Chapter 1
Introduction
1.1 Introduction

Nanotechnology is an interdisciplinary technology that has been booming in many areas including energy electronics, materials science, mechanics, optics, medical science and biotechnology [1]. Manufacturing nanomaterials such as clusters, nanoparticles, nanotubes, nanowires, nanorods and thin films is the key component for successful development of nanotechnology due to their chemical and physical properties resulting from the nanosize effect [2, 3]. Nanostructured materials have indeed become a very active research field in the area of materials science involving inorganic, organic and composite materials. The use of nanostructured materials is gaining importance in recent years because of their expected impact in biomedical sciences, optoelectronics, magnetics, catalysis etc. [4-10]. In the present thesis the research is directed towards the development of a simple synthesis route for producing zinc oxide nanoparticles. Further the work on zinc oxide-polymer nanocomposites has also been carried out.

This chapter will therefore include an introduction to nanomaterials followed by a brief overview on the ZnO semiconductor materials. Nanocomposites require specialized synthesis procedures for their preparation. Various synthesis approaches, which have been adopted for their preparation, are explained. The properties and applications associated with them have been discussed in detail. The chapter includes a brief overview of zinc oxide-polymer nanocomposites.

1.2 Nanomaterials: A Brief Introduction

The first so-called scientific study of nanoparticles took place way back in 1857, when Michael Faraday synthesized the ruby red colloids of gold and made public that the color was due to the small size of the metal particles. Gold and silver have found their way into glasses for over 2000 years, usually as nanoparticles. They have most frequently been employed as colorants, particularly, for church windows. Until 1959, nobody had thought of using atoms and molecules for fabricating devices. It was Nobel Laureate Physicist Richard Feynman who gave a visionary talk titled “There is plenty of room at the bottom” before the assembly of the American Physical Society, in which he talked about the possibilities of making things small [11]. His talk on nanoscience has become a classic milestone in nanotechnology although he never uttered the word ‘Nano’ or ‘Nanotechnology’. This
talk can be defined as the beginning of the nanotechnology. Nanotechnology is the
technology of making things small, light and cheap. The unit of nanometer derives its
prefix ‘nano’ from a Greek word meaning extremely small. Scientists use this prefix
to indicate $10^{-9}$ or one-billionth. One nanometer means $10^{-9}$ of a meter, is roughly the
length occupied by five silicon or ten hydrogen atoms aligned in a line.

In general terms, particles having any one, two or the three dimensions in the
range of 1-100 nm are considered to be nanoparticles. They can be roughly divided
into the three regimes as particles with (a) diameter $\leq 1-2$ nm where number of atoms
is $\leq 50$, (b) diameter $\leq 20$ nm where number of atoms is $\leq 5 \times 10^4$ (c) diameter $\geq 20$ nm
with number of atoms upto $\sim 5 \times 10^5$ [4]. At present, nanomaterials are at the most
advanced stage, both in scientific knowledge and commercial applications. Current
nanomaterials include multilayers, chains of atoms and atomic clusters on surfaces,
quantum dots, 3D nanostructured films, small atomic clusters and nanoscale materials
[12] Their unique size dependent properties give these materials superior and
controllable properties. Those extremely fascinating and useful properties can be
explored for various applications. Nanotechnology is sweeping through all the fields of
science and engineering. Large number of books and review articles has been
published in the past two decades on nanomaterials and Nanotechnology [5-10, 13-17].

Nanoparticles can be synthesized by growing, shaping or assembling the
materials by physical, chemical, biological or hybrid methods. Broadly speaking
synthesis of nanomaterials can be divided into two categories viz. top down and bottom up
approach [18]. In “top-down” approach, macroscopic particles can be reduced to the
nanosize by removal of material. This approach involves mechanical grinding, high-
energy milling, machining and lithography techniques. However, considering that
nanocomposites generally consist of a continuous phase/matrix including a nanosized
second phase/filler with particle sizes below 100 nm, this approach is not efficient
since particle sizes below 500 nm cannot be generated. On the other hand “bottom up”
approach involves aggregation of atoms to form particles of definite size, shape or
structure. Bottom up approach consists of physical as well chemical methods. In this
approach, materials and phases are created by physical or chemical means from
precursor compounds forming nanoscale or nanocomposite materials. The advantages
of chemical methods over physical methods are that they are relatively simple,
inexpensive, low temperature techniques and do not require sophisticated equipment.
The materials can be synthesized in various shapes, sizes and structures [4].
Chemical route has been employed for synthesizing zinc oxide nanoparticles
discussed in this thesis. Nanoparticles are characterized by size dependent properties. In case of nanoparticles the surface to volume ratio is extremely high. Hence surface atoms play an important role in governing the properties of nanoparticles. The fundamentals of nanotechnology lie in the fact that the properties of substances dramatically change when their size is reduced to the nanometer range.

When a bulk material is divided into small size particles with one or more dimension ‘length, width or thickness’ in the nanometer range or even smaller, the individual particles exhibit unexpected and interesting properties, different from those of the bulk material. This is due to the surface energy of nanoparticles, which increases with a decrease in Nanoparticle size. Thus the pressure required for changing the crystal structure also increases with decreasing size.

Another reason for change in the properties of nanomaterials is that in nanosize regime the wavelength of the electron wave function is comparable to size of the particles. It can be predicted by simple particle in a box model where density of states changes with the confinement of charge carriers. Figure1.1 shows schematic representation of the variation of density of states for different nanomaterials

![Figure 1.1 Variation of density of states with energy as a function of dimensionality for a bulk (3D), a quantum film (2D), a quantum wire (1D) and a quantum dot (0D) [19]](image)

As shown in the Figure 1.1, the density of states $N(E)$ in a three-dimensional (3D) semiconductor is continuous at all energies. The quantum well is a two
dimensional (2D) structure in which charge carriers are restricted in the direction normal to layers, and move freely in the plane of the layer. In quantum wires, which are one dimensional (1D) structure, the charge carriers are already restricted in two directions and move freely only along the wire axis whereas, the quantum dot is a zero dimensional (0D) structure where the charge carriers are restricted in all three directions and are characterized by a completely discrete energy spectrum. The bulk semiconductor materials are characterized by a small but nonzero bandgap. In the band dispersions, the curvature of the bands at the edges is high as compared to the center of the band. As size is reduced energy levels at the edges become discrete first as compared to centre of the band. This happens, as density of states is less at the edges than that in the centre of the band. Hence as the size of the bulk semiconductor is reduced to nanometer scale the band edges shift-giving rise to an increase in the band gap and the energy levels close to the edges become discrete.

Figure 1.2 illustrates the change in the band structure and band gap as one goes from bulk to nanoparticles.

![Figure 1.2 Schematic diagram for energy gap in case of semiconductors for bulk, nanoparticles and molecules](image)

The negatively charged electron and positively charged hole may interact to form a hydrogen-atom-like complex in which two carriers orbit each other. The bandgap of a semiconductor represents the energy required to break an electron and hole pair such that there is no coulomb attraction between the two. The attractive interaction between electron and hole leads to the formation of an electron-hole pair, which is termed as an exciton [20]. Exciton levels lie just below the conduction band minimum and are observable at low temperature. In semiconductors a pair of weakly bound electron and hole is called as Mott-wannier exciton. The separation between the
electron and the hole in the exciton is known as the Bohr diameter of exciton \((D_B)\) and is given as follows.

\[
D_B = \frac{2\hbar^2}{e^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right)
\]  

(1.1)

where, \(m_e\) = effective mass of electron

\(m_h\) = effective mass of hole, &

\(\varepsilon\) = dielectric constant of the material

When the size of the semiconductor material is reduced to such an extent that it is comparable to the Bohr radius of exciton, the situation may be visualized as that of a particle in a box model. In this model the particle is confined to move in a box (for simplicity we consider 1-D). The motion of the particle is assumed to take place with zero potential energy over a fixed distance i.e. inside the box. At extremities i.e. on and outside the walls of the box the potential is infinity. The energy and size of the particle can be found by solving time independent 1-D Schrödinger equation.

\[
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x)\psi(x) = E\psi(x)
\]  

(1.2)

Solution for this equation can be written in the form as

\[
\psi (x) = A \sin \left( \frac{2mE}{\hbar^2} \right)^{1/2} x + B \cos \left( \frac{2mE}{\hbar^2} \right)^{1/2} x
\]

Solving the equation we get the energy, which is expressed as

\[
E = \frac{n^2 \pi^2 \hbar^2}{2ma^2} = \frac{n^2 \hbar^2}{8ma^2}
\]  

(1.3)

Thus it is clear that energy is inversely proportional to the square of the particle size. As one goes on reducing the particle size energy difference between two consecutive energy states (e.g. energy states for \(n = 1\) and \(n = 2\)) will increase. Thus as the size reduces the band gap increases which results in a blue shift observed in the optical absorption spectrum.

Various theoretical approaches are employed for more quantitative analysis of the variation of energy gap and energy structures with size of the nanoparticles. The first attempt for explaining the spectral shift of absorption
spectra of CuCl was carried out by Ekimov and Onushchenko [21] where they considered the particle to be spheroid. For investigating the quantum confinement effect in various confinement regimes Efros and Efros used the effective mass model (EMM) [22]. However, these approaches were very elementary as they neglected the Coulomb attraction between the electron and the hole. Brus incorporated the Coulomb effect for correct explanation of the spectral shift as discussed below.

