Chapter 1

Introduction

"Science is a way of thinking much more than it is a body of knowledge."

- Carl Sagan

1. 1 Introduction

In the last 2 decades, escalating development of nanoscience and nanotechnology can be attributed to fascinating properties as well as advanced & multifunctional applications of nanomaterials. The research in this field is fuelled chiefly because of the accessibility of new methods of synthesizing nanomaterials as well as tools for characterization and manipulation [1].

The complete spectrum of contemporary activities towards the proposed industrial revolution is expected to revolve around nanotechnology and its associated research discipline of nanoscience. The framework for this field was originally proposed by Richard Feynman through his very famous lecture in 1959 [2]. He opined that nanoscience and nanotechnology would encompass the entire gamut of physical, chemical, biological, mathematical and engineering sciences needed to develop the purposeful capabilities of nano-manipulations, nano-structural modifications, miniaturization and bottom-up technology. Accelerated and incredible developments have been witnessed in this field since then. It is noteworthy that most of the work covered in the present thesis deals with nanostructured materials, and therefore, it is appropriate, to begin with, a brief introduction to nanotechnology and nanomaterials to put the subject matter in proper perspective.

1. 2 Nanoscale Phenomena

Tokyo Science University Professor Norio Taniguchi coined the term "nanotechnology" in 1974 via a research paper as follows: 'Nanotechnology' mainly consists of the processing, separation, consolidation, and deformation of materials by one atom or by one molecule [3]. The prefix nano in the word nanotechnology means a billionth (10^{-9}) of a meter. Thus, nanotechnology can be termed as the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. Nanotechnology deals with the study of materials and systems having at least one dimension in between 1 nm to 100 nm. This definition, however, is fussy and needs to be taken with a pinch of salt. It is the generalization of many definitions stated by different researchers and institutions. In the 1980s, the basic idea of this definition was explored in much more depth by Dr. K. Eric Drexler, who promoted the technological significance of nano-scale phenomena and devices through speeches and the books like Engines of Creation: The Coming Era of Nanotechnology [4] and *Nanosystems: Molecular Machinery, Manufacturing, and Computation* [5], and henceforth the term 'nano' acquired its current sense. The earlier book [4] is considered the first book on the topic of nanotechnology.

1.3 Different Types of Nanostructures

After the experimental research work on nanomaterials had started, various types of interesting nanostructures were synthesized. Some of the most significant alterations of nanostructured materials are enlisted in Table 1.1.

Sr. No.	Nanostructure	Size	Material Form
1	Clusters, Nanocrystals, Quantum dots	Diameter: 1–10 nm	Insulators, semiconductors, metals, magnetic materials
2	Spherical nanoparticles	Diameter: 1–100 nm	Ceramics
3	Nanobiomaterials	Diameter: 5–20 nm	Membrane protein, Photosynthetic reaction center
4	Nanowires	Diameter: 1–100 nm	Metals, semiconductors, oxides, sulfides, nitrides
5	Nanotubes	Diameter: 1–100 nm	Carbon, semiconductors, oxides, nitrides
6	Nanobiorods	Diameter: 5 nm	DNA
7	2D arrays of nanoparticles	Area: several nm^2–μm^2	Metals, semiconductors, magnetic materials
8	Surfaces and thin films	Thickness: 1–1000 nm	Insulators, semiconductors, metals, DNA, graphene
9	3D superlattices of nanoparticles	Diameter: several nm	Metals, semiconductors, magnetic materials
10	Hierarchical nanostructures: Nanoflowers, Sea urchins, Chest-nut husks, combs, etc	Dimensions: few nm to few hundred nm	Metals, semiconductors, insulators, magnetic materials

Table 1.1 *Nanostructures and their assemblies [6-8].*

Apart from these different nanostructures and their assemblies, nanocomposites are recently developed which constitute technologically an important class of materials where nanoparticles in size range of 1-100 nm with wide variety of morphologies viz. nanoplates, nanotubes or nanoclusters are dispersed in a suitable matrix such as glass, ceramic, metals, polymers, etc.

