Chapter I

Introduction
I.1 Nanomaterials: A preview

A time has come when the quote of famous chemist and Nobel laureate Richard Smalley: “just wait – the next century is going to be incredible. We are about to be able to build things that work on the smallest possible length scales. These little nanotings will revolutionize our industries and our lives” [1.1] has come to reality. Nanotechnology is sweeping through all the fields of science and engineering. Large number of books and review-articles have been published in the past two decades on nanomaterials and nanotechnology [I.2-I.10]. Research in the nanoscience has gained tremendous momentum all over the world due to large funding provided by governments of developed as well as developing countries. Why nanomaterials have been considered so much important? What are the uses of nanotechnology? These nanomaterials have potential applications as catalysts [I.11-I.14], as materials for in cell pharmacy, as cancer fighting nanoparticles, improved drugs [I.10], refrigeration [I.15], sensors due to their increased surface area [I.16-I.18], electrodes [I.19], solar cells [I.20-I.23], opto-electronic devices [I.24, I.25], memory devices [I.26-I.28] etc.

What are these nanomaterials? Usually they are defined as materials having one, two or all the three dimensions restricted in the range of 1 to 100 nm. They lie in the domain which is in between that of molecules and solids and show properties which are entirely different from both of them. Nanomaterials are attracting tremendous attention because their physico-chemical properties are size dependent. For example, in case of CdS, melting temperature reduces from 1600 °C for bulk to as low as 400 °C as we reduce the size up to 2 nm [I.29]. Another effect is that pressure required to transform the phase from four- to six – coordinate increases from 2 to 9 GPa. Also the radiative rate of lowest allowed optical excitation ranges from several nanosecond down to few pico seconds as size is reduced. All these properties can be altered just by changing the size and no change in their chemical composition is done.

Two major effects responsible for governing the properties of these nanomaterials are
1) In case of nano crystals surface to volume ratio is high, which means that larger fraction of the atoms is present on the surface, and

2) Due to quantum size effects intrinsic properties of the interior of the nanocrystals differ from that of bulk.

In case of small particles more number of atoms are present on the surface than that in the bulk of it. As the surface atoms try to be coordinatively unsaturated, there is a high energy associated with them. The surface energy is always lower in case of liquid than that in solid. By melting, total surface energy is reduced and stability is achieved. Thus smaller the particle; higher is the surface energy and lower is the melting point.

![Diagram showing variation in density of states with energy as a function of dimensionality](image)

Figure 1.1 Variation of the density of states with energy as a function of dimensionality for three, two, one and zero dimensional materials [1.9].

Another reason for change in the properties of nanomaterials is that the wavelength of the electron wave function is comparable to size of the particles. It can be predicted by simple particle in a box type model how density of states changes as one goes from bulk to quantum films which are confined in one dimension to quantum wires confined in two dimensions and finally to quantum dots which are confined in all the
three dimensions. Figure 1.1 shows schematic representation of the variation of
density of states for different nano materials.

Electrical transport properties of nanocrystals are also size dependant. In a nanocrystal, presence of one charge prevents the addition of another. Thus current – voltage curves in case of metals and semi conductors look like a staircase due to this Coulomb blockade [I.30].

In case of semiconductor nanocrystals strong variation in their optical properties can be observed as the size is changed. This happens due to quantum size effect. Nanocrystals lie in between the bulk; which has continuous bands of electronic levels and that of molecules; which has discrete states of electronic levels. A drastic change in the optical properties of these materials can be observed as the size is reduced below certain threshold. Main difference between metals and semiconductors is tuning of the band gap with size. In metals there is no band gap so one has to reduce the size to such an extent so that energy levels become discrete and band gap opens up.

As size is increased, centre of the band develops first and then the edges. Curvature of the band is high at the edges. The change in the band structure is dependent on the curvature; it is more where the curvature is high. 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. In case of metals Fermi level lies at the centre of the band so spacing in the energy levels is still very small and the properties resemble to that of the bulk. In case of semiconductors fermi level lies in between the two bands so edges of the bands dominate the properties of the semiconductor nanocrystals. In this case as one goes on reducing the size (top-down approach), bands shift giving rise to an increase in the band gap and edges of the bands becomes discrete. Reverse thing happens as one goes on adding up the molecules to build a nanoparticle (bottom-up approach). Variation of the bands with size is depicted in Figure 1.2.

