

Nanomaterials

Basic Concepts and Applications

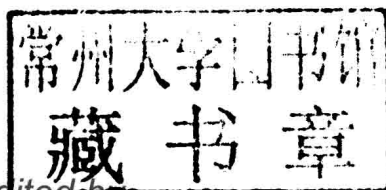


Edited by
Hardev Singh Virk

Nanomaterials

Basic Concepts and Applications

Special topic volume with invited peer reviewed papers only.



Edited by

Hardev Singh Virk



Copyright © 2015 Trans Tech Publications Ltd, Switzerland

All rights reserved. No part of the contents of this publication may be reproduced or transmitted in any form or by any means without the written permission of the publisher.

Trans Tech Publications Ltd
Churerstrasse 20
CH-8808 Pfaffikon
Switzerland
<http://www.ttp.net>

Volume 222 of
Solid State Phenomena
ISSN print 1012-0394
ISSN cd 1662-9787
ISSN web 1662-9779

(Pt. B of Diffusion and Defect Data - Solid State Data (ISSN 0377-6883))

Full text available online at <http://www.scientific.net>

Distributed worldwide by

Trans Tech Publications Ltd
Churerstrasse 20
CH-8808 Pfaffikon
Switzerland

Fax: +41 (44) 922 10 33
e-mail: sales@ttp.net

and in the Americas by

Trans Tech Publications Inc.
PO Box 699, May Street
Enfield, NH 03748
USA

Phone: +1 (603) 632-7377
Fax: +1 (603) 632-5611
e-mail: sales-usa@ttp.net

printed in Germany

Nanomaterials

Basic Concepts and Applications

Edited by
Hardev Singh Virk

Editor's Note

The present volume “Nanomaterials: Basic Concepts and Applications”, as the title suggests, deals with basic concepts and applications of nanomaterials, a buzz word in the modern world of Science and Technology. Because of advanced characterization and new fabrication techniques, nanomaterials are now central to multiple disciplines, including materials science, chemistry, physics, engineering and medicine. This special volume under Solid State Phenomena series will present an overview of recent research developments, including synthesis, characterization and applications in Nanoelectronics, Luminescence, Drug Delivery, Memristors, Solar Cells and Semiconductors.

There are 8 Chapters in this volume. First Chapter: “Luminescence of II-VI Semiconductor Nanoparticles” is the longest chapter in this volume. Luminescence of II-VI semiconductor nanoparticles such as ZnS, CdS, ZnO, etc. has attracted a lot of attention in the last two decades due to their unique properties and potential applications in electronics, lighting industry, displays, DNA markers and other medical fields. In the present chapter, the history, preparation, characterization, and optical absorption of nanoparticles are discussed in great detail; and the challenges and applications of the luminescence of semiconductor nanoparticles are explored. It is believed that the systematic investigation of a ‘synthesis-property-application’ triangle for the nanoparticles will inspire more research activities to solve the current challenges and promote deep curiosity and intense interest in the study of inorganic semiconducting nanoparticles.

Second Chapter “Oxide Nanomaterials and their Applications as a Memristor” outlines the unique properties, synthesis techniques and applications of oxide nanomaterials. The important and unique properties of TiO_2 and ZnO nanomaterials with their possible crystal structures have been discussed. In application part, the oxide nanomaterials, especially ZnO has been discussed for memory device applications. Oxide nanomaterials find application in memristor device application, which are becoming the hotspots in the field of physics, electronics as well as materials.

Third Chapter “Nano Electronics: A New Era of Devices” is a noteworthy contribution by Biomolecular Electronics and Nanotechnology Division (BEND) Group of CSIO, Chandigarh. Many molecules show interesting electronic properties, which make them probable candidates for electronic device applications. The challenge is to interpret their electronic properties at nanoscale so as to exploit them for use in new generation electronic devices. The authors

look around for alternative materials, for example, organic molecules, proteins, carbon materials, and DNA, for electronic device application and new methods for electronic device fabrication.

Fourth Chapter “Progress in Plasmonic Enhanced Bulk Heterojunction Organic/Polymer Solar Cells” discusses the enormous potential of thin-film photovoltaic technologies. Organic/polymer solar cells have many intrinsic advantages, such as their light weight, flexibility, and low material and manufacturing costs. This Chapter reviews the different plasmonic effects occurring due to the incorporation of metallic nanoparticles in the polymer solar cell. It is shown that a careful choice of size, concentration and location of plasmonic metallic nanoparticles in the device result in an enhancement of the power conversion efficiencies, when compared to standard organic solar cell devices.