A composite material is an amalgamation of two or more materials possessing utterly different yet exclusive physical and chemical properties that are recognized at the interface of the materials. Nanocomposite materials are typically composed of an inorganic solid host containing an organic component or vice versa. They may also consist of two or more inorganic/organic phases involving combination in tangible form with the condition that at least one of the phases or features exist in the nano size regime [9]. Thus, nanocomposites are materials wherein a small amount of the nanomaterials or nanofillers are dispersed uniformly in the matrix, usually a polymer [10]. As part of the study presented in this dissertation pertains to the synthesis of semiconductor nanostructures in a polymer matrix, henceforth, we confine our discussion on nanocomposites to polymer nanocomposites only.

Nanoscale particles or fillers are especially attractive to the creation of composite materials based on polymer matrices, as they have some properties which are not unique to bulk materials. Polymer nanocomposites are defined as materials in which wide variety of nanostructure morphologies viz. nanoplates, nanotubes, nanoclusters or nanoparticles ~ 1-100 nm size are dispersed in the polymer matrix. Remarkable impact on the physical, chemical, mechanical, thermal, magnetic and electrical properties of the resultant nanocomposites can be induced by the sheer presence of few weight percent of these nanostructures. They are investigated in numerous fields due to an optimum balance of characteristics such as ease of processing, light weight, excellent thermal and chemical resistance, etc. Such characteristics can be favourably exploited for engineering applications and in next-generation smart device fabrication.

1. 4 Nano-Length Scale Dependent Properties

In general, nanostructures exhibit changes in their properties when the size is reduced below a particular nanoscale regime where it shows a drastic deviation in the property when compared to its bulk counterpart. This generalization allows accommodation of a vast array of materials and their various nanoscale dependent properties. Figure 1.1 summarizes the characteristics length scales associated with various solid-state-science phenomena.