Theoretically this can be explained by considering a particle in a box type of model. In the model a particle is supposed to be confined in a box (for simplicity
consider one dimensional) of dimension 'a'. Inside the box potential is zero and outside it is infinity.

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

(Eq. 1.1)

Solution for this equation can be taken in the form as

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

(Eq. 1.2)

Solving the equation we get the energy which is expressed as

\[
E = \frac{n\hbar^2}{2m}
\]

for \( n = 1, 2, 3, \ldots \)
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. This is true for both the bottom up approach and top down approach.

In the thesis properties of the nanocrystals, which are synthesized using a bottom-up approach will be studied.

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

**1.2: Theoretical models used for the semiconductor nanocrystals**

**1.2.1: Effective mass approximation**

In a semiconductor, absorption of light excites an electron from the top of the valence band to the bottom of the conduction band leaving a hole behind in the valence band. Interaction of these excited electron and hole with the lattice and with each other is such that their masses are usually different than that of the free electron mass \( m_0 \). These are called the effective mass of electron denoted by \( m_e \) and for hole denoted by \( m_h \).

In effective mass approximation model introduced by L. E Brus [1.31-1.33], a particle with spherical shape is considered. Let \( R \) be the radius of the sphere with dielectric constant \( \varepsilon \) as shown below.

The lowest possible exciton state will have the wave vector given by
Consider an electron excited in the conduction band at \( k = 0 \) state. Smaller the cluster larger is the region of \( k \) space necessary to confine this electron inside the spherical cluster. The expectation value of the electron energy can be given as

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

(1.5)

Where, \( E_c \) is the conduction band energy and \( \psi_i \) is the wave function of an electron in excited state.

Effective mass is defined as

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

(1.6)

Substituting for \( \frac{\partial^2 E}{\partial k^2} \) 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 highest occupied molecular orbital (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
Combining equations (1.7), (1.8) and (1.9), the equation for the first excited electronic state is given as

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

Equation (1.10) is the effective mass approximation formula derived by L. Brus [1.31-1.33]. As can be seen from the equation the coulomb term shifts \( E^* \) to the lower energy as \( R \)' becomes large. The quantum localization term shifts the \( E^* \) towards higher energy as \( R \)'' becomes small. Thus the overall effect is that \( E^* \) will be always shifted to higher energy side for small \( R \).

There are two major problems in the application of effective mass approximation formula [1.34].

1) **Effective masses** are assumed to be independent of \( \vec{k} \). The band structure in real materials deviates from free electron parabolic form for larger \( \vec{k} \). 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.

Thus effective mass approximation is not too much useful in case of very small particles.

**1.2.2 Pseudo potential method**

Due to the limitations in effective mass approximation, another approach was described to obtain energy levels of the valence electrons and subsequently the band structure of the semiconductor crystal under study.

There are few approximations which are made to make this problem numerically tractable.
1) The electrons in the inner orbits are assigned to the nuclei to obtain charged cores.

2) The Born-Oppenheimer approximation is imposed to clamp the cores to fixed lattice sites.

3) Each electron is assumed to move independently in the mean field of fixed cores and other valence electrons.

The energies of the electronic states were determined using Schrödinger equation

$$H \psi_{n,k}(r) = E_n(k) \psi_{n,k}(r) \quad (I.11)$$

Hamiltonian $H$ in the above equation becomes

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V_p(r) \quad (I.12)$$

Where $V_p(r)$ is the effective potential also called as pseudo potential, which is the crystal-field potential experienced by the valence electrons under the approximations stated earlier.

Due to the contributions from all the atoms in crystal, $V_p$ becomes

$$V_p(r) = \sum_{k,j} v_j(r - R - d_j) \quad (I.13)$$

$v_j$ is the atomic pseudo potential of the $j^{th}$ basis atom at a lattice site $R$. $d_j$ is the position vector of $j^{th}$ basis atom relative to $R$.