Chapters 5 and 6 review an important application of Carbon nanotubes and potential of nanomaterials, respectively, as drug delivery vehicles to treat cancer and other maladies effectively. Carbon nanotubes are enjoying increasing popularity as building blocks for novel drug delivery systems as well as for bioimaging and biosensing. The recent strategies to functionalize carbon nanotubes have resulted in the generation of biocompatible and water-soluble carbon nanotubes that are well suited for high treatment efficacy and minimum side effects for future cancer therapies with low drug doses. Currently a number of nanomaterials are under investigation for their suitability as sustained, controlled and targeted drug carriers. However, authors of Chapter 6 confine their discussion to lipidic and polymeric nanomaterials, the two most commonly promoted, and safe nanosystems for delivery of both the chemical or small molecular entities (SME) and the macromolecules including genes and siRNA.

Chapter 7 is a research paper based on “Photoluminescence in a Novel Aldo-Keto Synthesized $\text{YPO}_4:\text{Eu}^{3+}$ Nanophosphor”. The luminescence studies were carried out by photoluminescence (PL) spectroscopy. The PL spectra reveal that the orange emission ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) was more intense than a normal red emission ($^5\text{D}_0 \rightarrow ^7\text{F}_2$). Chapter 8 “Recent Advances in the Synthesis and Characterization of Chalcogenide Nanoparticles” discusses in detail the synthesis strategies of size and shape controlled nanoparticles belonging to II-VI group of semiconductor chalcogenides. Nanoparticles and self-assemblies of CdSe, CdTe, HgTe and ZnSe are synthesized and characterized using new and facile single source molecular precursors based noble route by the authors. Some recent applications of chalcogenides QDs in the fields of solar cell, optical fibre amplifiers, biosensing and bo-imaging are discussed in this Chapter.

H.S. Virk

Table of Contents

Editor's Note

v

Luminescence of II-VI Semiconductor Nanoparticles	
B.P. Chandra, V.K. Chandra and P. Jha.....	1
Oxide Nanomaterials and their Applications as a Memristor	
S.K. Tripathi, R. Kaur and M. Rani.....	69
Nano Electronics: A New Era of Devices	
I. Kaur, S. Yadav, S. Singh, V. Kumar, S. Arora and D. Bhatnagar	101
Progress in Plasmonic Enhanced Bulk Heterojunction Organic/Polymer Solar Cells	
S.K. Tripathi, S. Sachdeva, K. Sharma and J. Kaur.....	119
Carbon Nanotubes as Drug Delivery Vehicles	
S. Arora, V. Kumar, S. Yadav, S. Singh, D. Bhatnagar and I. Kaur	147
Potential of Nanomaterials as Movers and Packers for Drug Molecules	
I.P. Kaur, M. Singh, M. Yadav, S.K. Sandhu, P.K. Deol and G. Sharma	163
Photoluminescence in a Novel Aldo-Keto Synthesized $\text{YPO}_4\text{:Eu}^{3+}$ Nanophosphor	
K.A. Koparkar, N.S. Bajaj and S.K. Omanwar.....	183
Recent Advances in the Synthesis and Characterization of Chalcogenide Nanoparticles	
P.K. Bajpai, S. Yadav, A. Tiwari and H.S. Virk.....	191
Keyword Index	235
Author Index	237

Luminescence of II-VI Semiconductor Nanoparticles

B.P.Chandra^{1a}, V. K. Chandra^{2b} and Piyush Jha^{3c}

¹Emeritus Professor, School of Studies in Physics and Astrophysics, Pt. Ravishankar Shukla University, Raipur- 492010 (C.G.), India

²Department of Electrical and Electronics Engineering, Chhatrapati Shivaji Institute of Technology, Shivaji Nagar, Kolihapuri, Durg 491001 (C.G.), India

³Department of Applied Physics, Raipur Institute of Technology, Chhatauna, Mandir Hasuad, Raipur 492101 (C.G.), India

^abpchandra4@yahoo.co.in(corresponding author); ^bvivekchandra1@rediffmail.com
^cpiyushjha22@rediffmail.com

Keywords: Nanoparticles, Synthesis, Characterization, II-VI Semiconductors, Luminescence