1.2.1 Effective mass approximation (EMA)

The first approach to obtain a quantitative understanding of the quantum confinement effects in nanocrystal as a function of its size was given by the effective mass approximation (EMA). As stated earlier Brus [23, 24] modified the hydrogenic Hamiltonian function. He included the potential energy due to dielectric polarization. Thus a model for the particles that incorporated

(a) The effective mass approximation for the kinetic energy of the electron and the hole,
(b) An electrostatic potential term from classical continuum polarizability theory and
(c) Tunneling of electrons and holes out of the crystallite at the surface for finite barrier height was considered.

In effective mass approximation model a crystal with spherical shape is considered. Consider the sphere of radius ‘R’ having a dielectric constant \( \varepsilon_2 \) for the semiconductor medium inside the sphere. Outside the semiconductor particle a dielectric medium with a value \( \varepsilon_1 \) is assumed as shown below.

Let \( R \) be the radius of the sphere with dielectric constant \( \varepsilon \) as shown below.

\[ \varepsilon \]
\[ R \]

The lowest possible exciton state will have the wave vector given by
Consider an electron excited into the $k=0$ state at the bottom of the conduction band. The smaller the cluster, the larger the region of $k$ space necessary to localize the electron inside the spherical cluster. The expectation value of the electron energy can be given as

$$E_i = \langle \psi_i | \hat{H} | \psi_i \rangle = E_c + \frac{\pi^2}{2R^2} \sum_{i=x, y, z} \left[ \frac{\partial^2 E}{\partial k_i^2} \right]$$

(1.5)

Effective mass is defined as

$$m^* = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}}$$

(1.6)

Substituting for $\left( \frac{\partial^2 E}{\partial k^2} \right)$ in equation (1.5) we get

$$E_i = E_c + \frac{\pi^2 \hbar^2}{2R^2 m_e}$$

(1.7)

meaning of the eq. (1.7) is that energy of an electron in tiny crystallite is the conduction band energy $E_c$ plus the quantum localization energy of an electron with effective mass $m_e$. Similarly for a hole in the HOMO, localization energy is given by

$$\frac{\pi^2 \hbar^2}{2R^2 m_h}$$

(1.8)

Electron and hole interact with each other via a shielded coulomb interaction which can be given as

$$= \frac{1.8e^2}{\varepsilon R} + \text{polarization terms}$$

(1.9)

Combining equations (1.7), (1.8) and (1.9), the equation for the first excited electronic state is given as

$$E^* = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\varepsilon R} + \text{small terms}$$

(1.10)
Equation (1.10) is the effective mass approximation formula derived by L. Brus [24]. As can be seen from the equation the coulomb term shifts $E^*$ to the lower energy as $R^{-1}$. The quantum localization term shifts the $E^*$ towards higher energy side as $R^{-2}$. Thus the overall effect is that $E^*$ will be always shifted to higher energy side for small $R$.

Although EMA is useful to understand the variation of band gap with size, there are two major problems in the application as follows. There are two major problems in the application as follows.

1. Effective masses are assumed to be independent of $k$. The band structure in real materials deviate from free electron parabolic form for larger $k$. Thus there will be significant error in calculations for smaller particles.

2. Lattice structure is assumed to be same for small clusters as that for their corresponding bulk. If it happens to be different in smaller crystals then the effective mass also will be different.

Apart from this model other approaches such as empirical pseudo-potential method [25,26] effective bond orbital method [27], tight binding (Tb) [28-30] method have also been developed for quantitative explanation of very small particles. Thus effective mass approximation is not too much useful in case of smaller particles.

1.2.2 Tight Binding Approximation (TBA)

An alternative method for the calculation of electron states in small crystallites is the tight binding method. It takes care of the structure of the crystallite and is applicable in principle to very small crystallites up to the size of molecular clusters. The other advantage is that it is less demanding in terms of computational efforts. Briefly, the fact of realistic description of structural and dielectric properties in terms of chemical bonds and its simplicity in handling very large systems is the backbone for the increasing popularity of this method. In tight binding method, the wave functions of the crystallites are constructed as linear combinations of orbitals on each site of the crystallite. The absence of translational symmetry leads to a large Hamiltonian matrix, which has to be diagonalized. Later, to keep the size of Hamiltonian within manageable limits several approximations are made and the matrix is solved for determining the properties. Slater and Koster were the first to suggest the tight binding model as an interpretation scheme for explaining the
electronic structure in solids [28]. However, their model posed one difficulty. The \( \text{sp}^3 \) model failed to explain the indirect band gap in some III-V semiconductors satisfactorily at the X point. Messmer et al. [29, 30] used the tight binding calculations in finite size to systems to treat defects in bulk materials using a cluster approach. Later, in order to mimic the influence of the excited d states, Vogl et al. [31] modified the method of Slater and Koster. They used the \( s^* \) orbital, in an ad hoc manner to explain the band gap at the X point correctly. By adopting Vogl’s parameters, Lippens and Lanoo [32] described the band gap variation with size for direct band gap materials of the type \( \text{A}_\text{II}\text{B}_\text{VI} \) semiconductor nanoparticles, where \( \text{A} = \text{Zn}, \text{Cd} \) and \( \text{B} = \text{S}, \text{Se}, \text{Te} \). They considered 17 to 2356 atoms with \( \text{sp}^3\text{s}^* \) of \( \text{CdS} \) and \( \text{ZnS} \). It was found that contrary to EMA, TBA agrees better with experimental results, especially in case of small particles.

For zinc oxide, the tight binding model was described by Vishwanatha et al. [33]. They have deduced the ab initio band structure of wurtzite \( \text{ZnO} \) using the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method. Band dispersions and density of states (DOS) were calculated to obtain the realistic TB model. In this work effective mass approximation as well as tight binding model will be employed to calculate the size of the zinc oxide nanocrystals synthesized using a chemical route. So far we have discussed about nanoparticles and the theoretical models used for semiconductor nanoparticles. In the following sections we will review the research work that has been carried out on these materials.

1.3 Zinc oxide (\( \text{ZnO} \)) : Introduction and General properties

Zinc oxide (\( \text{ZnO} \)) is one of the extensively studied semiconductor material belonging to II-VI group in the periodic table. zinc oxide (\( \text{ZnO} \)) is a piezoelectric, transparent semiconducting oxide. It is the hardest of the II-VI semiconductors therefore more resistant to wear. In addition, Zinc oxide is an important material for a variety of practical applications. Structurally, \( \text{ZnO} \) has a non-centrosymmetric Wurtzite crystal structure with polar surfaces. It is categorized as a hexagonal Bravias lattice with \( a = 0.325 \text{ nm} \) and \( c = 0.512 \text{ nm} \) with 6 mm point group symmetry. The Zn atoms are tetrahedrally coordinated to four O atoms [34] as in figure1.3. The oxygen anions occupy the octahedral sites. Wurtzite structure for zinc oxide is given in the Figure 1.3. In addition to the wurtzite phase, \( \text{ZnO} \) is also known to crystallize in the zinc blende and cubic rocksalt (\( \text{NaCl} \)) structures. Jaffe et al. [35] have calculated the
total energy for all three possible crystal structures of ZnO using the Hartree-Fock calculation method.

![Wurtzite crystal structure for zinc oxide](image)

**Figure 1.3 Wurtzite crystal structure for zinc oxide**

From the comparison of the total energy for all three possible crystal structures for ZnO, it is clear that wurtzite structure is having the lowest energy, thus it is thermodynamically most stable structure for ZnO. ZnO is a technological important material due to its various properties. Some important physical properties of ZnO are tabulated below.

**Table 1.1 Physical properties of ZnO [36]**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass</td>
<td>81.389</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>5.6803</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1975</td>
</tr>
<tr>
<td>Point group</td>
<td>6 mm (Wurtzite)</td>
</tr>
<tr>
<td>Specific gravity at 300 K (g/cm$^3$)</td>
<td>5.642</td>
</tr>
<tr>
<td>Lattice constants at 300 K (nm)</td>
<td>$a = 0.32495, c = 0.52069, c/a = 1.602$</td>
</tr>
<tr>
<td>Energy gap (eV)</td>
<td>3.4, direct</td>
</tr>
<tr>
<td>Exciton binding energy (meV)</td>
<td>60</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24</td>
</tr>
<tr>
<td>Electron Hall mobility at 330 K (cm$^2$/Vs)</td>
<td>200</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.59</td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K</td>
<td>5.50 cm$^2$/Vs</td>
</tr>
</tbody>
</table>
1.3.1 Zinc oxide Nanoparticles: A Brief Review

ZnO is a promising material for the realization and future of nanotechnology. In the group of II-VI compound semiconductors, ZnO has received intense attention due to its remarkable combination of physical and optical properties. It has a wide band gap (3.37 eV at room temperature), large exciton binding energy of 60 meV and its diverse growth morphologies make ZnO a key material in the fields of wide band-gap semiconductors and Nanotechnology. As a source of unique properties, zinc oxide has been widely studied as a novel material for its practical and potential applications in optoelectronic, switches, high-efficiency photonic devices, and near-UV lasers, and for assembling complex three dimensional nanoscale systems [37-39]. It is also used in applications such as micro, nano-electronics and micro, nano-robotic (machining) technology [40].