Replacing $(r-R-d_j)$ by

$$-\frac{1}{N N_a} \sum_G v_j(G) \exp[iG \cdot (r - R - d_j)] \quad (I.14)$$

Where $G$ are the reciprocal lattice vectors, $N$ are the number of lattice sites, $N_a$ are the number of basis atoms at each lattice site.

Final form of the pseudo potential is given as

$$V_p(r) = \frac{1}{N N_a} \sum_G \sum_{k,j} v_j(G) \exp[iG \cdot (r - R - d_j)] \quad (I.15)$$

All the parameters in the equation I.15 can be found out by fitting the experimental optical data. By putting the value of $V_p$ in equation I.11 and I.12 one can find out considerably accurate energy levels of the valence electrons and thus the band structure of the material under investigation.
Rama Krishna et al. [1.34] have proposed this approach and have demonstrated it in case of zinc blend cadmium sulphide crystals. Their results are in fairly good agreement with the experimental values. The model has been also demonstrated recently in the case of Si, CdSe, InP etc. [1.35 - 1.41].

1.2.3 Tight Binding Method.

Slater and Koster [1.42] have first discussed the tight-binding (TB) scheme for the determination of electronic structure of solid. Tight binding can be used even for complex systems and also for complex alloys and doped compounds.

Tight binding method was first used by Lippens and Lannoo [1.43] to describe the size dependant band gap for CdS and ZnS nanocrystallites. The calculations were carried out for crystallites with different sizes ranging from clusters with 17 atoms in 3 shells upto 2563 atoms in 15 shells. The calculated results were compared with existing experimental data [1.44, 1.45].

For zinc oxide, the tight binding model was described by Vishwanatha et al. [1.46]. They have deduced the ab initio band structure of wurtzite 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.

Hamiltonian used in this case is as follows

\[ H = \sum_n \epsilon_n a_n^\dagger a_n + \sum_{n'} \sum_{n''} \left( t_{n'n''} a_{n'}^\dagger a_{n''} + \text{h.c.} \right) \]  

(1.16)

where, \( a_n^\dagger \) and \( a_n \) are the creation and annihilation operators for electrons at the atomic site \( i \) in \( l^{th} \) orbit. \( \epsilon_{n'} \) gives the onsite energy for the orbital \( l \) at the site \( i \). Hopping interaction strength is given be \( t_{n'n''} \).

The DOS calculations were done for the nano-crystal whose effective diameter “d” was calculated to be

\[ d = \left[ \frac{3N_{\text{at}} a^2 c}{2 \pi} \right]^{\frac{1}{3}} \]  

(1.17)
Where, $a$ and $c$ are the bulk lattice parameters and $N_a$ is the number of atoms in the nanocrystal.

The calculated curve for the dependence of band gap variation with respect to nanocrystal size was compared to the available experimental data as well as with that calculated using effective mass approximation. It was shown that the TB model fits very well with that of experimental data than the EMA.

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.

1.3. Properties of zinc oxide (bulk)

1.3.1 Crystal structure

Like most of the II-VI group elements, zinc oxide can exist in either Rocksalt, zinc blend or Wurtzite crystal structure. Though wurtzite structure is the normal low pressure phase and is the most stable as well as common structure for zinc oxide. Zinc oxide can transform from normal wurtzite to rock salt structure at modest hydrostatic pressure, and remains metastable even at zero pressure [1.47].

Jaffe et al [1.48] have calculated the total energy for all three possible crystal structures of ZnO using the Hartree-Fock calculation method. Values calculated by them are given in the Table 1.1.

Table 1.1 Structural parameters for the three phases of ZnO calculated in the reference [1.48]. $E_0$ is total energy, $V_0$ is the volume per ZnO formula unit and $B_0$ is the bulk modulus at zero pressure.