Abstract. Nanoparticle or an ultrafine particle is a small solid whose physical dimension lies between 1 to 100 nanometers. Nanotechnology is the coming revolution in molecular engineering, and therefore, it is curiosity-driven and promising area of technology. The field of nanoscience and nanotechnology is interdisciplinary in nature and being studied by physicists, chemists, material scientists, biologists, engineers, computer scientists, etc. Research in the field of nanoparticles has been triggered by the recent availability of revolutionary instruments and approaches that allow the investigation of material properties with a resolution close to the atomic level. Strongly connected to such technological advances are the pioneering studies that have revealed new physical properties of matter at a level intermediate between atomic/molecular and bulk. Quantum confinement effect modifies the electronic structure of nanoparticles when their sizes become comparable to that of their Bohr excitonic radius. When the particle radius falls below the excitonic Bohr radius, the band gap energy is widened, leading to a blue shift in the band gap emission spectra, etc. On the other hand, the surface states play a more important role in the nanoparticles, due to their large surface-to-volume ratio with a decrease in particle size (surface effects). From the last few years, nanoparticles have been a common material for the development of new cutting-edge applications in communications, energy storage, sensing, data storage, optics, transmission, environmental protection, cosmetics, biology, and medicine due to their important optical, electrical, and magnetic properties.

Luminescence of II-VI semiconductor nanoparticles such as ZnS, CdS, ZnO, etc. has attracted a lot of attention in the last two decades due to their unique properties and potential applications in electronics, lighting industry, displays, DNA markers and other medical fields. In the present paper, the history, preparation, characterization, and optical absorption of nanoparticles are discussed. Then, the photoluminescence, electroluminescence, electrochemiluminescence, thermoluminescence, and elastico-mechanoluminescence of II-VI semiconductor nanoparticles are described. Finally, the challenges and applications of the luminescence of II-VI semiconductor nanoparticles are explored. It is mentioned that the great efforts made in the nanoparticle research during the last decade have gathered enormous knowledge related to nanoparticles and pointed out many important challenges. It is believed that the systematic investigation of a 'synthesis-property-application' triangle for the nanoparticles will inspire more research activities to solve the current challenges and promote deep curiosity and intense interest in the study of inorganic semiconducting nanoparticles.

Contents of Paper

1. Introduction
2. Historical Background
3. Preparation of Nanoparticles

4. Characterization of Nanoparticles
 - 4.1 X-Ray Diffraction (XRD)
 - 4.2 Field Emission Scanning Electron Microscopy (FESEM)
 - 4.3 High Resolution Transmission Electron Microscopy (HRTEM)
 - 4.4 Photoluminescence Spectroscopy
 - 4.5 Fourier Transform Infrared (FTIR) Spectroscopy
 - 4.6 UV-Vis Spectroscopy
 - 4.7 Raman Spectroscopy
5. Absorption Spectra of Nanoparticles
6. Luminescence of Nanoparticles
 - 6.1 Photoluminescence
 - 6.2 Electroluminescence
 - 6.3 Electrochemiluminescence
 - 6.4 Thermoluminescence
 - 6.5 Elastico-luminescence
 - 6.6 Mechanism of the Elastico ML of ZnS:Mn Nanoparticles
7. Applications of the Luminescence of Nanoparticles
8. Conclusions

1. Introduction

The term 'nano' is a Greek word, meaning 'dwarf', but in scientific jargon, nano means 10^{-9} . Thus, a nanometer (10^{-9} meter) is a billionth of a meter, that is, ten times the diameter of a hydrogen atom, or 1/80,000 of the diameter of a human hair. In fact, nanoparticle or an ultrafine particle is a small solid whose diameter lies in the range of 1 to 100 nanometers. Nanotechnology is an emerging manufacturing technology that allows thorough inexpensive control of the structure of matter at the nanometer scale- the scale of small number of atoms, thus leading to the production of machines or devices at nanometer scale. In fact, nanotechnology is the coming revolution in molecular engineering.

Semiconductor nanoparticles having size comparable with the characteristic wavelength of charge carriers are called quantum dots. Nanophase materials generally include nanocrystalline thin films, sintered materials with an ultrafine grain structure and loosely aggregate nanoparticles. Size reduction affects most of the physical properties (structural, magnetic, optical, dielectric, and thermal, etc.) due to surface effects and quantum size effects. Owing to the extremely small dimensions, these materials exhibit properties, which are fundamentally different from, and often superior to those of their conventional counterparts. In recent past, there has been considerable interest in the study of size effect in semiconductors of reduced dimension (in nanometer scale) due to their applications in solar cells, light emitting diodes, resonant tunneling devices, laser, catalysis, etc. Optical spectroscopy, being the non-contact method, has proved to be the most suitable technique to monitor the size evolution of the electronic structure.

