PREFACE

The world of materials science is witnessing a revolution in the exploration of matter at the small scale. Sub-atomic particles have been a fascination since the first half of the 20th century. High-energy accelerators allow us now to penetrate the constituents of sub-atomic particles. This is an ongoing quest. New and improved properties of materials whose constituting units are nanosized objects make one explore these objects in further detail. When matter at nanoscales can perform functions hitherto done by bulk materials and their assemblies, many things inconceivable in the past can be achieved. Imagine devices such as moving bodies 1000 times smaller than a bacterium. Imagine complex machines as small as a virus. In fact the virus itself is such a machine, created by nature.

Obviously reducing dimension and consequent exploration of properties has no limit. This takes one to the famous, oft-repeated statement of Feynman, "there's plenty of room at the bottom." One can start arranging molecules to achieve the functions of a complex machine. A future with controlled molecular assemblies of this kind, the molecular nanotechnology, will revolutionize everything—from food to thought will change with this newly acquired power.

Atoms and typical molecules are a few angstroms long. That is 10^{-10} m or 10 billionth of a meter. Numbers of this kind are very hard to comprehend as they are not in everyday use. This length is as small as a millimeter if one were to take a wire stretched between Chennai and Kanyakumari, the southern tip of India. In order to understand 10^{-10}, it is useful to imagine 10^{10}, a number which is astronomically big. The distance of 10^{10} m is 10 million kilometers or it is 26 times the distance between the earth and the moon. Obviously no one, except astronauts, travel that kind of distances. In day-to-day life we feel distances of the order of meters and centimeters, the smallest distance one can see without instruments is 0.1 mm, or the thickness of a cotton fiber. This is 10^{-4} m. The distance of 10^{-10} m is a million times smaller, or it is about 1 mm if the cotton fiber were to be expanded to appear like a 100 m wide highway. We are talking about very small things, and consequently we need the right tools to see these objects.

In order to get a nano object to function, it is necessary to assemble the constituent atoms or molecules, perhaps into a large single molecule such as a protein. These objects are of the size of a nanometer (10^{-9} m). The science of nanometer scale objects is nanoscience. The resulting technology is called nanotechnology. Nanotechnology involves achieving the capability to manipulate matter in a desired fashion, atom by atom. At this scale, the constituents of matter do functions, which are different from those of the constituents or bulk materials. While molecular properties bridge material functions at this interface, a wide gap opens up in our understanding of properties in this size domain. This makes it necessary to do additional investigation. Obviously there are many surprises in such studies which make this area scientifically fascinating.

The advances in this area will result in newer technologies: nanoscience and nanotechnology market in 2015 is predicted to be worth 350 billion dollars. That consequently calls for new investments in human resource development. These people must have strong foundation in nanoscience and technology with a fair background in chemistry, physics, mathematics and biology as well as in electrical, mechanical and chemical engineering. While the basic science and engineering degrees are absolutely essential, training in nano related areas with a desire to constantly update their knowledge will be necessary to launch them into the demands of the world. It is not possible to bridge the gap within the undergraduate curriculum alone by offering a few additional courses. Postgraduate programmes may have to be thought of in nanoscience and technology.

Such programmes must provide sufficient information on experimental methodologies with necessary theoretical background. Current undergraduate curriculum does not provide an introduction to the modern experimental tools, at least in India, where the author has first hand knowledge. It is also impossible to expect it at this level, considering the time available and the advances in the respective fields. Therefore, any programme directed towards nanoscience and technology has to be done at the postgraduate or graduate level. While a devoted postgraduate course in the area may be useful, this has to be done with sufficient practical exposure to all the areas and experimental methodologies. This calls for large scale investment on infrastructure, especially in countries such as India, as most universities are ill equipped to meet the demands in instrumentation intensive areas. The few who have the necessary competence both in terms of the infrastructure and human resource may initiate such programmes. Courses at the graduate level are certainly useful, but considering the selected few that one takes during the graduate programme, this may not provide an overall perspective of the area, unless one is pursuing research in it.

This book has been written to provide an overall appreciation of the area, starting from the basics. The subject matter can be easily comprehended by an undergraduate student in science or engineering. Certain details are omitted deliberately, but sufficient directions are given to both students and teachers who require detailed understanding in any specific area. For the benefit of those interested in further exploration, a brief summary of the discoveries in the area is given at the end of the book with original references. This may be useful for a person completing a master's degree yet unsure of the area in which he would like to specialize. A glossary of nano terms is also included.