<table>
<thead>
<tr>
<th></th>
<th>Zinc blend</th>
<th>Rock salt</th>
<th>Wurtzite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$ (eV)</td>
<td>-5.606</td>
<td>-5.416</td>
<td>-5.658</td>
</tr>
<tr>
<td>$V_0$ ($\text{Å}^3$)</td>
<td>24.551</td>
<td>19.799</td>
<td>24.570</td>
</tr>
<tr>
<td>$B_0$ (GPa)</td>
<td>156.8</td>
<td>203.3</td>
<td>154.4</td>
</tr>
</tbody>
</table>
From the comparison of the total energy for rock salt, zinc blend and wurtzite crystal structures for ZnO, it is clear that wurtzite structure is having the lowest energy, though the difference is very small (~0.05 eV) between the energies of zinc blend and wurtzite, thus it is thermodynamically most stable structure for ZnO.

Wurtzite structure for zinc oxide is given in the Figure 1.3. It consist of two hexagonal closed pack (HCP) structures, one for oxygen and another for zinc, interpenetrated in one another. They are displaced along c –axis by $\frac{1}{3}c$. It can also be described as a number of alternating planes composed of tetrahedrally coordinated $\text{Zn}^{2+}$ and $\text{O}^{2-}$ ions, stacked alternatively along the c-axis.

![Wurtzite Crystal Structure](image)

**Fig. 1.3:** Wurtzite crystal structure for zinc oxide.

Lattice parameters for zinc oxide are as follows

- $a = 3.2501 \, \text{Å}$ and $c = 5.2071 \, \text{Å}$
- $c/a = 1.6021$

The most common polar surface in zinc oxide is the basal plane, (0001). The oppositely charged ions produce positively charged Zn – (0001) and negatively charged O – (0001) surfaces resulting in a normal dipole moment and spontaneous polarization.
1.3.2 Mechanical properties of ZnO

Mechanical properties of ZnO are very important for its consideration and actual use in the applications. Mechanical properties are generally given by hardness, piezoelectric constant, bulk modulus, yield strength etc. Values for hardness and modulus for bulk ZnO are given in Table 1.2

Table 1.2 Hardness and modulus for bulk ZnO along a- and c- axis. [1.49]

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a – axis</td>
<td>2 ± 0.2</td>
<td>163 ± 6</td>
</tr>
<tr>
<td>c – axis</td>
<td>4.8 ± 0.2</td>
<td>143 ± 6</td>
</tr>
</tbody>
</table>

From the table it is clear that ZnO is harder in c-axis than in a-axis. Similarr study was done on the ZnO epitaxial layers grown on sapphire substrates by Coleman et al. [1.49]. They have shown that the epitaxial layers are harder than the bulk ZnO. Bradly et al [1.50] have studied the contact induced mechanical defects in single crystal ZnO. They have concluded that due to the soft nature of ZnO, relatively small loads result in significant mechanical damage.

Soft nature of ZnO can be expected due to the low melting point (~ 1975 °C). More ionic nature of ZnO (ionicity ~ 0.616) is expected to facilitate the nucleation and propagation of dislocations via the ease of bond angle distortion compared to purely covalent bonding [1.51].

1.3.3 Thermal properties

(i) Thermal expansion coefficient (TEC)

Variation of lattice parameters with change in the temperature is an important property. In case of zinc oxide many articles have been published on the TEC properties of ZnO [1.52].

Figure 1.4 gives the TEC data taken from the reference [1.53]. Lattice parameters are plotted as a function of temperature in the temperature range of 4.2K to 296K. X-ray powder diffraction method was used to determine the expansion coefficients.
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Fig. I.4: Lattice parameters as a function of temperature in case of ZnO [1.53].

(ii) Thermal conductivity

Thermal conductivity is an important quantity to measure if the material is to be used in high power, high temperature or optoelectronic devices. Thermal conductivity measurements were performed by Florescu et al [1.54] the results are shown in Figure I.5.

Fig. I.5: Thermal conductivity of ZnO heated from room temperature to 1000 °C. [1.54]
1.3.4 Electrical properties

Zinc oxide always exhibits strong n-type conductivity with electrons in the conduction band as charge carriers. Large number of efforts have been made to understand the origin of n-type conductivity in ZnO. Earlier it was assumed that either the oxygen vacancy, $V_O$ or Zn interstitial $Zn_I$ are the dominant donors \[1.55\]. Kroger \[1.56\] has proposed $V_O$ and $V_{Zn}$ as the main donor acceptor species taking part in the conductivity of ZnO.