Semiconductors in nano-crystallized form exhibit markedly different electrical, optical and structural properties as compared to those in the bulk form [1-10]. Out of these, the ones suited as phosphor host material show considerable size dependent luminescence properties when an impurity is doped in a quantum-confined structure. The impurity incorporation transfers the dominant recombination route from the surface states to impurity states. If the impurity-induced transition can be localized as in the case of the transition metals or the rare earth elements, the radiative efficiency of the impurity- induced emission increases significantly. The emission and decay characteristics of the phosphors are, therefore, modified in nanocrystallized form. Also, the continuous shift of the absorption edge to higher energy due to quantum confinement effect, imparts these materials a degree of tailorability. Obviously, all these attributes of a doped nanocrystalline phosphor material are very attractive for optoelectronic device applications.

It is to be noted that for each kind of material there is always a 'critical size' below which properties are size dependent. Generally, this critical size is in the range of a nanometer to few hundreds of nanometers. For the particle having diameter less than about 1 to 2 nm there are about less than 50 atoms; for the particle having diameter less than about 20 nm, the number of atoms would be less than $\sim 10^4$; and for larger particles it may be upto 10^5 to 10^6 . If the material dimensions are below ~ 20 nm, their dimensions are either comparable to wavelength associated with electron or hole or at least a few tens of their wavelengths [10]. In fact, larger particles upto a few hundreds of nanometers would be still interesting as long as the number of surface atoms is comparable to the number of bulk atoms. Such particles are important because of their surface effects rather than size effect and they are of interest especially in catalysis or chemical reactions. At such sizes materials cannot be considered either as large molecules or as periodic or aperiodic solids, and consequently, their properties cannot be described by any theory for molecules or that for solids.

Nanometer range semiconducting materials have been a subject of intense study for last several years due to their size dependent physical and chemical properties [1-10] below a critical size characteristic of the material. Blue shift in the optical absorption spectrum, size dependent luminescence, enhanced oscillator strength, and nonlinear optical effects are some examples of the interesting properties exhibited by the nanocrystals. All these properties are various manifestations of the so called size quantization effect which arises due to the increasing quantum confinement of the electrons and holes with diminishing size of the crystallites and the consequent changes in the electronic structures. In fact, their electronic structure is between that of a molecules and a bulk responsible to give rise to profound modification of the physical properties. Nanoparticles have been suggested for various potential applications in electronics where quantum confinement effects may be of significant advantage. For example, quantum confinement effects in nanostructured semiconductors result in widening the band gap of semiconductor and act as an efficient light emitter.

In fact, II-VI compound semiconductors include the cations of zinc, cadmium and/or mercury combined with anionic oxygen, sulfur, selenium and/or tellurium. These semiconductors have been found to generally crystallize in both a face-centered cubic (zinc blende) and a hexagonal (wurtzite) crystal structure. The equilibrium crystal structure of both ZnO and ZnS is hexagonal; however, ZnS often also exhibits a metastable cubic or a mixed hexagonal/cubic structure. As the II-VI compound semiconductors possess a direct band gap, they may exhibit good luminescence. Many of the II-VI semiconductors are often used as a host for luminescent activators, for example, ZnS doped with Mn^{2+} , which emits yellow light. In addition, near band edge emission from excitons can be observed from II-VI semiconductors, especially at low temperatures, from those materials with a low exciton binding energy.

Considering the development in the field of both theory and well planned experiments, further investigations on structure, shape, absorption, luminescence, Raman, electrical, interfacial and device properties of nanoparticles are attracting the interest of a large number of workers. The present review discusses the preparation, characterization, and luminescence of II-VI semiconductor nanoparticles and explores their applications.

