelengths as a function of its size [**Fig. 1.20**].

Why is this? We discussed earlier how gold changes color with respect to size– that down to approximately 10-nm, gold is still considered to be a bulk material and its color is determined by the shrinking boundary as it were. Gold colloids therefore can present a veritable rainbow of colors just based on this principle. It is the nature of the surface plasmon, and its various levels of resonance, that work collectively to produce the color when excited by light– a property dependent on the size of the gold. The optical repsonse of the quantum dot is also dependent on size but for a different reason. The electrons of a dot form Highest occupied (HOCO) and lowest unoccupied (LUCO) cluster orbitals with specufuc electronic transitions. Inother words, although based on size, QDs behave very much like large molecules, complete with allowed and forbidden electronic transitions. there will be more discussion later on in the text (of course).

1.3 ***Tools of Nano***: Nanoscience and nanotechnology require tools– tools to observe and measure and tools to fabricate. Just like with anything else, tools have also undergone, in parallel fashion, evolutionary developments that have helped bring on the *Nano Age*.

The SEM was invented in the early part of the twentieth century, the AFM and STM in the latter. Their impact is directly related to the size of the structure being observed– in the most modern versions, the atoms themselves. This landmark work, although simplistic in design, was simply the placement of xenon atoms to spell IBM by Donald Eigler et al. at the IBM Almaden Research Center. That work indeed put nanotechnology into the spotlight.

The details of SEM, AFM and other nanotools are provide in *Chapter 3*, Characterization Methods.

1.4 We emphasize the importance of nature in nanotechnology and nanoscience. Starting with biological materials, understand how all are built from the bottom up. Investigate the complexity of a selected hierarchical family– e.g. the tendon and its micro and nanostructure.

Discussion Topic: Why do you think biological materials and organisms are built from the bottom up? What is so special about the nanoscale in biology? And what of inorganic nature? Where are the nanomaterials? how are they formed?

1.5 The Nano Perspective is provided to emphasize the role of nanoscale materials in natural and synthetic materials.

Discussion Topic: Are all natural materials (inorganic, organic and biological) made of nanomaterials?

Chapter Summary:

- Nanoscience is the study of nanomaterials, properties and phenomena. Nanotechnology is the application of nanoscience to produce devices and products for commercial purposes

- Nanotechnology is, at the same time, enabling, horizontal, interdisciplinary, disruptive and convergent with a high barrier of entry

- The societal implications of nano are expected to impact all aspects of our society at the local, regional, national and global levels of complexity

- Please familiarize yourself with some of the well-known names associated with NT– e.g. the likes of Democritus, Boyle, Dalton, Michael Faraday, Richard Smalley, Richard Feynman, Ruska, Binnig and Rohrer, Eric Drexler, Gordon Moore, Langmuir and Blodgett, Günter Schmid, Alivisatos, Mihail Roco, Ray Baughman and many more.

- The concept of atomism is an ancient one that remained dormant for 2000 years until the likes of Boyle, Dalton and others revived it for good

- The color in many colored glasses is due to the inclusion of nanoparticles of certain metals– an ancient technology to be sure. There are many examples of old cultures utilizing nanomaterials.

- Catalysts and photography serve as another example of historical nanotechnology.

- The primary tools of nanocharacterization are the scanning electron microscope (SEM) and the atomic force (or scanning tunneling) microscope (AFM or STM). Other tools are refinements of preexisting tools such as x-ray diffraction and various spectroscopies. Specific nano-methods also include Raman spectroscopy, especially surface enhanced Raman spectroscopy (SERS) that employs metallic nanofacets to enhance the signal from organic molecules.

- Lithography, as a tool used to fabricate micron-size structures and facets, was extremely fundamental to the development of the integrated circuit and hence, our computers. It represents the consummate top-down method of fabrication of materials. Lithography is a well-established widespread commercial success. optical-UV-x-ray lithography is defined (and limited) by the wavelength of the excitation source.

- The importance of computer modeling and simulation cannot be understated. Because nanomaterials consist of a defined number of atoms (or molecules), a number amenable to facilitative computer simulation, computer assisted design of nanodevices is fast becoming an important engineering tool.

- Nature is the ultimate nanotechnologist (note, not nanoscientist). All of its biology is constructed from the bottom up– from atoms and molecules. We have much to learn from this master. Throughout the text, we make reference to nature and its wondrous structures and functions.

- The scale of things is an important visual tool. It compares synthetic and natural materials of decreasing size to the electromagnetic spectrum– an interesting and useful correlation.

- NS and NT face many grand challenges. It is one thing to fabricate something on a small scale, test it and write about it; it is quite another to turn it into a product that is sold worldwide. Upscale (or scale-up) is just one issue facing commercialization of nano. **Figure 1.28** summarizes some of the challenges facing both NS and NT.

Resources and Links

www.nano.gov

www.ipt.arc.nasa.gov

www.nuc.berkeley.edu/courses/classes/E-124/NanoTech.ppt

www.nanohub.org/local/ipod/Hersam_NANO101_Nanometer_Scale_Science(PDF).pdf

www.ncnano.org/nanotech2003.pdf

www.chemeng.ed.ac.uk/~mbiggs/mjbc_teaching/nanotechnology/2004-05/ohs/Introduction.pdf

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