Look et al. \[1.57\] have studied the origin of n-type conduction by creating the defects using high energy electrons (~ 2.0 MeV). From the observations on the carrier concentration Vs temperature, Hall concentration and Hall mobility Vs irradiation number, they have concluded that interstitial zinc ($Zn_I$) is the dominant donor in their system and zinc vacancy ($V_{Zn}$) is the dominant acceptor.

In another paper Van de Walle \[1.58\] has proposed that native defects are not responsible for the n-type conductivity in ZnO and it must be due to some impurity which is unintentionally incorporated during the synthesis. He has proposed hydrogen as the main source of charge carriers in zinc oxide.

Simillar kind of work has been performed by Kohan et al \[1.59\] and Van de Walle et al \[1.60\]. Still the origin of n-type conductivity observed in ZnO is not well understood. ZnO can be converted to p-type by doping.

1.3.5 Optical properties of ZnO

Zinc oxide is a well-known phosphor material that exhibits an efficient blue-green luminescence. Very important property of ZnO is its high exciton binding energy of 60 meV. ZnO has been used in plenty of applications like vacuum fluorescence displays (VFDs), Field emission displays (FEDs) etc. In 1999 edition of Phosphor Handbook it is written that “The origin of the luminescence centre and the luminescence mechanism of ZnO phosphors are barely understood” \[1.61\]. Large number of efforts have been devoted to understand the origin of visible luminescence in case of ZnO. Earlier it was associated with divalent copper impurities \[1.62\]. Intrinsic defects like interstitial zinc \[1.63\] or oxygen vacancies \[1.64-1.66\] were also considered to be the possible source.
Dijken et al. [1.67, 1.68] have studied the luminescence behavior in ZnO and proposed a model for the origin of visible green luminescence. The model in the pictorial form is given in Fig. 1.6.

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 somewhere 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 $O^{2-}$ ions at the surface.

As given by Dijken et al. [1.68] the model given in Figure 1.6 shows three possible paths for the recombination of photoexcited electron with the corresponding hole. 1) Exciton emission, 2) Trap emission and 3) non-radiative recombination. Origin of green luminescence was explained as follows.

The photo generated hole gets trapped by the surface states. The surface trapped hole tunnels back to combine with an electron in a deep trap. $(V_o^\bullet)$ centre. $(V_o^\bullet)$ centre is a singly ionized oxygen vacancy. It gets converted to doubly ionized oxygen vacancy $(V_o^{\bullet\bullet})$ after capturing the hole, which is the recombination centre for the visible luminescence observed in case of ZnO. The whole process is shown in Figure 1.6, path (B-D-G).

Process of excitonic or band edge emission is depicted in Figure 1.6 (A). Paths (B-E-H) or (C-F-H) give non radiative recombination in ZnO.
Fig. I.6: Possible recombination paths of photo excited electron with photo generated hole in zinc oxide [1.68].
Some important properties of ZnO

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>II-VI semiconductor</td>
</tr>
<tr>
<td>Bandgap</td>
<td>3.3 eV at room temperature</td>
</tr>
<tr>
<td></td>
<td>3.44 eV at 2K</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Wurtzite (Hexagonal)</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>a = 3.25 Å, c = 5.21 Å (c/a=1.603)</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Dielectric constant (ε)</td>
<td>9.1</td>
</tr>
<tr>
<td>Effective mass of electron</td>
<td>0.28</td>
</tr>
<tr>
<td>Effective mass of hole</td>
<td>0.49</td>
</tr>
<tr>
<td>Molecular mass</td>
<td>81.389</td>
</tr>
<tr>
<td>Specific gravity at room temp</td>
<td>5.642 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>2250 K</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.125 cal/gm</td>
</tr>
</tbody>
</table>