2. Historical Background

The application of nanosized materials is much older than today's science, and dates back to ancient Egyptian, Chinese, and Roman times. Egyptian and Chinese authors around 5th century BC were the first to mention the solutions of liquid gold. In fact, ancients believed in the metaphysical and healing powers of the solutions of liquid gold [11]. Colloidal gold and silver have been used since Ancient Roman times to colour glass with intense shades of yellow, red, or mauve, depending on the concentration of the two metals. In the ancient times metal nanoparticles were formed in molten

glass, and used to make stained glass objects. Such a magnificent example of ancient glass is the famous Lycurgus Cup (Fig. 1) (AD fourth century), housed up at the British Museum, illustrating myth of King Lycurgus [12]. The dispersed gold nanoparticles in the glass make it to appear green, when viewed in reflecting daylight. But, when the cup is illuminated from the inside it appears red by the transmitted light. In the middle age, believing in curative properties of Au colloids, they have also been used in medicine for various diseases [11].

In fact, in 15th century, Italian artisans in Gubbio and Deruta were able to prepare brightly coloured porcelain, called luster, containing silver and silver - copper alloy nanoparticles. Such technique was developed earlier in the Islamic world during the 9th century who exploited the reducing atmosphere obtained by heating dried genista up to 600 °C to obtain nanoparticles by reducing metal oxides or metal salts previously deposited on the ceramic piece from a vinegar solution [11, 13]. In the 17th century Andreus Cassius and Johann Kunchel further refined the process of glass-colouring by contriving “Purple of Cassius”, a precipitate of colloidal gold and stannic hydroxide they added to the base glass [11].

The first “scientific” study of metal nanoparticles is dated back to the seminal work of Michael Faraday around 1850 [14]. Faraday was the first to notice that the red colour of gold colloid was due to the minute size of the Au particles and that one could turn the preparation blue by adding salt to the solution. He was able to obtain gold colloids reducing $AuCl_4^-$ by phosphorus, following a procedure already reported by Paracelsus in 16th century about the preparation of “Aurum Potabile” and based on a two phase water / CS_2 reaction. It is to be noted that some of Michael Faraday’s preparations are still preserved today in the Faraday Museum in London [15].

In fact, other synthetic methods for colloidal metal particles have been developed in the early 20th century, both physical or chemical, until the fundamental work of Turkevitch in 1951 [16]. Interestingly, he started a systematic study of gold nanoparticle (NP) synthesis with various methods by using transmission electron microscopy (TEM) analysis to optimise the preparative conditions until obtaining what is commonly known as the Turkevitch method.

Carbon black is the most famous example of a nanoparticulate material that has been produced in quantity for decades. Roughly 1.5 million tons of the material is produced every year. Nanotechnology, though, is about deliberately and knowingly exploiting the nanoscale nature of materials, which would, for many, exclude early use of carbon black from being given the nanotechnology label. However, new production and analysis capabilities at the nanoscale and advances in theoretical understanding of the behavior of nanomaterials certainly mean nanotechnology can be applied to the carbon black industry. Nanoparticles can exist in nature such as the structures on the wing of a butterfly, the skin of a shark or the surface of the lotus leaf. Throughout history, people have been exposed to nanoparticles such as smoke, dust, ash and fine clays through air, food or water. Nanoparticles are not solely a product of modern technology, but are also created by natural processes such as volcano eruptions or forest fires. Naturally occurring nanoparticles also include ultrafine sand grains of mineral origin (e.g. oxides, carbonates). In addition to commercially produced nanoparticles, many are unintentionally created by the combustion of diesel fuel (ultrafine particles) or during barbecuing.

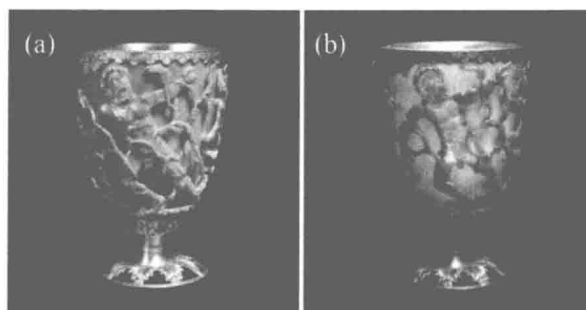


Fig. 1: The Lycurgus Cup (British Museum).

The idea of nanotechnology was first floated by the Nobel Laureate in physics, Richard Feynman on December 1959 in the annual meeting of American physical society, where he delivered a lecture "There is a plenty of room at the bottom-an invitation to enter a new field of physics". In the lecture he said, "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. Subsequently, Eric Drexler popularized Feynman's philosophical thinking in a most influencing and stimulating manner in his book "Engines of creation, the coming age of nanotechnology". Drexler described, "Nanotechnology is the principle of manipulation atom by atom, through control of the structure of matter at the molecular level. It entails the ability to build molecular systems with atom-by-atom yielding a variety of nanomachines".