So since last two decades many groups have worked on zinc oxide nanoparticles to understand its properties and its use in many applications. Here we discuss the work done so far on zinc oxide nanoparticles. This will include the different aspects like synthesis, morphologies, properties and applications of ZnO as majority of the work presented in this thesis is carried out on zinc oxide nanoparticles. To prepare ZnO nanoparticles or thin films, several methods such as chemical vapor deposition, molecular beam epitaxy, metal organic vapor-phase epitaxy, Spray pyrolysis and wet-chemistry colloid preparation have been developed. A variety of methods exist for Zno deposition and growth.

Koch et al. [41] have synthesized colloidal ZnO nanocrystallites with methanol and propanol as medium. Zn(ClO$_4$)$_2$ was used as a salt for zinc. Their UV-Vis absorption spectra show that particles are in the nanoregime with absorption edge recorded in between 300 to 350 nm. 0.1% Cu$^{2+}$ ions were doped in ZnO particles to study the effect of it on luminescence of ZnO. They found that presence of Cu$^{2+}$ inside the ZnO enhances the efficiency of visible luminescence by ~30 % while Cu$^{2+}$ ions are adsorbed on the surface of colloidal particles, intensity is quenched by ~50 %. Effect of irradiation (UV light with 330 nm wavelength) was also studied and they have reported that irradiation quenches the visible luminescence almost 100 %, which was recovered after 30 minutes of solution ageing. The phenomenon was explained with Hauffe mechanism as shown in Figure 1.4.

Meulenkamp [42] isolated pure ZnO nanoparticles from the colloids through a precipitation-redispersion method. In his report organic “nonsolvents” were used to
precipitate ZnO gels from the colloids, and the gels could be redispersed in solvents. Therefore, ZnO nanoparticles either in solvents or in solid states can be investigated without the influence of impurities.

Figure 1.4 (a) Absorption and fluorescence spectra of ZnO sol in water, (b) ZnO sol in propanol-2 at various times of aging [41]

Spanhel and Anderson [43] have explained the synthesis of nanocrystals of zinc oxide using distillation set-up starting with products of zinc acetate and ethanol. They have obtained highly concentrated colloidal nanocrystals of ZnO of size varying from 3.5 to 5.5 nm with aging and shown that these crystals remain in a dispersed state for weeks. The same sol-gel technique was used by another group [44] to synthesize transparent conducting thin films of ZnO. Zinc nitrate hexhydrate was used as a starting precursor and ethylene glycol as a reaction medium. Films were prepared by spin coating. Effect of indium doping on the resistivity was studied. It was found that
undoped ZnO films show lowest resistivity. Tokumoto et al.[45] have also used sol-gel route to synthesize ZnO nanoparticles and zinc acetate derivatives to study the chemical and structural nature of them. Zinc acetate and different catalysts viz. lithium hydroxide, succinic acid and glacial acid were used for the hydrolysis. Authors have concluded that the chemical and structural nature of the ZnO nanoparticles is strongly dependant on the temperature and type of catalyst used during the synthesis. Most pure zinc oxide sample could be synthesized at lower temperatures (< 20°C) without catalyst or using LiOH as a catalyst.

Chemically capped ZnO nanoparticles were reported by Tong et al. [46] in which polyvinyl butyral was used as a capping agent. PVP-capped ZnO quantum dots have been widely studied [47, 48]. Capping of ZnO nanoparticle surfaces by using polyvinyl pyrrolidone (PVP) also exhibited enhanced UV photoluminescence and reduced green emission of ZnO nanoparticles [47]. This is attributed to the nearly perfect surface passivation of the ZnO nanoparticles by the PVP molecules.

Bendre et al. [48] have used poly vinyl pyrrolidone (PVP) as a capping molecule. They have studied effect of capping on the PL spectrum of ZnO. Vishwanatha et al. [33] have used PVP and 1-decanethiol as capping agents. ZnO nanoparticles having sharp absorption edges with four different sizes have been reported. Figure 1.5 shows the UV-Vis absorption spectra for the samples.

![Figure 1.5 Optical absorption spectra for capped ZnO nanoparticles](image)
Thin films of polyvinyl pyrrolidone (PVP) -capped ZnO nanocrystalline were successfully prepared on glass substrate by sol-gel dip-coating method by Suwanboon et al. [49]. All films were dipped five times and calcined at 550°C in air for 1 hour. It was found that all the thin films exhibited preferred orientation along (002) plane when increasing PVP concentration into solution and the direct optical band gap of the films was in the range of 3.80-4.08 eV. Authors have concluded that this large band gap may be due to the high crystalline quality and lattice-match to the substrate.

Pesika et al. [50] have used octanethiol to quench the growth of ZnO nanoparticles. The reaction was carried out in ethanol, 1-propanol, 1-butanol, 1-pentanol and 1-hexanol as solvent. The influence of the solvent provides a means to achieve control over the ZnO nanoparticle size and size distribution. The evolution of the particle size distribution and the rate constant on an Arrhenius plot is as shown in the Figure 1.6.

![Figure 1.6](image1.png)

**Figure 1.6** (a) and (b) selected size distribution at 35°C in 2-propanol (c) Arrhenius plot of the rate constant for growth of ZnO particles at different temperatures [50]
Seeling et al. [51] have reported monodispersed and well organized ZnO spherical particles in the size range from 115 nm to 610 nm. The particles were synthesized using a chemical route. Zinc acetate and di-ethylene glycol were used as starting precursors in the reaction. Sridevi and Rajendran et al. [52] were reported the successful synthesis of ZnO nanoparticles by hydrothermal method using zinc acetate and oxalic acid as the reactants. They found that the size of the particles determined by XRD was in good agreement with TEM analysis. They have also studied the optical properties of ZnO nanomaterials by absorption and photoluminescence spectra.

Thareja and Shukla [53] synthesized zinc oxide nanoparticles by pulsed laser ablation of a zinc metal target at room temperature in different liquid environment. These nanoparticles were characterized by photoluminescence, atomic force microscopy and X-ray diffraction techniques. The sample ablated in deionized water showed the photoluminescence peak at 384 nm (3.23 eV), whereas peaks at 370 nm (3.35 eV) were observed for sample prepared in isopropanol. The use of water and isopropanol as a solvent yielded spherical nanoparticles of 14–20 nm while in acetone they found two types of particles, one spherical nanoparticles with sizes around 100 nm and another platelet-like structure of 1 μm in diameter and 40 nm in width.

A physical vapour condensation method was used to synthesise ZnO nanoparticles by Tripathi et al. [54]. The size of these nanoparticles varied from 40 nm to 100 nm. Mostly, these nanoparticles are spherical in shape but contain some impurities. From UV visible absorption spectra of these nanoparticles, peaks at 381 nm and 373 nm are observed. The XRD data shows a sharp peak at 36.87°, which is very close to that of zinc oxide nanoparticles grown by oxidation in the presence of ambient gases i.e., oxygen mixed with argon.

Meruvu et al. [55] have reported an easy pathway to synthesize the ZnO nanoparticles with narrow size distribution. Synthesis of zinc oxide nanoparticles was achieved by using zinc acetate, polyethylene glycol and ammonium carbonate by precipitation method. Detailed structural characterizations demonstrate that the synthesized products are spherical and crystalline in structure and their diameter was about 30 nm. These structures clearly evident from SEM as shown in Figure 1.7. Further they studied its antimicrobial activity against Bacillus subtilis and E. Coli. Composites of zinc oxide have also been synthesized and studied.
Nemeth et al. [56] have reported the synthesis of ZnO nanoparticles on clay mineral surface. They showed that presence of clay mineral stabilizes the particles. Synthesis of zinc oxide on the surface of silica particles was demonstrated by Xia and Tang [57]. Simultanious addition of triethanolamine and zinc acetate into SiO$_2$ ethanolic solution gives the ZnO coated silica particles. TEM is shown in the Figure 1.8.

Wang et al. [58] reported chemical synthesis of water-soluble ZnO-Au NCs by a simple and effective route to obtain semiconductor and metal heterostructure composites that are soluble in aqueous media and have expanded functionalities of nanostructured materials. The structures and sizes of ZnO-Au NCs with dumbbell-like shape were identified to be wurtzite ZnO and fcc Au with 4.9 and 7.1 nm diameters, respectively. They found that the surface plasmon band of the ZnO-Au NCs was broadened and red-shifted by about 17 nm relative to monometallic Au nanoparticles.
The UV emission of the ZnO-Au NCs was about 1 order of magnitude stronger than that of pure ZnO nanocrystals, which reflect the strong interfacial interaction between ZnO and Au.

Hong et al. [59] synthesized ZnO nanoparticles by calcination of precursor prepared by the precipitation method. Polystyrene was grafted onto the surface of ZnO nanoparticles to improve the dispersion of the particles and to reduce their photocatalytic activity. The obtained particles were characterized by Fourier transform infrared spectroscopy, X-ray powder diffraction, and transmission electron microscopy. The photocatalytic activity of bare and modified ZnO nanoparticles was studied. Experimental results show that well dispersed ZnO nanoparticles were obtained after surface modification. ZnO nanoparticles possess high photocatalytic activity, whereas the photocatalytic activity can be significantly reduced when polystyrene was grafted onto the particle surface.