The entire material can be structured as a one semester course, with about 36 lectures, the suggested number of lecture hours is only a guideline. Lectures may also be added to bring more quantitative aspects into the classroom, especially in specific areas such as self assembled monolayers (e.g. experimental structure of monolayers), metal nanoparticles (e.g. electronic absorption spectrum) and quantum dots (e.g. size effects). This may be done in several different ways. An example would be 20–25 classroom lectures followed by student presentations, which can include additional material from current research or cited references. The summary of discoveries in the area may be used to pick topics for presentations. It is also possible to cover selected areas using this book while a course on a more focused subject is presented.

Subject matter of the kind discussed in this book is rapidly evolving. Therefore, any book of this kind has to be updated at periodic intervals. Science at the nano-bio-mechanical-electrical interfaces is opening up newer disciplines. Advanced technology is rapidly changing instrumentation, which in turn makes it possible to explore newer things. The problems and the way they are looked at are changing. All of these would suggest a more frequent revision of the book than would be necessary in more traditional areas.

This book has also been written in view of specific demands of our times. There is a realization that nano is the direction to go in the years to come. This has come to the minds of educationists, planners and administrators alike—thanks to the media. As a result of this, several institutions are planning to establish courses and programmes in the area. This book may be used at least as a pointer while designing the course content and structure of such programmes. The present book along with the suggested references will be adequate for an elective course. A more detailed textbook with lot more material covering additional subject areas such as nanotechnology will be necessary for a specialized degree programme on nano.

The author is always receptive to constructive criticism and can be contacted at *pradeep@iitm.ac.in*.

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ACKNOWLEDGEMENTS

This book became a reality due to the continuous support of several people. First of all I should thank my students in the undergraduate, masters and graduate levels at the Indian Institute of Technology Madras, who were instrumental in making me organize bits and pieces necessary for this writing. The courses, CY305-Molecular architecture and evolution of functions, CY653-Electron spectroscopy and CY722-Novel materials, which I have been handling for the past several years contributed to the evolution of the contents of this book. My graduate students have contributed heavily to the writing, in fact several of the chapters are largely due to them. I thank the following students for their contributions in writing the chapters: D.M. David Jeba Singh (Gas Phase Clusters), V.R. Rajeev Kumar (Self-assembled Monolayers and Monolayer-protected Metal Nanoparticles), A. Sreekumaran Nair (Core-shell Particles), M.J. Rosemary (Nanoshells), Renjis T. Tom (Nanobiology) and C. Subramaniam (Nanosensors). Three of my undergraduate students, Anshup (Nanomedicines), Sahil Sahni and Richie Khandelwal (Nanotribology) also contributed. Although their contributions have been substantial, the errors are mine. Dr Birgit Bürgi, who spent a few months in our lab, with whom I wrote an article on societal implications of nanoscience and technology was kind to permit the use of the article in this volume. The article was published originally in *Current Science*. Similarly, another article of mine, on fullerenes, published in the same journal also finds place in this book, although with some modifications. Support of C. Subramaniam and V. Sajini for preparing the history and index, respectively, are acknowledged. My former assistants, K.A. Arun and K.R. Antony helped me at various stages of manuscript preparation.

I thank all my present and previous students whose contributions enriched my understanding of the subject.

All the publishers and authors readily agreed to reproduce their work, for which I am grateful. There have been a few websites from which we have used figures and I thank them for their kind permission. Several textbooks, monographs, review articles and websites have helped me in gathering information and it is my earnest hope that all the intellectual property has been adequately acknowledged. In spite of the best intention, if any material has not been referenced adequately or appropriately I request the reader to point out such lapses, which will be corrected at the earliest available opportunity.

This work reaches you with the hard and sustained work of an excellent team at McGraw-Hill Education (India) Ltd. I thank the support of each one of them.

I thank the Indian Institute of Technology Madras for encouragement. Financial support of the Curriculum Development Cell of the Centre for Continuing Education is acknowledged.

Finally, I thank my wife and children for their patience.

