

Nanotechnology: Principles and Practices

Sulabha K. Kulkarni

Nanotechnology: Principles and Practices

Third Edition

 Springer



Sulabha K. Kulkarni
Physics Department
Indian Institute of Science
Education and Research
Pune, India

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To my family

Preface to the Third Edition

Over the past 15 years, the scientific world has witnessed a dramatic interest in nanotechnology with research contributions from physicists, chemists, biologists as well as scientists working in the medical, agricultural, textile and environmental fields. The varied inputs from different disciplines and their complementary nature in the synthesis, characterization, understanding and applications from household items to space technologies have enriched the nanotechnology basics. This can be easily understood as about 80 journals have emerged on nanotechnology and hundreds of thousands of papers have been published in the last 12 years or so. Lecturers aware of this fact naturally want to introduce the new knowledge to the young generation and prepare their students for the great challenges of sustainable management of energy, water and environment faced by mankind.

The availability of a large number of books, review articles and journals on nanotechnology is essential in order to get an overall picture of such a vast field, which is a very difficult task. Particularly in the case of beginners in the field as well as students at the graduate level, the complex terminologies can prevent them from exploring the fascinating world of nanotechnology.

This book makes an attempt to introduce students, teachers and research scientists trying to enter the vast field of nanotechnology to nanosynthesis and various analysis methods and applications in a simple way, without overlooking the necessary principles underlying nanoscience. Continual attempts have been made right from the first edition (2006) to cover the contemporary ideas in the field. Due to the fast growth in the field by the launch of the second edition (2011), some more synthesis and analysis techniques which were becoming popular and newly discovered phenomena and effects were added to the basic contents of the first edition.

In the third edition, the book has been further reorganized keeping Chaps. 1, 2, 3, 4, 5, and 6 as in the second edition with some additional material on fuel cells and solar cells as well as including separate chapters on nanoelectronics and on nanotechnology and environment. The latter chapter, although briefly, gives an idea

of how nanotechnology can help in the detection of air and water pollution and in its remedial approaches. It also describes the negative aspects of nanotechnology that can be harmful to the environment or have adverse effects on human health. The chapter is rather brief because much research is awaited in this area. However, due to its importance, it is included as a separate chapter. In the chapter on nanoelectronics, single electron transistor and spin field-effect transistor are explained in more detail. Besides, two new appendices on the Kronig–Penney model and a data table on bulk semiconductors are included, which will provide some ready data for solving small problems like determination of band gaps in nanomaterials.

It is expected that this edition would give a good overview and provide a strong foundation of nanotechnology to its students. Most part of the book was prepared through my teaching notes, which were updated from time to time, while teaching nanotechnology at the University of Pune and the Indian Institute of Science Education and Research (IISER), Pune, for more than a decade. The book also contains some part of my own research (as well as that of my PhD and postgraduate students) in Nanotechnology and Condensed Matter Physics. Many of my students have contributed by way of preparing diagrams and sketches and providing photographs as well as carefully going through some parts of the book. For the third edition, I would like to thank Dr. Pavan G.V. Kumar, Dr. Smita Chaturvedi, Ms. Rashmi Runjhun, Mr. Prashant Bhaskar, Mr. Amey Apte, Mr. Arshad Nair and Ms. Supreet Singh for reading the drafts, making suggestions and drawing figures. I also thank the Director of IISER Pune Prof. K.N. Ganesh and Chair of the Physics Programme at IISER Pune Prof. Sunil Mukhi for their generous support while preparing this edition.

Last but not the least, I would like to thank Capital Publishing Company and Springer for their help, suggestions and careful proofreading of this edition.

Pune, India
May 2014

Sulabha K. Kulkarni

Preface to the Second Edition

Nanotechnology has now become a buzz word all over the world. Even the common man and school children hear the word “Nano”—may be through the cars rolling on the streets, housing projects and products like washing machines or mobiles. In some products there may not be any use of nanomaterials but the word indeed has become popular to indicate ‘small’. This indeed shows to some extent awareness, importance and acceptance of nanotechnology and nanoscience.