Karimi et al. [60] synthesized ZnO and MgO nanoparticles and ZnO/MgO nanocomposite by the sonochemical method. Under optimum conditions, spongy shaped, uniformed and homogeneous nanostructured zinc oxide and magnesium oxide powders were obtained with particle sizes of 25–50 and 30-60 nm, respectively. ZnO/MgO nanocomposite was also obtained with more spongy morphology and particle size about 65 nm. The synthesized nanoparticles and nanocomposites were successfully applied to the preparation of zinc polycarboxylate dental cement. This study showed that mechanical strength of dental cements is dependent on composition size scale.

Fernandez et al. [61] reported one-pot surfactant-assisted procedure to prepare ZnO-SiO₂ lamellar nanocomposites with high zinc content. Quantum confinement effects have been observed in the optical response of the ZnO nanoparticles included in these nanocomposites. Impedance spectroscopic analysis of nano ZnO and ZnO-Al₂O₃ nanocomposites containing varying wt% percentage of nano Al₂O₃ from 5 to 20 nm has been recently reported by Jose et al. [62].

Similarly the contributions by grains and grain boundaries to the electrical conductivity of ZnO-Ag nanocomposites were studied in detail by Jose et.al. using the same technique [63]. It was found that at higher temperatures, the conductivity of the nanocomposite samples increased with increasing wt % of nano-Ag and then decreased as shown in Figure 1.9.
Chapter 1

Introduction

The variation must be originating from the changes in the grain boundary structure of nano ZnO and the effects of the Ag₂O layers on the diffusion of charge.

![Graph showing variation of dc conductivity of ZnO-Ag nanocomposite sample with wt % of nano Ag](image)

**Figure 1.9** Variation of dc conductivity of ZnO-Ag nanocomposite sample with wt % of nano Ag [63]

Virat et al. [64] have studied a new type of composite material, consisting of metallic cobalt nps dispered within a piezoelectric ZnO matrix. Well-oriented ZnO (SEM, Figure 1.10) is obtained by a heat treatment in air above 500 °C. Because ZnO is sensitive to a reducing heat treatment in air above 500 °C, in order to obtain well oriented ZnO as well as metallic cobalt, optimized reducing treatments had to be performed in a mild reducing atmosphere.

![SEM image of the as deposited film heat treated at 600°C](image)

**Figure 1.10** SEM image of the as deposited film heat treated at 600°C [64]

Shi et al. [65] found that ZnO nanoparticles in AAO membrane may cause luminescence enhancement. They fabricated purpose-built ZnO arrays directly on ITO
conductive glass and in nanochannels of polycarbonate membrane, and investigated their photoluminescence properties. The former sample exhibited only two peaks at 360 and 390 nm, which correspond to the recombination of e–h⁺, and UV band emission, which confirms minimal defects, existed. After annealing, the second kind of samples showed an additional two peaks, located at 488 and 540 nm. This fact may be explained by the defects in the newly formed ZnO, which is derived from Zn²⁺ adsorbed on the surface of the ZnO nanoparticles in the nanochannel.

Monticone et al. [66] have investigated the UV and visible fluorescence of colloidal ZnO particles by time resolved spectroscopy. Time-resolved spectroscopy of colloidal ZnO nanoparticles has been carried out with a laser excitation at 248 nm. Except for the known band gap 370-nm and impurity 510-nm emissions, they had found additional continua at ~300, 430, and 545 nm. These continua were developed in solutions of different composition, with excess Zn²⁺ and OH⁻ ions, and in function of time. All but 510-nm fluorescence bands exhibit short nanosecond or subnanosecond decays. The green fluorescence at 510 nm originating from 4-nm particles in Zn²⁺-rich solutions is a much longer-lived, 1.0 μs. Cluster size distribution and growth kinetics have been recovered from spectral measurements.

Dijken et al. [67] also discussed the mechanism of the two emission bands by measuring the steady state luminescence of nanocrystalline ZnO particles with different size. They have studied the luminescence behavior in ZnO and proposed a model for the origin of visible green luminescence. Intensity of green luminescence is more than that of UV (band edge) luminescence in zinc oxide. This means there is one step involved in which photoexcited hole is trapped some where in the particle and trapping is much faster than the radiative recombination rate of the band edge emission. Surface sites are considered to be the most efficient traps for these photoexcited holes. Dijken et al. have reported that probable candidate for such traps is the O²⁻ ions at the surface. PVP-capped ZnO quantum dots also exhibited enhanced UV-photoluminescence and reduced green emission of ZnO nanoparticles. [68].

An interesting study has been performed recently by Andelman et al. [69]. They have studied the effect of particle morphology on photoluminescence of ZnO particles. Depending on the solvent used three different morphologies have been synthesized viz. triangles, rods and spheres. Photoluminescence investigations show that green luminescence observed in case of ZnO nanoparticles is strongly dependant on the particle morphology.
The strongest green band intensity corresponded to the shape with the largest surface/volume ratio and could be attributed to surface oxygen vacancies. Photoluminescence measurements indicated that the green band emission is associated with surface defects and shows a strong dependence on morphology, with suppression of the green band emission in the case of spherical nanoparticles and nanotriangles. In their another study Andelman et al. [70] reported a simple solution method to control the diameter of ZnO nanorods by increasing the chain length of the amine solvent used. They have studied the effect of particle diameter on photoluminescence of ZnO particles. It was found that the small ZnO nanorods have strong green emission, while the large diameter nanorods exhibit a remarkably suppressed green band.

There are few reports about the electrical conduction mechanism in ZnO. Studenkin et al. [71] reported that the effect of H incorporation increases the number of zinc rich defects and therefore n type conductivity. It has been reported that many factors affect the electrical properties of the ZnO thin films such as film thickness, grain and agglomerate size, grain boundary and impurity distribution all of which are determined by the synthesis conditions.

Hartmann et al. [72] have showed that copper implantation of ZnO thin films deposited by sputtering decreases the resistivity while oxygen annealing increases the resistivity of the ZnO thin film due to electron trapping by the Cu 3d states. It has been recognized that the presence of Al or Co has the effect of enhancing the electrical conductivity of ZnO thin films [73]. The electron hall mobility in zinc oxide single crystals is in the order of 200 cm²/V.s at room temperature. In case of undoped ZnO, electron doping has been attributed to Zn interstitials, oxygen vacancies or hydrogen. The electrical properties of ZnO are hard to quantify due to large variance of the quality of samples available. ZnO nanostructures show better electrical transport properties than thin film.

Zinc oxide has received considerable attention in recent years because of its potential applications associated with it. The principal advantage is that ZnO possesses a larger exciton binding energy than that of GaN, which will allow devices operating with higher efficiency and lower power threshold for lasing by optical pumping at room temperature. Valued for its ultra violet absorbance, wide chemistry, piezoelectricity and luminescence at high temperatures, ZnO is one of the critical building blocks in today’s modern society [74].
It can be found in paints, cosmetics, plastic and rubber manufacturing, electronics and pharmaceuticals, to name just a few other applications in optoelectronics as blue colour light emitting phosphors [75,76], as nanosensors of various gases and also in cosmetic industry, as a component of sun screens, are envisioned [77-80]. Also it can be used as nanorod UV light emitters [81], as fluorescence labels in medicine and biology, in controlling units as UV photodetectors [82].

Recently Padmavathy and Vijayaraghavan et al. [83] reported the enhanced bioactivity of ZnO nanoparticles by studying the antimicrobial activity of suspensions with various particle sizes using a standard microbial method. ZnO nanoparticles were found to be more abrasive than bulk ZnO, and thus contribute to the greater mechanical damage of the cell membrane and the enhanced bactericidal effect of ZnO nanoparticles.

Transparent conducting zinc oxide films have been extensively studied in recent years for solar energy conversion applications. Transparent conducting films deposited on polymer substrates can be used in plastic liquid crystal displays transparent electromagnrtic shielding materials, flexible electro-optical devices, touch sensitivity overlay and unbreakable heat-reflecting mirrors [84]. Additionally, the radiation hardness of ZnO to MeV proton irradiation makes it an ideal candidate for space applications [85]. The applications of ZnO to the UV-emitting diodes, cathode-ray phosphors, transparent conductor, varistors, chemical sensors, UV-protection films and ultrafast nonlinear optical devices have been performed [86]. Piezoelectricity is one of the important properties of ZnO, which has been extensively studied for various applications in force sensing, acoustic wave resonator, acousto-optic modulator [87-90].

Our group [91] has reported efficient field electron emission from ZnO nanoparticles synthesized by a chemical route. Nanostructures were synthesized in three different morphologies, namely needles, rods, and spheres. The observed results indicate that the field emission characteristics of chemically grown ZnO nanostructures are at par with those reported for solid–vapour phase grown ZnO nanostructures.

The field emitters prepared by the chemical method have been found to be quite stable with respect to the emission current as well as having mechanical stability.
Field emission images of ZnO particles are shown in Figure 1.11.