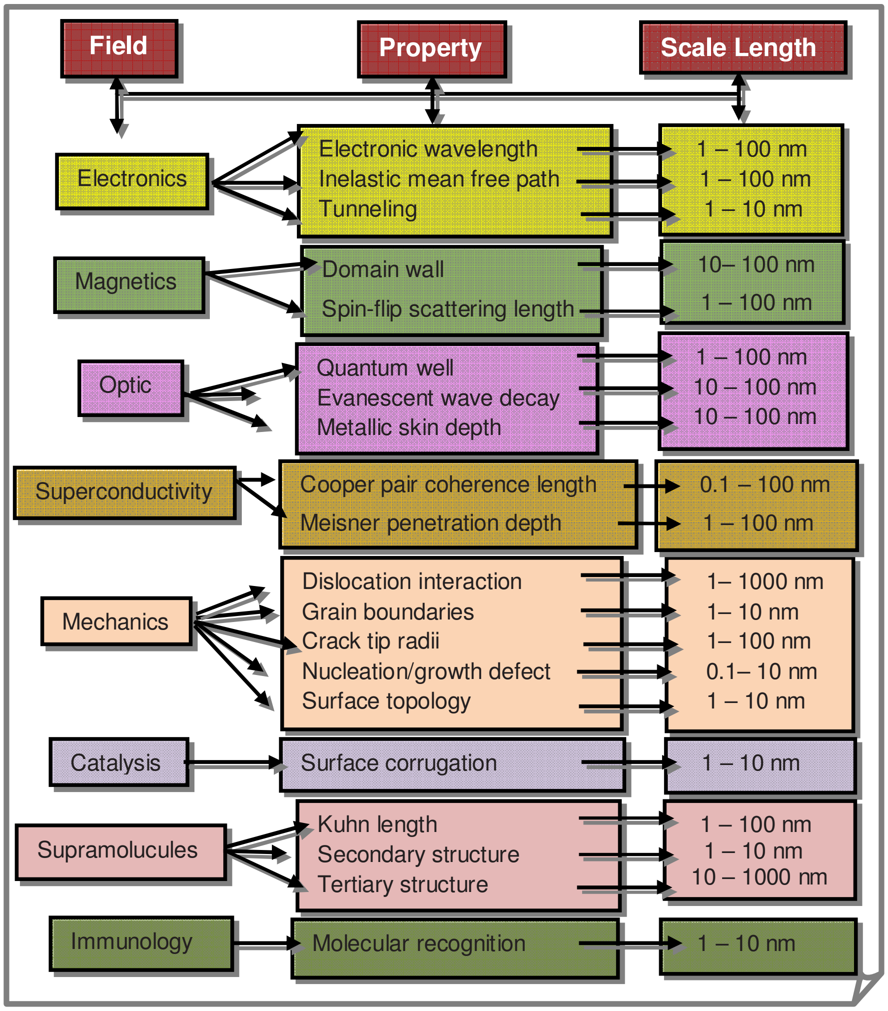

Figure 1.1 *Characteristic nanoscale length-scales in solid-state science phenomena [11]*

It is evident that most of the solid-state materials science phenomena occur at length scales in the range of 1-100 nm. Therefore, the general definition of nanostructures has been restricted to the 1-100 nm scale by most researchers. In this context, nanomaterials bridge the gap between nanoscience and nanotechnology and link the two areas together. It is recognized that the size range that provides the greatest potential and, hence, the greatest interest is below 100 nm. It has been observed that the physical properties of nanomaterials are substantially different from that of the corresponding bulk materials. The considerable difference in properties can be ascribed to high surface to volume ratio and high surface energy of the nanoparticles as compared to the bulk counterpart materials. On account of these properties, numerous applications have been credited to the nanomaterials.

1.5 Applications of Nanomaterials

At present, nanoscale materials are being developed at accelerating pace for a variety of applications in all kind of sectors and products, e.g. electronics, cosmetics, automobiles, building and construction materials, medical & pharmaceuticals, energy and environmental, etc. All these modern applications are based on their specific properties that are related to nanoscale properties. Many possible applications are also in the pipeline. Quite interestingly, nanotechnological applications in different fields are based on distinctly different demands, and, in turn, face very different challenges. Moreover, different strategies are developed accordingly. For example, molectronics has been developed as a branch which requires different approaches, such as molecular electronics in which single molecules are expected to be able to control electron transport. Nanorobots are envisioned to act as vehicles for delivery of therapeutic agents, detectors, or guardians against early disease and perhaps repair of metabolic or genetic defects, molecular recognition in biological molecules, etc.

Apart from these novel futuristic applications, some of the nanomaterial based applications are on the verge of commercialization or have already reached the market.

Biophysics, Biochemistry, biotronics (biomolecules on chips), biofabrication, computational biology, etc. are the broad areas where nanomaterials normally used in the field of bioscience. Medical and health biology nanotechnologies already use quantum dots or synthetic chromophores to selected molecules (e.g. proteins) for intracellular imaging [12]. Here, nanomaterials help in gene and drug delivery system to improve therapy efficacy. The challenge is to make nanoparticle device capable of targeting specific diseased cells, which contains both therapeutic agents that are released into the cell and an onboard sensor that regulated the release. Intense research efforts the in this direction are going on. In cosmetics, nanoparticles are already being used in sunscreen lotions which absorb UV rays. In engineering sectors, nanomaterials are regularly used in various types of devices and components. Few nanometer thick surface coating of certain materials improves the properties like wear and scratch-resistance, hydrophobic properties. Photocatalytic titanium dioxide (TiO_2) coatings on windshields and mirrors of automobiles assist in rapidly removing for and improving visibility for drivers. Some hard nanomaterials such as tungsten carbide, tantalum carbide and titanium carbide that have more wear and erosion resistance, durability, and toughness than their counterparts are now used for making cutting tools (e.g. mill machine tools). Nanoparticles of zinc oxide (ZnO),

TiO_2, etc. are also used in paint industry to get better paint properties. Carbon nanotubes based field emission displays (FED) for the next generation of monitor and television are already in the market. Supercapacitors (based on graphene and allied nanomaterials) are being used in the various application, for example, to reduce cranking while starting an automobile. Various nanomaterials based such as lithium (Li), sodium (Na), manganese (Mn), ion batteries are also available in the market. However, this is just beginning, and in the near future, nanomaterials are expected to span all areas of human life through concentrated efforts.