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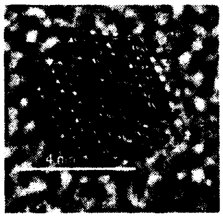
PART ONE

Introduction

Contents:

Chapter 1

INTRODUCTION—THE CANVAS OF NANO



Nanoscience and nanotechnology refer to the control and manipulation of matter at nanometer dimensions. This control has made it possible to have life, which is a collection of most efficient nanoscale processes. The best eco-friendly and efficient processes must learn from nature. When we explore life around us, it is found that organization of nanomaterials is central to biology. Architectures made by organisms are all based on nanoassemblies. Today we know that it is possible to use biological processes to make artificial nanostructures. Chemically synthesized nanostructures have been used at various stages of civilization.

Learning Objectives

- Why nanotechnology?
- What are the connections between nanotechnology and biology?
- What are wet and dry nanotechnologies?
- What are the historical landmarks in this area?

1.1 Nano and Nature

This chapter should begin with an apology. In it, you will find a popular science introduction to nano, not the one commonly found in textbooks. Yet, this needs to be done as science at the nanoscale has larger implications and needs to be understood from diverse viewpoints.

Man has learnt a lot from nature. Yet his manufacturing practices are primitive. Everyone knows that a lot more needs to be done to get closer to nature. For example, no one has reached the efficiency of photosynthesis in storing energy. No one can facilitate energy transfer (or electron transfer) as efficiently as biomolecules. No factory does water purification and storage as efficiently as coconut trees or water melons. The brain of one person can, in principle, store and process more information than today's computer. It is unlikely for any movie camera to capture visuals more vividly than the human eye. The olfactory receptors of the dog are much more sensitive than the sensors we have developed, though single molecule detectors have been reported. Most early warning systems are primitive when compared to the sixth sense of animals. Well, all these functions are performed in nature without any fanfare; this has been happening since time immemorial and with precision each time.

Conventional wisdom says that what happens in a factory is high-tech. Technology converts primitive, unusable materials into modern, useful materials. But technology has a much greater impact on nature especially as the complexity of the technology increases. The impact of the wheel is not as significant as that of the automobile. When spaced in time, the impact of technology increases along with the progress of civilization. The chisel symbolized the highest technology of the Neolithic era. The man who could make his chisels better would get a greater share of food. The best or most high-tech product today would be the super chips used in the fastest computers. These, in the course of production from sand to wafers and then to integrated circuits, have caused severe damage to the environment, even as they contribute to the information explosion. The impact of modern technology is evident on all natural resources—water, air and everything around us. Of course, what we have developed is not high-tech in totality.

The use of conventional technology has not ensured optimum efficiency in energy conversion. Our best photovoltaic devices convert light with only 16 per cent efficiency. Our best internal combustion engines work at around 52 per cent efficiency. While cooking, we use 38 per cent (at best) of the thermal energy produced by gas. But our body utilizes almost the entire chemical energy it produces. Plants utilize this energy much better, as do bacteria. If we were to be as inefficient as an electric motor we would be consuming several times more food than we do today and there would not be enough food for all of us! It is therefore clear that ultimate efficiency or value for money is achieved only if we traverse nature's way.

Nature as a whole fixes about 110–120 billion tonnes of carbon per annum through photosynthesis. We humans emit only 0.65 billion tonnes of carbon dioxide through respiration. But carbon emissions due to human activity constitute about 8 billion tonnes, 77.5 per cent of which is due to the burning of fossil fuels alone. During this process, we produce a lot of other wastes such as smoke, complex organic compounds and oxides of nitrogen. Obviously, the technologies we have developed are much less efficient than those operating in nature. But most importantly, the benefits accruing from the processes and machines developed by us are incongruent with the huge amounts of resources we utilize for these developments.

Eric Drexler (Ref. 1) has suggested an alternate way of producing things, by assembling things from the bottom, which can be called molecular nanotechnology. This is akin to the humble way in which plants take carbon dioxide and water from the environment to produce organic compounds like carbohydrates in the presence of sunlight. A vast majority of living beings on this planet subsist on these carbohydrates, excepting a few organisms, which abstract other forms of chemical energy. In fact, one carbon CO_2 is assembled by a series of chemical processes to yield complex structures. This one-by-one assembly has facilitated functions with single molecules. Examples of this include molecular motors, muscle fibres, enzymes, etc., each of which is designed to perform a specific activity. The complexity of this molecular architecture is such that one molecule can communicate precisely with another so that the structure, as a whole, achieves unusually complex functions, that are necessary to sustain life. Nature has taken a long time to master this complexity. Maybe, that is the path one must pursue if one has to look toward the future.