![Figure 1.11 Field emission from ZnO particles (A) Needles, (B) Rods and (C) Spherical particles [91]]

ZnO also presents suitable characteristics useful in the development of gas sensing devices [92]. Yi and coworkers [93] demonstrated ZnO nanorod sensors for detection of biological molecules. Thus ZnO could be one of the most important nanomaterials for future research and applications.

### 1.4 Polymers: A Brief Introduction

A Polymer is a large molecule (macromolecule) composed of repeating structural units. Polymer has gained its name from two Greek words, Poly means ‘many’ and mer means ‘unit or part’. The individual small molecules from which the polymer is formed are called monomer—means single polymer and are linked to each other by covalent bonds [94]. The process by which the monomer molecules are linked to form a polymer is called ‘polymerisation’. Polymers are classified as either Natural or synthetic based on the source. Natural rubber, cellulose, and proteins are examples of natural polymers. Synthetic polymers, on the other hand, are human-made materials such as polyamide, silicone, and polyurethane.

Based on structure of polymers it can be classified as linear polymers, branched chain polymers and cross-linked or network polymers. Linear polymers contain linear chains having some branches, e.g., low-density polythene. Branched chain polymers consist of long and straight chains. e.g. high density polythene, polyvinyl chloride, etc. Cross linked or network polymers are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains. e.g. bakelite, melamine, etc.
Polymers can have different structures and these can affect their properties, some examples are shown in figure 1.12. The chains when heated can flow easily this is a good example of the chain of a thermoplastic. Properties often associated with this type of chain are a weak material, ductile with a low density and melting point.

![Figure 1.12 Sketches of Linear polymers, Branched chain polymers and Cross linked polymers [94]](image)

Branched chains will not flow as easily when heated they will have a higher melting point than linear chains and typically have the properties of a slightly less ductile material (stronger and stiffer). The Cross linked bonding retains its shape when heated and is a good example of the bonding found in thermo set plastics. These also have a higher melting point than linear and branched bonds, they are usually a harder material but also more brittle.

A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains. Under this category, the polymers are classified into the following four sub groups on the basis of magnitude of intermolecular forces present in them.

**Elastomers and Fibres**

These are rubber-like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few ‘crosslinks’ are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc. Fibres are the thread forming solids which possess high tensile
strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

**Thermoplastic and Thermosetting polymers**

These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

Thermosetting polymers are cross-linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.

**Organic and Inorganic polymers**

A polymer whose backbone chain is made mainly of carbon atoms is known as organic polymer. Most of the synthetic polymers are organic polymers. On the other hand, those which contain no carbon atoms in their chain backbone are called inorganic polymers. e.g. glass and silicone rubber.

Lightweight, low cost, and ease of processing are the main reasons that motivate the use of these materials, especially in today’s market. Neat polymers do not usually attain all the property requirements in certain applications and thus a composite is required. One of the most economical ways to improve properties of polymeric materials is via the fabrication of multi-component materials, or polymer composites.

Subsequent to the commercialization of nanosize oxide particles, polymer nanocomposites have been the subject of intense research and development in academia and industry. The polymers provide a processable matrix in which to disperse the particles. Polymers are able to produce required immobilization of nanoparticles avoiding their coalescence or segregation; thus protecting the novel size dependent properties of nanomaterials [95]. The polymers commonly used are as follows [96].
Polyvinyl alcohol (PVOH, PVA)

Polyvinyl alcohol (PVOH/ PVA) is a water-soluble synthetic polymer. PVA is fully degradable and is a quick dissolver. Due to large range hydrogen bond formation ability it is extensively used as a binder for the synthesis of composite materials [97]. It decomposes rapidly above 200°C as it can undergo pyrolysis at high temperatures. The properties and molecular formula for PVA is as follows.

<table>
<thead>
<tr>
<th><strong>Polyvinyl alcohol (PVA)</strong></th>
<th><strong>Properties</strong></th>
<th><strong>Chemical structure</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>((\text{C}_2\text{H}_4\text{O})_n)</td>
<td><img src="attachment" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Density</td>
<td>1.19-1.31 g/cm³</td>
<td></td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>(10^{15}) (ohm-cm)</td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>230°C</td>
<td></td>
</tr>
<tr>
<td>Boiling point</td>
<td>228°C</td>
<td></td>
</tr>
</tbody>
</table>

Polyvinylpyrrolidone (PVP)

PVP (Polyvinylpyrrolidone) is highly soluble in polar solvents such as alcohol. Therefore it is preferable to avoid phase separation in the reaction. The pyrrolidone group of PVP prefers to complex with many inorganic salts resulting in fine dispersion and surface passivation of them. It has good film-forming and its films exhibit good optical quality and mechanical strength [98]. The properties and molecular formula for PVP is as follows.

<table>
<thead>
<tr>
<th><strong>Polyvinylpyrrolidone (PVP)</strong></th>
<th><strong>Properties</strong></th>
<th><strong>Chemical structure</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>((\text{C}_6\text{H}_9\text{NO})_n)</td>
<td><img src="attachment" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Density</td>
<td>1.19-1.31 g/cm³</td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>150 - 180 °C</td>
<td></td>
</tr>
<tr>
<td>Boiling point</td>
<td>228°C</td>
<td></td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>(10^{17}) (ohm-cm)</td>
<td></td>
</tr>
</tbody>
</table>

Polyaniline (PANI)

Polyaniline (PANI) is a conducting polymer. Amongst the family of conducting polymers and organic semiconductors, polyaniline is unique due to its ease of synthesis, environmental stability, and simple doping/dedoping chemistry. Although the synthetic methods to produce polyaniline are quite simple, its
mechanism of polymerization and the exact nature of its oxidation chemistry are quite complex. Because of its rich chemistry, polyaniline (PANI), is one of the most extensively studied conductive polymers in past few decades. Polyaniline has a great deal of potential for applications due to its lightweight, conductivity and chemical properties.

Polyaniline is especially attractive because it is less expensive, and has an acid/base doping response as was described above in the oxidation states. This latter property allows polyaniline to be used in chemical vapor sensors. PANI has applications in batteries, microelectronics, electrochromic materials for displays, antistatistia additives to plastic and in sensors. Among all the conducting polymers it is the most environmentally stable polymer with good electrical conductivity [99].

The properties and main chemical structure of PANI is as follows.

<table>
<thead>
<tr>
<th>Polyaniline (PANI)</th>
<th>Properties</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>((\text{C}_5\text{O}_2\text{H}_8)n)</td>
<td><img src="image" alt="Polyaniline Chemical Structure" /></td>
</tr>
<tr>
<td>Density</td>
<td>1.19g</td>
<td></td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>(10^3) (ohm-cm)</td>
<td></td>
</tr>
</tbody>
</table>

**Poly (methyl methacrylate) (PMMA)**

Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic, often used as a light or shatter-resistant alternative to glass. It is sometimes called acrylic glass. Chemically, it is a synthetic polymer of methyl methacrylate. PMMA transmits up to 92% of visible light (3 mm thickness). PMMA swells and dissolves in many organic solvents, it also has poor resistance to many other chemicals on account of its easily hydrolyzed ester groups. Nevertheless, its environmental stability is superior to most other plastics such as polystyrene and polyethylene. It has good insulating properties, a high dielectric strength. Besides it is a versatile polymeric material that is well suited for many imaging and non-imaging microelectronic applications [100]. It is also widely used as a housing material or surface coating material of machinery because of its excellent weather resistance and high transparency. The properties and chemical structure of PMMA is as follows.
Chapter 1

Introduction

<table>
<thead>
<tr>
<th>Poly(methyl methacrylate) (PMMA)</th>
<th>Properties</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>(C₅O₂H₈)ₙ</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Density</td>
<td>1.19 g/cm³</td>
<td></td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>2 x 10^{15} (ohm-cm)</td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>160 °C</td>
<td></td>
</tr>
<tr>
<td>Boiling point</td>
<td>200 °C</td>
<td></td>
</tr>
</tbody>
</table>

1.5 Nanocomposite particles: An Overview of Synthesis, Properties and Applications

Nanocomposite materials have attracted large attention [101-103] these days as they are novel materials, which combine the advantages of different constituting materials. The term “nanocomposite” describes a two-phase material where one of the phases is dispersed in the second one on a nanometer level. The solid phases can be organic or inorganic or both with amorphous semi-crystalline or crystalline phase or combinations of those phases. The reason why nanocomposites arise significant interest in the scientific community is that the extremely small size of the fillers not only leads to unique properties themselves, but also attributes to unprecedented morphologies of the composites.