Nanotechnology is being introduced in many curricula at post-graduate and under-graduate levels although research in this field has not reached its saturation. It has therefore become indeed difficult to find any book which will be able to give all the new developments in the field with enough coverage keeping basic components intact.

In this edition attempt is made not to remove almost any of the original material of the first edition but add more material like ‘*Self Assembly*’ as a separate chapter (No. 6) and an Appendix (IV) on ‘*Vacuum Techniques*’. Although the word and some examples of ‘self assembly’ were part of the previous edition, progress in ‘Self Assembly’ and its importance is so overwhelming that it deserved a separate chapter in this book. However, I am quite aware that more material in this chapter also would have been in order. The appendix on ‘Vacuum Techniques’ would serve the readers to at least get an idea of this essential technology needed to synthesize nanomaterials like in physical and chemical vapour deposition systems. It also forms an integral part of numerous analysis instruments like ‘Electron Microscopes’ or spectroscopy techniques like ‘Photoelectron Spectrometer’ discussed in Chap. 7. In Chap. 7 the readers will also find some techniques like ‘*Dynamic Light Scattering*’ and ‘*Raman Spectroscopy*’ introduced in this edition. There are more illustrations introduced in this chapter. In Chap. 4 on Chemical Synthesis, additional techniques like ‘*Hydrothermal Synthesis*’, ‘*Sonochemical Synthesis*’, ‘*Microwave Synthesis*’ and ‘*Micreactor*’ or ‘*Lab-on-Chip*’ are introduced in the new edition. Similarly, in Chap. 9 on Nanolithography, the concepts of ‘*Nano Sphere Lithography*’ and ‘*Nanoimprint Lithography*’ are introduced.

Chapter 8 has a separate section on '*Clusters*' and has been named as 'Properties of Clusters and Nanomaterials' as against the 'Properties of Nanomaterials' in the previous edition. In Chap. 10 on Some Special Nanomaterials one would find '*Graphene*' and '*Metamaterials*' or '*Negative Refractive Index*' materials being introduced. Chapter 11 on applications is a chapter for which sky is the limit! Therefore attempt is made to introduce only the '*Solar Cells*' and '*Lotus* (as well as *Gecko*) *Effect*' which perhaps needed more attention. There is a considerable concern now on developing renewable, inexpensive, clean or pollution-free energy sources and solar cells based on nanomaterials open up a challenge for the scientists and technologists. Similarly with understanding of lotus effect, many new self cleaning products are around and deserve an introduction. One more experiment on making ordered pores in aluminum foil (*AAO templates*) is given in the new edition. This itself can be an interesting experiment as well as some may find it useful to deposit later materials in pores to make ordered nanorods for some applications like solar cells.

Thus it is hoped that the readers would find lot of new concepts, materials, techniques and application areas introduced in the second edition of the book.

Pune, India
March, 2011

Sulabha K. Kulkarni

Preface to the First Edition

Periodic table with 118 elements is quite limited in number. But by combination of different elements in certain proportions, nature has produced a number of gases, liquids, minerals and above all, the living world. Mankind too, ingeniously working, learnt to make a large number of materials and even cast or shape them for desired functions or operations. Starting with stone implements man learnt to separate metals and make alloys. He made wonderful organic and inorganic materials.

Now we use wood, metals, alloys, polymers etc. for our comforts. Some materials are directly taken from the nature and some are man-made. All the materials used today have a variety of functions, which is the fruit of skill and intellect of many generations of mankind. All this has led to wonderful electronic systems, communication tools, transport vehicles, textile, utensils, architectural materials, medicines etc.