Key Advantages of ZnO

1) High Piezoelectric Effect (ε33 = 1.2 C/m², among highest of all semiconductors)
2) High Thermal Conductivity of 0.54 Wcm⁻¹K⁻¹ (compared with 0.5 for GaAs)
3) Largest Exciton Binding Energy of II-VI & III-V Semiconductors, 60 meV = excitonic stimulated light emission up to 550 K
4) Even more radiation resistant than GaN (up to 2 MeV, 1.2 x 10¹⁷ electrons/cm²)
5) Drift Mobility Saturates at Higher Fields & Higher Values than GaN = attractive for high frequency devices
6) Very Low Dark Current UV Detectors with maximum spectral response at 350 nm.
7) Strong Two-Photon Absorption with High Damage Thresholds, = attractive for optical power limiting devices
8) Very Large Shear Modulus ~45.5 Gpa (indicates stability of the crystal) = compared with 18.35 for ZnSe, 32.60 for GaAs and 51.37 for Si.
1.4 Overview of zinc oxide nanoparticles

Due to the possibility of tuning various properties viz. optical, mechanical, electrical etc., with size and shape, nanoparticles and nanotechnology has become a subject of interest in recent years. Various metals, semiconductors, composites etc. in the nano regime have been studied extensively in last two decades. Variety of II-VI and III-V semiconductor nanoparticles have been synthesized and characterized for various properties.

Zinc oxide is a wide band gap (direct band gap with energy $E_g = 3.3$ eV at room temperature) II-VI semiconductor material. Zinc oxide is a well known phosphor material [1.61, 1.66]. It is used in many applications like photocatalysis [1.69], gas and chemical sensor [1.70-1.74], varistors [1.75], flat panel displays and field emission displays [1.76], UV semiconductor lasers [1.77, 1.78] etc. So since last two decades many groups have worked on zinc oxide nanoparticles to understand the properties and its use in many applications. Here we discuss some of the work done so far on zinc oxide nanoparticles as majority of the work presented in this thesis is carried out on zinc oxide nanoparticles. Different aspects like size, shape, synthesis, properties etc. will be considered.

Koch et al [1.79(a)] 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 nano regime 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 if Cu$^{2+}$ ions are adsorbed on the surface, 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 phenomena was explained with Hauffe mechanism [1.79(b)].

Spanhel et al. [1.80] have studied the effect of illumination of 436 nm light on the absorption spectrum of solution containing ZnO nanoparticles along with CdS nanoparticles. The ZnO particles have been synthesized by hydrolyzing Zn(ClO$_4$)$_2$
with NaOH in methanol as a medium. They recorded the shift in the absorption edge with increasing the illumination time. They have attributed this blue shift to the electron deposition on the ZnO particles.

Detailed investigations on the synthesis and characterizations of zinc oxide quantum dots were carried out by Bahnemann et al [1.81]. ZnO particles were synthesized using zinc acetate and NaOH in 2-propanol. A temperature dependant growth was observed for the ZnO nanoparticles formation. UV-Vis absorption spectra show shift in the absorption edge from 306 nm towards 365 nm as time and temperature were increased. The spectra are shown in Figure I.7(a).

Fig: I.7: Temperature and time dependant shift in absorption (a), Photoluminescence of ZnO particles in propanol (b), and (c) effect of oxygen on PL intensity. [1.81]
Figure 1.7 (b) shows luminescence behaviour of ZnO nanoparticles with increasing size. Effect of oxygen on PL intensity was studied. Result (Figure 1.7(c)) shows that intensity of the green luminescence increases as the pressure of oxygen was increased. So they concluded that oxygen is essential to covert UV luminescence to visible luminescence. Titration experiment was also been carried out to investigate the acid-base properties of colloidal ZnO. Results indicate that colloidal ZnO has buffering capacity towards acid.