In fact, the discovery of transistor by John Bardeen, William Shockly and Walter Brattain in 1947 laid the foundation of miniaturized devices. On one hand, miniaturization enabled to save the space by making the various pieces of equipments compact and on the other hand, it gave rise to the invention of many novel devices. Presently, semiconductor devices are finding several applications right from kitchen appliances to space-craft covering between them a large range of other applications. Today, using the deposition techniques like molecular beam epitaxy or metallo-organic chemical vapour deposition combined with lithography, it has become possible to make as large as 10^8 to 10^9 components on a single chip. In fact, real breakthrough in nanostructuring of semiconductors took place in 1970 when L. Esaki and his collaborators at IBM in USA produced quantum wells of GaAs and AlGaAs by alternately stacking these two materials on atomic scales. They used molecular beam epitaxy to produce this novel structure. In such structure the charge carriers are periodically confined in the plane of the film due to change in potential that will be faced at alternate material (GaAs or Al GaAs). By carving lithographically a thin film, a wire can be obtained and by cutting the wires lithographically, one can achieve the quantum dots. Such techniques are difficult as well as expensive and also they are not accessible to most of the scientists. As such, until 1980, the research work on semiconductor quantum devices could be carried out only at few laboratories.

As shown in Fig. 2, when the reduction in physical size of a material is only in one direction, it gives rise to a thin film; when the reduction is in two directions, it gives rise to a wire; and when the reduction is in all directions, it gives rise to a point. This puts certain restrictions on the motion of charge carriers. In a bulk (3-D) material the charge carriers are free to move in all directions, whereas in a planer material or thin film (2-D) charge carriers are confined only in a plane. The charge carriers in a wire or 1-D material will be allowed to flow only in one direction. However, the charge carriers in a cluster, nanoparticles or quantum dot (0-D) are confined in a very small region in space. It is to be noted that although it has been said that, in a film charge carriers are constrained in a plane, in a 1-D material only in a line and in 0-D material only at a point, in actual practice, one has to relax these conditions for obvious reasons. In real life we cannot have a plane or wire or dot

of a material without certain thickness. However, the length of reduced dimension should be smaller than the phase coherent length or mean free path scattering length for electron in the material. In fact, this is known as mesoscopic regime or quantum confinement regime.

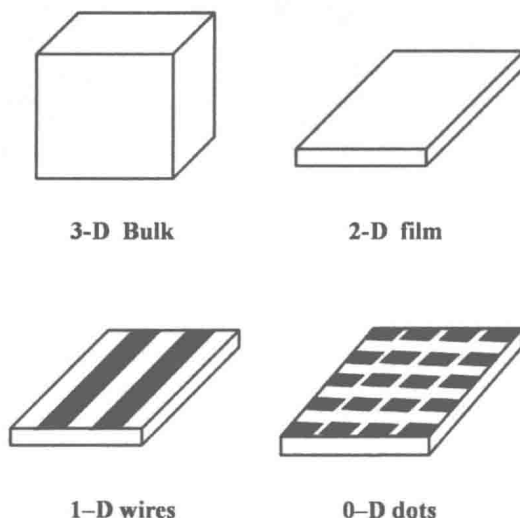


Fig. 2: Schematic diagram showing 3-D, 2-D, 1-D and 0-D materials.

In the year 1981, Ekimov and Onushchenko [17] of Ioffe Physical Technical Institute in St. Petersburg noticed a blue shift of the optical spectrum for nanometer sized CuCl in silicate glass. In 1982, Efros and Efros [18] of USSR put forward the theory for the first time that quantum size effects (the change of optical and optoelectronic properties with size) could be used to control the colour of glass by either changing the size or stoichiometry of $\text{CdS}_x\text{Se}_{1-x}$. In 1984, Ekimov and Onushchenko [19] reported an experimental evidence for quantum size effects in all three dimensions for microcrystallites of CdS dispersed in a silicate glass. In 1984, L.E. Brus [20] of USA developed a theory based on effective mass approximation which could qualitatively explain the size dependence of certain properties of semiconductor nanoparticles. Now, tight binding approximation modified forms of effective mass approximation, etc. are being used to explain the experimental observations, Brus group also reported that it is possible to obtain semiconductor nanoparticles in colloidal solutions or they can be grown in polymer matrix. After 1982, a sudden increase in the activity of nanoparticles research took place, when it was realized that nanoparticles could be produced by different means other than molecular beam epitaxy combined with lithography. Presently, several physical and chemical techniques of synthesizing nanoparticles are available.