Any production achieved through biological processes is extremely complex, but very cheap in real terms. The constitution of a water melon is more complex than the most complex integrated circuit, yet it costs far less. On the other hand, the power to manipulate atoms and arrange them in the way we please can facilitate the creation of complex inorganic structures merely at the price of vegetables. This power can, in fact, facilitate the creation of all man-made products. That is nanotechnology. In many ways, this is the wet side of nanotechnology (Ref. 2). There is a corresponding dry side wherein the ability to organize things atom by atom would make it possible to have structures and devices with functions. That would not only make computers smaller, and surgical procedures feasible without blood loss, but also help harness solar energy efficiently so that we can avoid climate changes. The organization of the molecules is such that they can communicate with one another. Such an arrangement enables the execution of usually complex functions necessary to sustain life.

1.2 Our Technologies and the World We Live in

Implementing nature's ways would imply a thorough understanding of molecular machinery. This knowledge, if applied to inorganic matter, results in functional materials. Through these, a superstructure may be built, which has functions similar to those encountered in biology. Think of molecules transferring matter from one end to the other. Think of molecules, which bend, stretch or curl in response to external stimulus such as temperature and come back to their original shape when the stimulus is reversed. Consider chemical reactions which can be turned on and off by light. Think of molecules converting one chemical into another without using anything else in the medium and assume that such transformation occurs with precision and within the shortest time. These kinds of functions and indeed many more have already been achieved and there is much greater scope for such achievements in the future.

In the course of the evolution of mankind, technologies have come and gone. One large difference between today's technology and that of the past lies in the time taken to perfect technology. The agrarian era, driven by the associated technologies of irrigation, tools, fertilizers, etc., took a few thousand years to evolve, with the time period varying depending on the location. The Industrial Age, which came just after the agrarian era, starting around the 1800s, took about 150 years in evolution. Then came the Information Age, starting from the 1950s and in many projections, it is said to have evolved, to a great extent. The impact of that evolution may not have been felt in many societies, as technologies are absorbed differently (see Chapter 16), but in the developed countries of the West can be said to be technologically fully evolved. The next age, at the threshold of which we stand today, is expected to evolve within a generation. But the way in which that technology is absorbed will be vastly different from the absorption of earlier technologies.

A partial list of technologies developed in the 1900s, along with the year of invention and names of the people who invented them, is given in Table 1.1.

It is important to note that many technologies took a long time to reach the marketplace, but the most recent technologies are already in the marketplace (see those of the 1990s).

Table 1.1: *Details of technological inventions of the 20th Century*

Year	Technology	Inventor
1920s:		
1924	Frozen foods	Clarence Birdseye
1926	Rocket engine	Robert Goddard
1926	Television	John Logie Baird
1928	Penicillin	Alexander Fleming
1930	Synthetic rubber	Julius Nieuwland
1930s:		
1930	Jet engine	Frank Whittle and Hans Von Ohain
1932	Automatic transmission	Richard Spikes
1934	Nylon	Wallace Hume Carothers
1937	Pulse code modulation to convert voice signals into electronic pulses	Alec Reeves
1937	Xerography or Xerox machines	Chester Floyd Carlson
1940s:		
1940	Radar	Robert Watson–Watt
1946	Microwave oven	Percy Spencer
1947	Cellular phone (conceptually)	D.H. Ring
1947	Transistor	Nillian Shockley, John Bardeen, and Walter Brattain
1949	Magnetic core memory	An Wang and then Jay Forrester
1950s:		
1951	The pill	Gregory Pincus
1952	Thorazine	Henri Laborit
1954	Fortran, the first high-level programming language	Griffith John Backus
1955	Polio vaccine	Jonas Salk
1956	Disk drive	Reynold B. Johnson
1958	Implantable pacemaker	Wilson Greatbatch
1958	Lasers	Schnwlow, Towens Basov, and Prokhorov
1959	Integrated circuit	Robert Noyce, Jack Kilby

Contd.

Table 1.1 Contd.