Nanocomposites have been fabricated in several interdisciplinary fields to produce and satisfy several functions simultaneously needed in many applications. The methods used for preparing nanocomposites may vary from chemical and mechanical routes to vapour phase deposition and mainly depending on the type of matrix used. The key issues in the development of nanocomposites are production of nanoreinforcements, control over distribution in size and their dispersions, tailoring interfaces at nanoscale between the constituents and understanding physical phenomena, in these composites [104]. There are various techniques to fabricate well-dispersed nanocomposites. In this kind of materials the nano-size fillers influence the composite’s properties to a much greater extent than corresponding conventional composites with micro-size fillers. Specially, the nanomaterials with their host polymer are often synthesized by embedding nanoparticles of metal or semiconductors in polymers [105,106]. Nanofillers restrict conformation of polymer chains and mobility, which might lead to changes in relaxation behaviour, free volume and thermal...
transitions like glass transition temperature, etc. For semi-crystalline polymers like polyethylene, poly (vinyl alcohol), polypropylene and nanofillers may even influence the degree of ordering and crystal packing, thus crystallinity or the micro-structure of the polymer will be altered. Nanocomposites offer opportunities of producing a new class of materials, which would demonstrate their own structure - property relationship [104-106].

Here first, we have to prepare the nanosized particles of inorganic moiety and then to incorporate them in the matrix. The research work reported in this thesis is concentrated on the synthesis and characterization of various polymer nanocomposites embedded with ZnO nanoparticles. The processing conditions were optimized to achieve good uniform dispersion of the nanoparticles in the polymer matrix. Poly (methyl methacrylate), polyvinyl alcohol, polyvinyl pyrrolidone, polyaniline were the polymers chosen as the host matrix.

Despite numerous challenges, considerable research has been done to develop appropriate synthetic techniques for making good polymer nanocomposites in the literature. The methods used in the preparation of nanocomposites range from chemical means to vapor phase deposition. One can classify these methods in different ways, e.g. chemical or physical synthesis routes. Methods in which one can make thin films or bulk nanocomposites, etc. Depending on whether the inorganic component is grown in presence of polymer matrix or pre-fabricated there are two principally different routes to incorporate inorganic particles into organic matrix. Generally these techniques can classified as ex situ and in situ methods.

The ex situ synthesis generally involves a homogenous mixing of chemically pre-synthesized nanoparticles with pre-synthesized polymer matrix.[107-110]. In the ex situ process, there are two subgroups: direct mixing and solution mixing. Direct mixing consists of elastomeric mixing or thermal mixing in which nanoparticles and polymers are mixed directly to make nanocomposites.

Some nanocomposites can be produced with this traditional method for example nanoscale silica (SiO$_2$) and polypropylene have been successfully mixed in a two-roll mill [111]. Some nano particle fillers in nylon matrix also have been processed using thermal spraying method [112]. Direct mixing is the fastest method for introducing new nanocomposites.

Hong and coworkers also reported that nano- ZnO and low density polyethylene were melt-compound in a high-shear mixer to prepare nanocomposites.
with an increase in the resistance to thermal degradation [113]. The main limitation of direct mixing process is that by increasing the filler concentration the viscosity increases rapidly which in turn can limit the viability of this technique.

Some of the limitations of direct mixing can be overcome if both the polymer and the nanoparticles are dissolved or dispersed in solution. This allows modification of the particle surface without drying, (like ligand-exchange process) among the polymer matrix, which reduces particle agglomeration [114]. After dispersion, the polymer nanoparticle solution can then be casted into a solid, or be isolated from solution by solvent evaporation or precipitation. Further processing can be done by conventional techniques.

Wei et al. [107] prepared platinum nanoparticles composite thin films by this method-using precursor (hydrate lead acetate and titanium butoxide). The ultrafine particles obtained with spheroid in shape and have size in the range 40 -80 nm. The platinum-polyetherketone nanocomposite formation was done by spin coating method-using chloroform as the solvent.

Zeng et al. [108,109] have produced Ag-polymer nanocomposite films using solution-mixing approach. They have synthesized spherical silver nanoparticles by the reduction of silver ions with hydrazine in a water-in-oil microemulsion system. Nanoparticles were further capped by n-dodecyl mercaptan (C_{12}H_{25}SH). For fabrication of nanocomposite films, the polymers including PMMA, polystyrene (PS) etc., were dissolved in chloroform subsequently. A given amount of the aforesaid silver nanoparticles were added to the polymer solutions and dispersed by ultrasonication. Finally, Ag-polymer nanocomposite films were made by static casting at room temperature.

Pan and Zou [110] have reported the fabrication of polyacrylonitrile (PAN)/antimony-doped tin oxide (ATO) nanocomposite using solution mixing method. They have reported first the preparation of nano ATO particle. These nanoparticles were dissolved in dimethyl sulfoxide (DMSO) and mixed with a DMSO solution of polystyrene. The mixture solutions were cast and left to dry in vacuum at 60\degree C for 48 h. The micrographs of the resulting nanocomposite materials were imaged by SEM and are shown in Figure 1.13.
Chloroform was used as solution for dispersing TiO$_2$ and paraxylene was used for dissolving LDPE. The solutions were later volatilized. Tong et al. developed a sol-gel approach to prepare and study polyimide/TiO$_2$ hybrid films from soluble polyimides and a modified titanium precursor [116]. Zhang et al. prepared High-impact polystyrene (HIPS)/nano-TiO$_2$ nanocomposites by surface pretreatment of nano-TiO$_2$ with special structure dispersing agent (TAS) to study the impact properties [117].

Carotenuto et al. [118] have introduced a method for fabrication of metal-polymer nanocomposite using solution mixing and subsequent annealing the samples. They have reported the preparation of Ag, Au, Co and Pd clusters dispersed in Polystyrene (PS) matrix. First, the alkanethiols capped nanoparticles were synthesized and then were dissolved in chloroform and mixed with a chloroform solution of polystyrene. After casting the nanocomposite solution onto a glass substrate annealing treatments were made at temperature above the polymer glass transition temperature, ranging from 120 to 230$^\circ$C.

In in situ formation of nanocomposites process, formation of the nanoparticles occurs in the presence of a protective polymer, which immobilizes the particles and limits the size of the particles. Once a stable suspension of particles is prepared in the presence of a polymer, the composite can be cast to form a nanocomposite.

Liu et al. [119] reported the preparation of CdS/ Poly (styrene-co-vinyl acetate) nanocomposites by the in situ simultaneous copolymerization technique with
CS$_2$ as the sulfur source. The sample was characterized by TEM micrograph as shown in the Figure 1.14. The figure showed the aggregates of the CdS particles, which were formed because of the high surface energy of the nanometer size crystals.

![Figure 1.14 TEM image of the CdS/PSV nanocomposites prepared at 130°C for 12 h](image)

**Figure 1.14 TEM image of the CdS/PSV nanocomposites prepared at 130°C for 12 h [119]**

In order to prepare a visually transparent material which absorbs UV light, nanocomposites of ZnO and a copolymer of ethylene and vinyl acetate (EVA) were produced starting from immersion of EVA in a diethyl zinc solution [120]. The zinc compound diffused rapidly into the polymer. The nanocomposites absorbed UV light up to 370-380 nm while light loss by scattering was virtually absent in the visible wavelength range. Visually transparent nanocomposites of ZnO and poly(propylene) (PP) or poly(ethylene) (PE) were also described [121]. Transparency, an increase in refractive index, and other optical gains resulting from the inclusion of nano-TiO$_2$ were also investigated into nanocomposites with the polymer matrices including PMMA [122,123].

Most of the properties observed in polymers-discontinuous reinforcement systems are directly related to their structure. For example, poly (styrene-alt-maleic anhydride) (PSM) /CdSe nanocomposite showed an emission peak at 540 nm in its photoluminescence spectrum, which was close to the absorption edge of the obtained CdSe particles. According to the authors, [124] this type of near band edge emission is typical of surface-passivated nanocrystalline CdSe. For nanoparticles, a large percentage of defects are located at the surface. If these defects are not passivated, non-radiative recombination will occur, as they act as traps for electron and hole annihilation. Therefore, PSM modified the surface structure and enhanced the luminescence properties of CdSe nanoparticles.
As can be seen from TEM image of this material (Figure 1.15), CdSe nanoparticles are monodispersed and uniform with an average size of about 17 nm. Here, PSM played an important role in controlling the size and the monodispersion of the nanoparticles. Interactions between PSM and CdSe particles were also investigated and are supported by IR and UV-visible spectroscopy.

![TEM image of PSM/CdSe nanocomposite](image)

**Figure 1.15** TEM images of the PSM/CdSe nanocomposite (size 17 nm) and corresponding absorption spectra is plotted for the same [124]

In a recent work, Lü et al. [125] synthesized blue emitting 5-(2-ethacryloylethoxymethyl)-8-quinolinol (MQ) surface coordinated ZnS NPs, with high quantum yield and good stability by a ligand exchange process. The high emitting MQ-ZnS NPs were integrated in polymer matrix obtained starting from DMAA/St/DVB monomers, resulting in transparent and blue emitting nanocomposites. The as-prepared hybrid functionalized NP–polymer materials can be therefore processed in the fabrication of multifunctional electro optical devices.

The electrical properties of the nanocomposites have significant interest due to possible applications in fluid sensors [126] and single electron transistors [127]. Reports by Athawale et al. [126], Sarma et al. [127], Sadik et al. [128] state that incorporation of nanoclusters into conducting polymer matrices resulted in enhancement in the electrical conductivity. They found that the conductivity increased with decrease in the particle size and increase in the nanoclusters content.

Ballav and Biswas prepared composites consisting of PTP and nanosized alumina (particle size: 22–74 nm) [129]. They found a slight increase in the electrical conductivity and an improved thermal stability in contrast to the pure homopolymer.