In fact, size dependent properties of materials have been a very interesting concept not only to fabricate technologically interesting devices but also to understand how starting from atoms, molecules, ensemble of molecules or clusters evolve ending up into a solid, and how the structure, binding, electronic structure and other properties change during the evolution. Lots of experimental data, theoretical predictions as well as applications are making the area of nanostructuring richer and richer. Certainly, a lot of unexpected things are expected to come out in the coming years.

3. Preparation of Nanoparticles

Synthesis is the most important step in the studies of nanoparticles. Nanophase materials generally include nanocrystalline thin films, sintered materials with ultrafine grain structure and loosely aggregate nanoparticles. Nanoparticles can be prepared by chemical and physical methods. Several methods have been used for the preparation of II-VI semiconductor nanoparticles [4-6]. There are two methods involved in nanomaterial synthesis and fabrication of nanostructures. These methods are: (i) Top-down method, and (ii) bottom-up method. Top-down method refers to a set of fabrication technologies which fabricate by removing certain parts from a bulk material substrate. The removing method can be mechanical, chemical, electrochemical, etc., depending on the material of the base substrate and requirement of the feature sizes. The formed structures usually share the same material with the base substrate. There are a couple of manufacturing technologies in the conventional scale which can be categorized top-down. Milling is a representative example. In the top-down approaches, a bulk semiconductor is thinned to form the Qdots. Electron beam lithography, reactive-ion etching and/or wet chemical etching are commonly used to achieve Qdots of diameter < 30 nm. Bottom-up method is opposite to top-down method. In this method, nanocomponents are made from precursors in the liquid, solid, or gas phase employing either chemical or physical deposition processes that are integrated into building blocks within the final material structure. In the bottom-up approach, molecular components arrange themselves into more complex assemblies, atom-by-atom, molecule-by-molecule, cluster-by-cluster from the bottom (e.g., growth of a crystal). Some methods for synthesizing II-VI semiconductor nanoparticles will be described.

(i) Chemical Precipitation Method: Bhargava et al. in 1994 were the first to report nanosize luminescent materials using chemical precipitation method [21]. They synthesized manganese-doped nanocrystals of zinc sulfide, in which the nanomaterials had external photoluminescence quantum efficiency of 18%. The synthesis involved reaction of diethyl zinc with hydrogen sulfide in toluene. The dopant manganese was added as ethylmanganese in tetrahydrofuran solvent to the parent solution of zinc salt before precipitation reaction. They used surfactant methacrylic acid to maintain separation between the particles formed. The dried material was further subjected to UV curing for possible polymerization of surfactant methacrylate capping film on the surface of Mn doped ZnS nanocluster for imparting true quantum confinement. They explained the enhancement of efficiency on the basis of surface passivation of the nanocrystals due to photo-polymerization of the surfactant. The photoluminescent (PL) and photoluminescence excitation (PLE) spectra of the nanophosphor were compared with bulk ZnS:Mn. The PL is found to be slightly shifted and a larger line width is found in the nanophosphor as compared to bulk.

Following the reports of Bhargava et al. [21] on ZnS:Mn nanophosphor, Khosravi et al. [22] in 1995 succeeded to prepare manganese doped ZnS nanoparticles by aqueous method. They prepared aqueous solution of zinc chloride with required amount of dopant manganese chloride and then mercaptoethanol was mixed slowly under constant agitation and subsequently reacted drop wise with sodium sulfide solution. In this experiment, the reaction was carried under nitrogen gas to avoid oxidation of freshly formed highly reactive nanoparticles. They observed PLE and PL peaks at 312 and 600 nm, respectively, and Mn concentration of 12 at wt % was found to be optimum. Khosravi et al. [23] also reported synthesis of copper doped zinc sulfide quantum particles, where synthesis was carried out in presence of sodium hexametaphosphate at pH 8-9. On a growing metal sulfide cluster, phosphate chains get attached through metal ions. These chains separate the clusters due to their length and avoid coalescence. Luminescence decay times were measured for both Cu doped and undoped ZnS, in which two exponential decay times of 2.9, 54.2 and 1.62, 22.12 ns were observed. In fact, shorter decay times were found in undoped sample. A lot of work [24-45] has been done on preparation of nanoparticles by the chemical precipitation and interesting results have been reported. In 2004, Karar et al. [46] prepared ZnS:Mn nanophosphor capped with ZnO,

whereby the nanophosphor was prepared by reacting acetates of zinc and manganese with sodium sulfide. Subsequently, in the same reaction medium zinc acetate along with ammonia solution were reacted which led to the formation of zinc hydroxide, i.e., ZnO on drying on zinc sulfide.