Year	Technology	Inventor
1960s:		
1962	Modem	US Airforce, AT&T
1968	Automated teller machines (ATMs)	Don Wetzel
1968	Mouse	Douglas Engelbart
1969	Charge-coupled devices	George E. Smith, Williard S. Boyle
1969	The Internet	UCLA, Stanford, among others
1970s:		
1970	Compact disc (CD)	James T. Russell
1970	Liquid crystal displays	James Fergason
1971	Microprocessor	Intel, Busicom
1972	Computed tomography imaging	Godfrey Housnfield, Allan Cormack
1972	Ethernet	Robert Metcalfe
1972	E-entertainment and precursor to video games	Nolan Bushnell
1974	Catalytic converter	Rodney Bagley, Irwin Lachman, Ronald Lewis
1975	Recombinant DNA	Herbert Boyer and Stanely Cohen
1979	Spreadsheet	Daniel Bricklin, Bob Frankston
1980s:		
1986	Automated DNA sequencing machines	Leroy Hood, Llyod Smith and Mike Hunkapiller
1987	Mevacor to reduce cholesterol	Merck
1987	Prozac to reduce depression	Ray Fuller of Eli Lilly Company
1989	World wide web	Tim Berners-Lee
1990s:		
1994	Viagra	Albert Wood, Peter Dunn, Nicholas Terrett, Andrew Bell, Peter Ellis
1996	Protease inhibitors for patients suffering from HIV	S. Oroszlan, T.D. Copeland

Although technologies have come and gone, it is important to assess what they have given us. The Industrial Age of the 1900s gave us advanced agricultural practices like the use of chemical fertilizers, radio, TV, air conditioning, car, jet planes, modern medicines, fabrics, etc., which can help the rich live like the kings of the past, and also enable paupers to become kings if they have an appropriate understanding of the markets. The Industrial Age removed the distinction between the king and the common man. The Information Age has given us mobile phones, Internet, cable TV, email, ATMs, administrative reforms, and reduced distances, among other things, which have transformed our neighbourhood completely. It has eliminated distances (and distinctions) of all sorts. The next era may remove the barrier between humans and their surroundings in every possible way; life may acquire a seamless link with nature. A prophetic statement indeed!

This change in our lives has occurred due to science. Chemistry has been the driving force in the front, which made major changes possible in the 19th and 20th centuries. The large production of ammonia, sulphuric acid, cement, iron, aluminum, drugs, fibres, dyes, polymers, plastics, petroleum products, etc. has changed the world. What the world of chemistry has produced drives society. Chemistry contributes to more than half the global production, including that of computers. Chemicals drive several economies. While this growth of chemistry was continuing, a major change occurred in 1947 with the discovery of the transistor. In the 1950s and beyond, the advent of semiconductor devices facilitated the development of consumer electronics. Everything that one purchases today has an integrated circuit in it. Gadgets from toys to cars function with these circuits. This, along with computers, helped build an era of physics. Many predict that the next era would be that of biology and materials. In that era, it is highly likely that the interfaces between disciplines rather than the disciplines themselves would contribute largely to developments.

The manner in which this change has occurred has left many distinct marks on society. The typewriter, which was a prized possession till recently, has disappeared completely. Electronic typewriters—manufactured in the era between typewriters and word processors—have also disappeared. The 'typist' has become non-existent in many institutions and there is no more recruitment under this category. Factories producing goods related to the typewriter have vanished before our eyes, in the recent past. This may be contrasted with the disappearance of the blacksmith from Indian villages. The blacksmith, a reminder of the agrarian era disappeared slowly as a result of the advent of new factory-made agricultural implements. While the former development took place over a few decades, the latter has taken centuries. As a result of the changing times, it became necessary to develop several other skills. Programming skills, which were expected to be specialized, became a part of the established set of skills. Today, computer knowledge is no longer considered special, but is expected to be part of the school training.

In spite of the large economic boom that has resulted from the developments in various fields, many problems remain. Poverty is widespread and several communities in the world still suffer from starvation. Clean drinking water is inadequate and many still have no access to it. In India, around 15 per cent of the population has no access to clean drinking water. The global estimate of power requirement for 2050 is 30 PW (P = peta, 10^{15}). Radically new forms of technology will be needed to harness that power. Maintaining a clean environment will be the biggest challenge that humanity will face in the years to come. The alarming depletion of non-renewable resources, forest areas and wetlands, the extinction of animal and plant species, and the deterioration in air and water quality are gigantic problems. These issues are of larger importance to marginalized societies where life is inexorably interlinked with nature. These and the associated problems of healthcare, education and housing are astronomical even with a nominal population growth rate of 1.14 per cent (2004 estimate), which would make us a country of 10 billion