Figure 1.2 presents the summary of the applications of the prepared nanostructures in different fields. As evident from this figure, nanomaterials have the enormous potential for applications in every aspect of enrichment of human life and the environment.

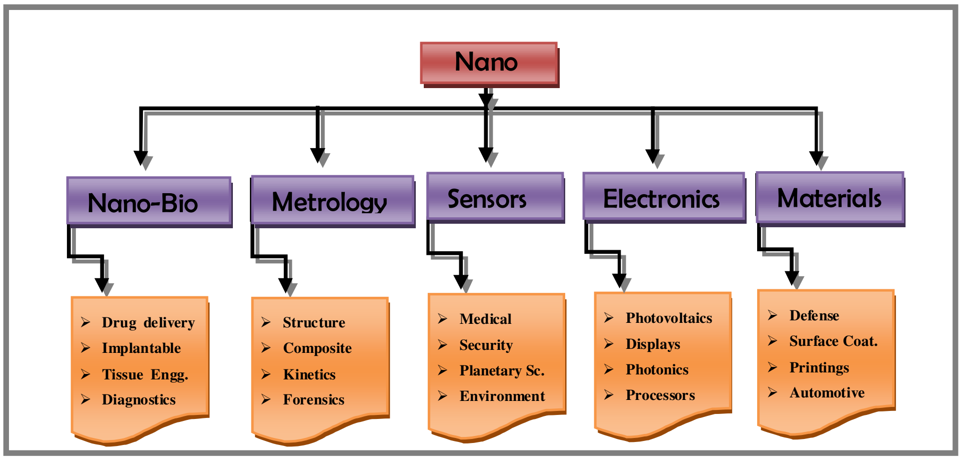

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Figure 1.2 *The Applications of nanomaterials*

These applications can be linked simultaneously to size and morphology dependent nanoscale phenomena occurring in different nanostructured material forms.

Apart from the above mentioned applications of various nanostructures, nanocomposites of inorganic materials in polymer matrices have also been considered as the technologically one of the most important materials because of their diverse range of applications in solar cells [13], polymer electrolyte membrane fuel cells [14], sensors for detection of different analytes [15,16], electrode for supercapacitors [17], membranes for gas separation [18]. Xin Zhao et. al. have reviewed the environmental applications of polymer nanocomposites [19]. Xiao Feng Lu et al. have conducted an extensive review of the applications of nanocomposites in electronic nanodevices, chemical and biological sensors, catalysis and electrocatalysis, energy, microwave absorption and electromagnetic interference shielding, electrorheological fluids, and biomedicine [20].

To realize these applications, controlled preparation of polymer nanocomposites is an important aspect. Such nanocomposites are in general created using four approaches as enlisted - (i) direct dispersion of nanoscale material into a polymer in molten or liquid form (for example: addition of several types of nanoscale metal oxide and hydroxide to polymeric matrix), (ii) production of nanoscale building blocks *in situ* in a polymer matrix via reduction of metal ions in polymer matrix, (iii) accomplishment of polymerization of monomers in the presence of nanoscale building blocks (e.g. polymerization of methyl methaacrylate or styrene in presence of nanoparticles), (iv) concurrent and *in situ* polymerization as well as formation of nanoscale building blocks (for example: polymerization of methyl methaacrylate or styrene monomers as well as reduction of metal ions during the same process). For the present work, solid-solid route (*chapter 4*) has been used for the synthesis of semiconductor based nanocomposites within the matrix of polyphenylene sulfide which can be linked to the (ii) approach mentioned above.

1. 6 Thesis Framework

In a nutshell, this chapter has provided a brief overview of nanoscale phenomena, its associated properties, and applications. In lieu of these fascinating properties and applications offered by nanostructures and nanocomposites, there are many technological challenges that need to be addressed such as development and production of more sophisticated and specialized materials with a minimal environmental blow. In this context, the first challenge is to garner precise control over the size, shape, composition, and yield as well as cost effectiveness of the synthesized nanostructured products which play a vital role in the synthesis procedure so as to realize their end application in any nanoscale materials based device. The second challenge is to explore suitable applications synthesized nanostructures. In the present dissertation, we have tried to address both these challenges. In this contact, the brief framework of each chapter of this thesis is given in figure 1.3 which pictorially summarizes the overall work.