Mankind has been constantly trying to overcome its physical limitations. Animals like horse can gallop at high speed and only the birds can fly. But by inventing the appropriate materials and understanding nature's aviation system, man has been able to develop vehicles that run faster than a horse and fly in the sky reaching a height impossible for a bird. He has developed the communication and navigation systems, which take him or his instruments to distant planets. He may not physically go everywhere but he has tried ingeniously to get some knowledge of different planets, stars or even the galaxies.

But in order to continue with such adventures, man needs more and more materials with controlled properties. He needs materials not known before. He needs materials, which are highly efficient, often small in size and novel. In the attempt of making lightweight and smaller and smaller electronic devices, scientists have reduced the size of materials to such an extent that it has reached nanometric dimensions. At such a scale new phenomena are observed for practically all the

materials known so far, leading to novel devices and potential applications in different fields from consumer goods to health related equipment. Perhaps we are now living in the age Nobel laureate Richard Feynman dreamt of in 1959. He, in his now very famous speech delivered to the American Physical Society, said that why not mimic nature and produce smaller and smaller functional materials, which will be highly efficient. At that time the computers were very big occupying large buildings yet only good enough to make calculations now done on a palm size calculator. Scientists used to be still proud of those computers. The radio sets used to be occupying large space and be power hungry. But now see the change of scenario after forty years. We have smaller and efficient Personal Computers (PC), Laptops, Compact Disc (CD) players, pocket transistors, mobiles with digital camera and what not. Although Feynman did not utter the words ‘Nanoscience’ or ‘Nanotechnology’ we see the advantages of making things small.

However, it may be remembered that nanomaterials are not really new. Michael Faraday synthesized stable gold colloidal particles of nano size in 1857 A.D. His gold samples are still in the British Museum in U.K. showing beautiful magenta-red colour (not golden!) solution. Decorative glass windows with beautiful designs in old churches and palaces indeed use nanoparticles of iron, cobalt, nickel, gold, silver etc. Photographic plates also have nanoparticles and whole branch of catalysis in chemistry has a variety of catalyst particles in nanometer range. However in all such examples there were systematic attempts to understand the size effects on properties—either lacking or insufficient. The lack of powerful microscopes, which would correlate the sizes to properties was the main barrier in early work. One can consider some of the milestones (or history) in Nanotechnology as given in Box 1.

Box 1: Milestones in Nanotechnology

- 1857—Michael Faraday synthesized gold colloids of nanosize
- 1915—W. Ostwald, a famous chemist, wrote a book ‘World of Neglected Dimensions’ in German
- 1931—E. Ruska and M. Knoll developed the first electron microscope
- 1951—E. Müller developed the Field Ion Microscope which enabled the imaging of atoms from the tip of metallic samples
- 1959—R. Feynman delivered his now very famous talk ‘There is Plenty of Room at the Bottom’ pointing out to the scientists that reduced dimensionality of materials would create fascinating materials
- 1968—A.Y. Cho and J. Arthur developed Molecular Beam Epitaxy technique for layer by layer growth of materials
- 1970—L. Esaki demonstrated the quantum size effect (QSE) in semiconductors

(continued)

Box 1 (continued)

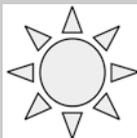
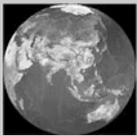
- 1980—A.I. Akimov showed QSE in CdS and CdSe particles dispersed in glass, triggering the research on nanoparticles
- 1981—G. Binnig and H. Rohrer developed the scanning tunnelling microscope (STM) by which atomic resolution could be obtained. This was also followed by a family of scanning probe microscopes of various types
- 1985—R.F. Curl, H.W. Kroto and R.F. Smalley synthesized sixty atom carbon molecule, later named as ‘Fullerene’
- 1989—D.M. Eigler wrote letters ‘IBM’ using xenon atoms
- 1991—S. Iijima discovered ‘carbon nanotubes’
- 1999—C.A. Mirkin developed the ‘Dip Pen Lithography’
- 2000—D.M. Eigler devised ‘Quantum Mirage’ using Fe atoms on the copper substrate.