Ma et al. reported that polystyrene resin/ZnO nanocomposites were prepared by melt blending [130]. The surface resistivity falls as the amount of ZnO increases.
Adding 30 wt % of ZnO spherical particles and ZnO whiskers reduced the surface resistivities of materials from $1.0 \times 10^{16}$ to $8.98 \times 10^{12}$ $\Omega$/cm$^2$ and to $9.57 \times 10^{10}$ $\Omega$/cm$^2$, respectively. The amount of ZnO in polystyrene resin can be gradually increased to form a conductive network. Dispersion of nanoparticles in conductive or insulating polymers can enhance their electrical conductivity. These nanocomposites have found various applications used for heating devices, antistatic materials, electromagnetic shielding and specially to the development of highly sensitive components for the measurements of temperature and pressure.

However, the resistivity of these nanoparticles-polymer nanocomposites shows dependence upon polymer species, size and shape, as well as concentration of nanoparticles. A maximum value of ionic conductivity was obtained at 10% nano-TiO$_2$ loading with a conductivity of $7 \times 10^{-7}$ S/cm, which was over an order of magnitude higher than that of the electrolytes without TiO$_2$, also higher than that of microsized-TiO$_2$ filled electrolytes.

The electrical breakdown strength of nano TiO$_2$ filled low-density polyethylene (LDPE) nanocomposites was investigated by Ma et al. [131]. It shows the breakdown strength at 63.2% cumulative failure probability ($E_0$) for the composites filled with dried nanoscale TiO$_2$ was similar to that of neat LDPE and 50% higher than that for the samples filled with as-received nanoscale TiO$_2$. It was also found that surface modification of nanoscale TiO$_2$ had a significant influence on the breakdown strength. Dispersion of nanoparticles in conductive or insulating polymers can enhance their electrical conductivity. In addition, the electric breakdown strength of nanocomposites can be enhanced [132].

Hsu et al. [133] studied the electrical properties of the composites $(La_{1.85} Sr_{0.15} CuO_4)_1-x(La_{0.3} Dy_{0.4} Sr_{0.3} MnO_3)_x$ with $x<1.5$. They studied these properties by resistivity measurements. The undoped $(La_{1.85} Sr_{0.15} CuO_4)$ undergoes a superconducting transition at ~40 K, whereas it exhibits an insulator-to-metal transition ~100$^0$K. and a spin glass transition ~70$^0$K. Figure 1.16 shows the resistivity plot Vs temperature.

In a recent work, Mukherjee and Nandi fabricated Schottky barrier diodes consisting of a conducting polymer, such as poly(o-methoxy aniline) (POMA) and Ag NPs [134]. Electrical measurements on the nanocomposites pointed out different I–V
behaviors depending on the size and density of NPs, that result in a tuning of the electronic properties from rectification behavior to switching behavior.

![Figure 1.16 Variation of the scaled resistivity of LSCO and the composites w.r.t to temperature. Conduction below ~ 120K (continuous line) and above ~180 K (dashed lines) [133]](image)

Nanocomposite materials have received considerable attention in recent years because of potential applications associated with them. A few applications are discussed here.

Zinc-based sol-gel inorganic paints were and are still employed as corrosion-resistant primers and high-temperature coatings for steel [135]. Farouk et al. [136] reported the synthesis and characterization of nanosize zinc oxide particles and applied it for the preparation of functional coating for inorganic-organic hybrid materials. These materials were modified with these particles and were applied to cellulosic cotton (100%) and cotton/polyester (65/35%) fabrics. The resulting textile materials achieve significantly improved UV-absorption of high durability, without affecting the textile, changing air permeability and even improving the wear resistance.

These modified inorganic/organic hybrids polymers were based on 3-glycidyloxypropyltrimethoxysilane (GPTMS). Complete finishing solution prepared in this work has remarked long stability for further processing. The effectiveness of the novel finishing was determined by UV-Vis spectroscopy and by evaluation of the
ultraviolet protection factor (UPF). The influences of the finishing for some general textile properties as e.g. tensile strength, elongation, air permeability, degree of whiteness, wear-resistance, stiffness as well as the durability of the treatments were investigated. Wypych and Satyanarayana [137] reported a variety of possible industrial applications for polymer nanocomposites such as automotive, construction, aerospace, food packaging and electrical and electronics etc.

Godovsky et al. [138] discussed in detail the advantages of using organic-inorganic nanocomposites for device applications. Composite electrolyte materials for applications such as solid-state lithium batteries or supercapacitors are produced using organic-inorganic polymeric systems formed by the mixture of organic polymers and inorganic moieties prepared by sol-gel techniques.

Park et al. [139] found that by embedding Ag or Pd nanoparticles in a polyaniline (PANI) matrix an increase in redox activity. The improved redox activity results in charge-discharge performance potentially making these useful as cathode materials in improved lithium rechargeable batteries.

Polymeric foams are extensively used in different applications such as aerospace, marine, automotive, packaging, and cushioning due to their energy absorption capabilities especially in the event of impact loading [140] good moisture resistance, dampening characteristics.

Mahfuz et al. [141-142] modified polyurethane foam by infusing 3%TiO₂ nanoparticles (spherical shape, diameter 29nm) through ultrasonic cavitation process. They found that nanophased foams are thermally stable and their strength and stiffness are greatly improved. On the basis of research results, it can be said that nanocomposite foam plays an important role in packaging industries and also for short-term disposal applications.

Various methods have been developed to produce nanocomposites which are biocompatible and found lots of applications as biosensor.

For example, functionalized platinum nanoparticles have been conjugated onto multiwall carbon nanotubes and the assemblies were incorporated into the polypyrrole matrix using electropolymerization technique [143]. Resulting nanobiocomposites exhibit a high electrocatalytic ability and high sensitivity useful for a biosensor. The biocompatible polymers like ‘Arabinnogalactan’ can be applied for reducing and stabilizing of noble metals e.g. Au, Ag, Pt, Pd [144].
1.5.1 Electrical conduction mechanism in composite materials
Tunneling effect and Temperature dependence of the electrical Resistivity

The resistivity as a function of temperature and or composition for a material can be represented as in Figure 1.17. The curve can be described as consisting of two different regions. In the low temperature regime, the resistivity increases with temperature and in the high temperature regime, the resistivity decreases with increasing temperature. The resistivity has a metallic behavior (d\(\rho\)/dT > 0) below the peak and a semiconducting (insulator) behavior (d\(\rho\)/dT < 0) above.

![Figure 1.17 A typical resistivity versus temperature and composition for a material [145]](image)

Temperature causes electrons to be excited into the conduction band and hence resistivity is considered as a thermally activated process. At the insulating regime, it can be considered that the electrical conduction in composites results from tunneling of electrons and holes from one isolated neutral particle to the next across the gaps. To generate the charge carriers, electrons have to be removed from one neutral particle to another. At low field regime, when the voltage difference between neighboring particles (\(\Delta v\)) is much smaller than KT/e, thermal activation is the main mechanism responsible for charge carrier generation.

The energy required to exchange charge between particles, is called activation energy (\(\Delta E\)). Only electrons and holes excited to states of at least this energy from the Fermi level will be able to tunnel from one neutral particle to another. The model described here is like the models which were considered for ‘Ultra thin metal films [146,147] or ‘cermets’ [147]. At equilibrium, and at any temperature above absolute zero degree, a number of particles are charged. They have gained or lost an electron from or to initially neutral neighbouring particles. If the activation energy is supplied
only thermally, the equilibrium number of charge carriers will be of the order of [148]

\[ n = N \exp \left(-\frac{\Delta E}{K T}\right) \]  

(1.11)

Where \( N \) is the total number of particles in the sample, \( \Delta E \) is the effective activation energy, \( K \) is the Boltzmann constant and \( T \) is the temperature in Kelvin. Here we neglect the electrostatic interaction between the charged particles. The probability that an electron will tunnel from one negatively charged particle, \( i \), to a neighboring neutral particle, \( j \), is proportional to the density of filled states in particle \( i \) and the density of empty states in particle \( j \) [148]:

\[ P \propto \int D_i (1-f_j) \, dE \]  

(1.12)

Where \( f \) is the Fermi function and \( D \) is the transmission coefficient, depending exponentially on the distance between the particles. This equation results to the random motion of the charge in no field. By applying a field, the relative position of the Fermi levels of neighbouring particles displace and the tunneling probability increases for a transition of charge in the field direction and decreases to a corresponding amount against the field direction. Figure 1.18 illustrates the relative position of the Fermi levels of neighbouring particles in an applied field.