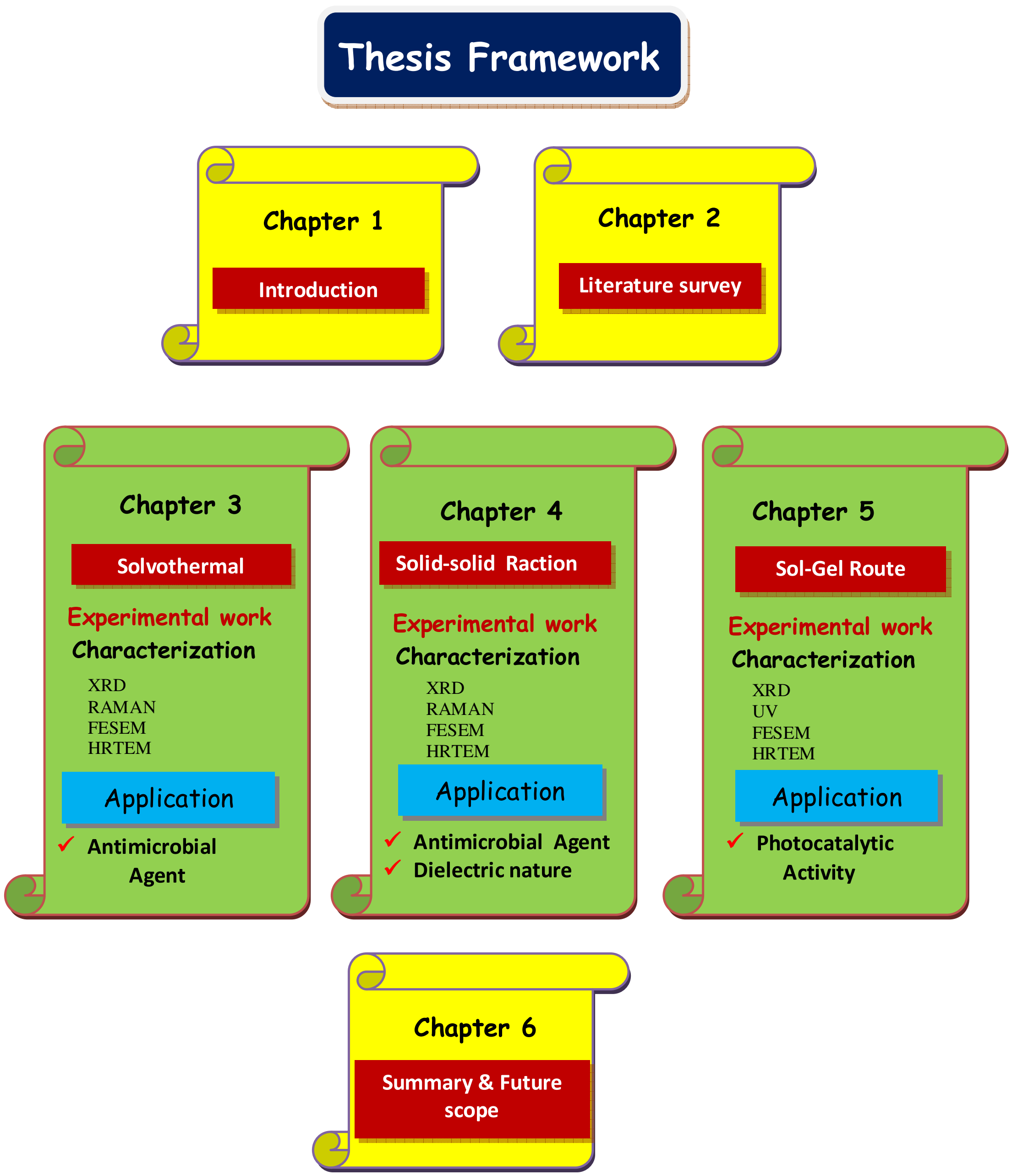

Figure 1.3 *Thesis framework*

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