Beginning of the twenty first century has witnessed a tremendous upsurge of scientific activity in the field of ‘Nanoscience’ and ‘Nanotechnology’, whose seeds were sowed in the last century. Scientists, technocrats and even governments of many countries all over the world are convinced that nanotechnology based on nanoscience is the technology of twenty first century. The terms ‘Nanotechnology’ and ‘Nanoscience’ are often used synonymously. The literal meaning of ‘nano’ is ‘dwarf’ or an abnormally short person. However in scientific language it is a billionth (10^{-9}) part of some unit scale, e.g. nanometre or nanosecond mean 10^{-9} m [see Box 2] or 10^{-9} s respectively. Nanometre is so small that if you imagine only ten atoms of hydrogen placed in a line touching each other it will measure one nanometre. To get a qualitative idea, see Box 3. Nanotechnology is thus the technology of materials dealing with very small dimension materials usually in the range of 1–100 nm. When at least one of the dimensions of any type of material is reduced below 100 nm, its mechanical, thermal, optical, magnetic and other properties change at some size characteristic of that material. Thus within the same material one can get a range of properties. For example [See Box 4] consider a semiconductor like CdS, which is normally reddish in colour. If one brings down the particle size (i.e. diameter) of CdS to say 10 nm, its powder still has red colour. But below about 6 nm size, a dramatic change occurs in the optical properties of CdS. As illustrated in the photograph the colour of 4 nm size particles is orange, 3 nm size particles is yellow and that of 2 nm size particles is white. Not only the visual appearance but other properties also change dramatically. Melting point for pure bulk solids is very sharply defined. If we measure the melting point for CdS nanoparticles (i.e. particles with diameter in few nanometres range) then we will find that the melting point reduces with the particle size. Therefore by changing the particle size of a material one can achieve a range of properties.

Box 2

Factor	Symbol	Prefix	Factor	Symbol	Prefix
10^{-18}	a	atto	10^1	da	deka
10^{-15}	f	femto	10^2	h	hecto
10^{-12}	p	pico	10^3	k	kilo
10^{-9}	n	nano	10^6	M	mega
10^{-6}	μ	micro	10^9	G	giga
10^{-3}	m	milli	10^{12}	T	tera
10^{-2}	c	centi	10^{15}	p	peta
10^{-1}	d	deci	10^{18}	E	exa

Box 3: Comparison of Different Objects

	Diameter of the Sun	1,393,000 km
	Diameter of the Earth	12,715 km
	Height of Himalaya Mountain	8,848 m
	Height of a Man	1.65 m
	Virus	20–250 nm
	Cadmium Sulphide Nanoparticles	1–10 nm

Box 4: CdS Nanoparticles (Colour Change with Particle Size)

Technologists thus find tremendous potential of nanomaterials from consumer goods to space applications. In a span of few years there have emerged a number of manufacturers selling products like cosmetics, clothes, TVs, computers, medicines, toys, sports goods, automobile etc. which use some nanomaterial or the other.

Nanotechnology is an interdisciplinary science. It needs Physics, Chemistry, Engineering, Biology etc. so that its full potential can be exploited for the advantage of mankind. What has been achieved in nanotech so far is only the tip of the iceberg. However to fully explore the potential of nanotechnology it is essential to know what are nanomaterials, how and why do they differ from other materials, how to synthesize/analyze the nanomaterials organize them and understand some already proven application areas.

There are several books available on nanotechnology written by the leading scientists working in nanotechnology. Most of the books, however, are collection of research articles. This means the reader is expected to have considerable background in basic sciences. Often there is a jargon of technical terms, which is difficult to understand.

This book aims at developing sufficient background for students of graduate and post-graduate levels. Some boxes are given so that without leaving the main flow of the text additional material could be given. The book is meant to be self-sufficient.

Pune, India
September, 2006

Sulabha K. Kulkarni

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