Figure 1.18 Schematic energy level diagrams of a composite consists of conductive fillers incorporated in insulating medium and effect of an electric field on the levels (a) Each metal particle is neutral before the tunneling takes place (b) After tunneling has occurred, a hole is left on one particle and an electron is added to the other particle [146]
The net probability of a charge transition between particles in the field direction due to an applied field can be written as [148]

\[ P_{\text{net}} = P_{+\Delta V} - P_{-\Delta V} \]  

(1.13)

Where \( \Delta V \) denotes the potential drop between two particles. The positive subscript sign is assigned for the transition in the field direction and the negative one for the same against the field direction. Using Fermi functions one can get

\[
P_{\pm \Delta V} \propto D \int_{-\alpha}^{+\alpha} \frac{1}{1 + e^{E/\Delta V}} \left( \frac{1}{1 + e^{(E \pm \Delta V)/\Delta V}} \right) dE
\]  

(1.14)

Which can be reduced to

\[ P_{\text{net}} \propto D e \Delta V \quad \text{(transmissions/cm².sec.)} \]  

(1.15)

By calculating the mobility of charge carriers in the applied field using equation (1.15) and knowing the charge carrier concentration from (1.11)

\[ n_r = 1/r^3 \exp(-\Delta E/\Delta V) \]  

(1.16)

(where \( r \) is the linear dimension of the particles) the conductivity becomes [142]

\[ \sigma = \sigma_0 \exp(-\Delta E/\Delta V) \]  

(1.17)

or the electrical resistivity can be given as [147]

\[ \rho = \rho_0 \exp(\Delta E/\Delta V) \]  

(1.18)

Where \( \rho_0 \) is a constant and independent of temperature. Equation (1.17) exhibits that the resistivity of composite consisting conductive particles embedded in insulating matrix is independent of the applied field and varies exponentially with the inverse temperature.

It is believed that the nature of conductivity is supposed to be an activated one in the most of the composites [149-153]. For example, Roy et al. [154] have synthesized composites of silica glass and metal nanoparticles of copper and nickel and investigated electrical resistivity of them in the temperature range \( \sim 100-340 \) K. Figure 1.19 (a) and (b) show the variation in logarithm of resistivity as a function of reciprocal temperature for different samples containing copper and nickel nanoparticles respectively. There is a sharp increase in the resistivity in the higher
temperature range, followed by a small change of resistivity down to low temperature. In these samples the resistivity change is characterised by semiconductor like behavior in the temperature range ~140–340 K metallic behavior in the range ~80-140 K. The metallic resistivity behavior is according to the evidence by the negative slopes of the curves at lower temperature. The results can be fitted by Eq. (1.17) with different slopes (activation energy) in different regions.

![Figure 1.19](image)

**Figure 1.19** Logarithm of resistivity as a function of inverse temperature for samples containing (a) copper nanoparticles (b) nickel nanoparticles with different particles size [154]

### 1.5.2 Zinc oxide- Polymer nanocomposites : A Brief Review

Zinc oxide is a widely applied filler to poly(hydroxyethylmethacrylate), polyacrylate, low-density polyethylene (LDPE), and many other polymers to prepare composites. Experiments have shown that nanoscale reinforcement brings new optical, electrical, mechanical phenomena, which contribute to material properties and correspondingly extended applications in coatings, plastics, rubbers, fibres and other applications [155]. Here we will discuss the reported literature on ZnO/Polymer nanocomposites.

Xiong et al. [156] have prepared poly(styrene burylacrylate)latex/ZnO nanocomposites by blending prepared poly(styrene burylacrylate ) latex with a water slurry of nano-ZnO particles. It was found that the tensile strength and ultraviolet and near infrared shielding properties of the nanocomposites increased with increasing nano ZnO content. Zheng et al. [157] reported that the addition of small amount of ZnO nanoparticles into a polyurethane matrix changes the mechanical behavior of the
polymer in ZnO/polyurethane nanocomposites. Addition of ZnO nanoparticles decreases the modulus and strain at fracture and increases the glass transition.

Abdullah and Kokuyarna [158] have succeeded in producing ZnO/Polymer nanocomposites with stable luminescence peaks down to 465 nm (blue region) by in-situ growth of ZnO nanoparticles in a poly(ethylene glycol) (PEG) matrix. Figure 1. 20 shows the excitation and photoluminescence spectra.

![Figure 1.20 (a) Excitation spectra and (b) Photoluminescence spectra of nanocomposite polymer electrolyte samples [156]](image)

Xiong et al. [159] produced PEO-ZnO and PEO-ZnO-LiClO$_4$ nanocomposite films through a film-casting method. They found that PEO-ZnO composite exhibited interesting photoluminescence properties and the ionic conductivity of the film increased significantly. Hong et al.[113] were able to make nanocomposites with low-density polyethylene (LDPE) matrix and ZnO nanoparticles through melt mixing of the components. They have reported that ZnO / low-density polyethylene nanocomposites had exhibited a slower decrease in resistivity with filler concentration compared to the conventional composite. The dielectric breakdown strength was also found to be higher for the nanocomposites at high filler concentration. Excellent dispersion of ZnO nanoparticles in the polymer matrix was achieved as shown in the Figure 1.21.

Zheng et al. [160] have reported excellent luminescent performance and high photoelectrochemical conversion efficiency of ZnO/PANI nanocomposite film. The film was prepared by electrochemical-assembly and sol-gel technique on PATP(p-aminothiophenol)/Au-substrate. Further in another study [161] they have synthesized an array of ZnO/PANI coaxial nanowires using an anodic aluminum oxide (AAO) membrane as the template. The PL spectrum of ZnO/PANI coaxial nanowires array in
AAO membrane displays a blue shift and a 100 times PL enhancement of the visible emission band of ZnO (from 530 to 400 nm).

![Figure 1.21](image_url) (a) FESEM image of ZnO/LDPE nanocomposites (b) dc resistivity of ZnO/LDPE nanocomposites [113]

Nanostructured multilayer ZnO/PANI films were studied by Kovtyukhova et al. [162]. The luminescence spectrum of the composite film displays a blue shift in the visible emission band of ZnO.

A few research efforts were reported on PMMA/ZnO nanocomposites. Liu et al. [163] prepared PMMA/ZnO nanocomposites through in situ polymerization of MMA and organic modified ZnO nanoparticles. The thermal stability and UV absorption of the nanocomposites were enhanced as ZnO concentration increased. Very recently, Chen et al. [164] have investigated the optical properties of zinc oxide/PMMA nanocomposites. It was found that the refractive index of the composite films scaled linearly with volume fraction of nanofillers. The surface resistivities of the films were decreased with a high content of zinc oxide nanoparticles.

Du et al. [165] used Sol-gel route to produce ZnO nanoparticles in lipophilic PMMA. It was found that ZnO nanoparticles are fine, well distributed in a PMMA matrix and passivated by the side chain of PMMA. The ZnO/PMMA nanocomposites exhibit pure UV light emission and visible light emission is quenched. Fortunato et al.[166] have reported that Ga doped ZnO thin films on PEN substrates and Al doped ZnO thin films on poly(ethylene-terephthalate) (PET) substrates by r.f. magnetron sputtering. The lowest resistivity obtained of Ga doped ZnO thin films was $5 \times 10^{-4}$ cm$^{-3}$ and an average optical transmittance in the visible part of the spectra of 80%.
Zhang et al. [167] have reported that highly transparent conducting Al-doped ZnO films with good adherence and low resistivity has been prepared on polyisocyanate and polypropylene adipate substrates by r.f. magnetron sputtering. Figure 1.22 shows Electrical resistivity of Al doped ZnO thin films.

![Figure 1.22 Electrical resistivity of Al doped ZnO thin films as a function of Al (OH)₃ content (wt%) (c) Transmittance spectra of the films with thickness (a) [167]](image)

1.6 Summary

In this chapter a brief overview and discussion of the nanoscience and nanomaterials specially on semiconductor nanoparticles and semiconductor-polymer nanocomposites in last few years is presented. Basic properties of nanomaterials, which make them, behave differently from their bulk counterpart is addressed. Various synthesis approaches required for their fabrication along with their properties and applications have also been discussed. A brief discussion of nanocomposites is presented. It is shown that these nanocomposites can be produced by either in situ or ex situ procedures. These advanced functional materials can find large applications in different area like optical, electronic, spintronic etc. The electrical conduction mechanism of composite materials is investigated. In the last section of this chapter a brief review on zinc oxide-Polymer nanocomposite has been given.
References

Chapter 1  Introduction

44. S Huang, T. Kaydanova, Aa. Miedaner, D. S. Ginley, U.S. Dept. of Ener. J. Undergraduate research 70
95. http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/polymers.htm
98. Lide, David R, Handbook of Chemistry and Physics, CRC (1998-99)
 Chapter 1

116. Tong Y., Li Y., Xie F., Ding M. Polymer International, 49 (2000) 1543

49
158. Abdullah T.M. Orionoto Kokuyarna Advanced functional materials 13 -
    10 (2003) 800
159. Xiong H.M., Xu Zhao , Jie-Sheng Chen, J.Phys. Chem. B., 105 (42)1
    10169-10174
162. N.I.Kovtyukhova, A.D.Gorchinskiy, C.Waraksa, Materials Science ,
    131-138
    5222 Nov.(2003) 158-162
165. Du Xi-Wen, Ying song Fu, Jing Sun, Xue Han , Jim LiuSemiconductor
    science , technology, 218 (2006) 1202-1206
166. Fortunato, P. Nunes, A. Marques, D. Costa, H. Águas, I. Ferreira M. E.
    V. Costa, M. H. Godinho , P. L. Almeida , J. P. Borges R. Martins ,
    surface , coatings technology, March (2002) 247-251