(ii) Heat Assisted Chemical Reaction Method: In 2000, Wang and Hong [47] described a new procedure for the preparation of nanosized zinc sulfide particles using heat assisted chemical reaction method. In this method, zinc acetate and thioacetamide were milled separately, mixed and further milled so that thorough and uniform dispersion of the components in the mass could be achieved. They confirmed the formation of nanocrystalline zinc sulfide where the size was 3.2 nm at 100 °C. TEM and PL studies also indicated the nanocrystalline nature of the sample. In 2001, Konrad et al. [48] prepared nanocrystalline cubic yttria and, in 2002, Ebestein et al. [49] reported fluorescence quantum yield of CdSe/ZnS core/shell nanophosphors prepared by them. The nanoparticles were prepared by them following the route of high temperature pyrolysis of organometallic precursors in coordinating solvents. Furthermore, they synthesized some samples with trioctylphosphine oxide (TOPO) and hexadecyl amine capping.

(iii) Chemical Reaction Method: In 2001, Dijken et al. [50] prepared colloidal solutions of nanocrystalline ZnO and studied the variation of luminescence quantum efficiency with particle size. In that experiment, NaOH solution was added slowly to zinc acetate solution. They prepared both the solutions in 2-propanol and pre-cooled to 0°C. They succeeded in preparing the colloidal suspension of ZnO particle of 0.7 nm radius. It was found that the particle size grew with time due to aging. In that experiment the growth up to 3 nm were recorded and analyzed.

(iv) Chemical Precipitation from Homogeneous Solution Method: In 2001, Yang et al. [51] were successful to prepare ZnS nanocrystals coactivated with Cu and rare-earth metals like Ce, Y, Nd, Er, Tb, where the doped zinc sulfide nanoparticles were synthesized by precipitation from homogeneous solution. In this method, zinc acetate solution with dopants in form of chloride salt and solution of thioacetamide were separately heated to 80°C and mixed; pH of the solution raised to 2.0 and reaction time of 30 min was given. In fact, the reaction was arrested by cooling the solution to less than 10°C. Although the PL spectra with rare-earth impurities showed practically no change in emission peak as compared to that of pure ZnS, the intensity enhancement by factor of 5-6 was obtained. For the case of double doping with Cu and rare-earth peak PL emission was around 540-550 nm with 15 times increase in intensity for Tb³⁺, Cu²⁺ sample as compared to the samples of pure ZnS. In 2002, Lee et al. [52] synthesized ZnS nanoclusters thin films by solution growth method. In 2004, Lee et al. [53] investigated the effect of preparation temperature on particle size/shape of ZnS:Cu nanocrystals. They measured the PL spectra at different synthesis temperatures and reported that Cu is transformed to CuO for preparation temperatures greater than 90 °C.

(v) Sol-gel Method: The sol-gel synthesis of nanosize ZnS was reported by Stanic et al. [54] in 1997. They used zinc tert-butoxide in butanol and water free toluene and high purity hydrogen sulfide gas was bubbled through the solution till complete gelation occurred. In this experiment, gel was aged and dried in vacuum. X-ray diffraction (XRD) and IR absorption spectra confirmed the formation of ZnS. Many other phosphors have also been prepared using sol-gel method. In 2004, Haranath et al. [55] reported controlled growth of ZnS nanophosphor in porous silica matrix in which organic capping agents was replaced by inorganic ones which are more stable and robust. Their experiment involved preparation of silica alcogel from tetraethylorthosilicate with ethanol and water as diluents and hydrochloric acid as catalyst. They added the aqueous solutions of zinc and manganese in colloidal solution of silica before gelling followed by addition of Na₂S solution. They prepared the samples with varying ratios of ZnS and SiO₂ and studied their annealing at different temperatures. They found that ZnS goes to wurtzite phase after annealing at 900 °C, which has been reported for the first time.