Spanhel et al [1.82] have used sol-gel technique to synthesize ZnO colloids. They used zinc acetate as zinc precursor and LiOH to hydrolyze the zinc salt. Reaction was carried out in ethanol as a medium. Particles in the range of 3 nm to 5 nm were synthesized. Spectroscopic properties of the particles in different levels of formation were extensively studied. The same sol-gel technique was used by another group [1.83] to synthesize transparent – conducting thin films of ZnO. Zinc nitrate hexahydrate 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 [1.84] have also used sol-gel route to synthesize ZnO nanoparticles and zinc acetate derivatives to study the chemical and structural properties of them. Different chemicals viz. lithium hydroxide, succinic acid and glacial acid were used as catalysts for the hydrolysis of zinc acetate. XRD, EXAFS and TG-DTA were

![Fig. 1.8: Fourier transform of EXAFS spectra for ZnO nanoparticles synthesized with different catalysts at various temperatures. (a) with LiOH, (b) with succinic acid and (c) with water.](image)
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, as shown in the Figure I.8. All the powders were reported to be composed of mixture of zinc oxide, zinc acetate and zinc hydroxyacetate. Most pure zinc oxide sample could be synthesized at lower temperatures ($< 20 \, ^\circ{C}$) without catalyst or using LiOH as a catalyst.

Similar kind of study was done to know the influence of precursor structure on the morphology of final ZnO nanoparticles was performed by Boyle et al. [1.85]. They have reported that depending on the morphology of the precursor different shapes of the ZnO nanostructures can be synthesized. Compounds with four different nuclearities, mono, di, tetra and hepta nuclear were selected for the synthesis of ZnO.

Various groups [1.86-I.102] have used different chemical routes to synthesize ZnO nanoparticles and to study their properties. Gattorno et al [1.89] have reported an easy pathway to synthesize the ZnO nanoparticles with narrow size distribution. Depending on the temperature and other reaction conditions particles with different sizes were synthesized. They have reported the co-existence of cubic rock salt phase along with the regular wurtzite phase when zinc cyclohexanebutyrate was used as the starting precursor. TEM is shown in the Figure I.9. The co-existence of Wurtzite and rock-salt structures has been discussed in section I.3.1.

![HR-TEM of the ZnO nanoparticle with cubic-rock salt structure.](image)

Fig. I.9: HR-TEM of the ZnO nanoparticle with cubic-rock salt structure. [1.89]
Hosono et al [I.90] have reported a non-basic synthesis route for the formation of ZnO nanoparticles. The synthesis was carried out using zinc acetate dihydrate in alcoholic medium. The reaction temperature was kept at 60 °C. Comparative study of the chemical reaction using different solvents show that layered hydroxide zinc acetate was formed as an intermediate which then transforms to ZnO. This transformation was reported to be influenced by type of the solvent used.

Chemically capped ZnO nanoparticles were reported by Tong et al [I.93] in which polyvinyl butyral was used as a capping agent. Particles were investigated using XRD, UV-Vis absorption and temperature dependant PL. Bendre et al [I.99] have used poly vinyl pyrrolidone (PVP) as a capping molecule. They have studied the effect of capping on the PL spectrum of ZnO. Vishwanatha et al [I.100] have used PVP and 1-decanethiol as capping agents. ZnO nanoparticles having sharp absorption edges with four different sizes have been reported. Figure I.10 shows the UV-Vis absorption spectra for the samples.

![UV-Vis absorption spectra for capped ZnO nanoparticles.](image)

Fig. I.10: UV-Vis absorption spectra for capped ZnO nanoparticles. [I.100]
They have studied electronic structure of ZnO and quantum size effects using tight binding model. Pesika et al. [I.97] have used octanethiol to quench the growth of ZnO nanoparticles.

Influence of the solvent on the growth of ZnO nanoparticles was studied by Hu et al [I.103]. The reaction was carried out in ethanol, 1-propanol, 1-butanol, 1-pentanol and 1-hexanol as solvent. The study shows that growth of the ZnO is faster as chain length of the solvent is increased, thus solvent is an important factor in obtaining ZnO nanoparticles.

Ramakrishna et al [I.104] have studied the effect of particle size on the reactivity of ZnO nanoparticles. Simillar study has been performed by Carnes et al [I.105]. ZnO particles in the size range of 3-260 nm have been synthesized and tested for their reactivity with chlorocarbon, acid gas and an organophosphorus compound. It has been shown that particles with smaller size are more reactive due to the higher surface area.

Composites of zinc oxide have also been synthesized and studied. Nemeth et al [I.106] 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 et al [I.107]. Simultaneous addition of triethanolamine and zinc acetate into SiO2 ethanolic solution gives the ZnO coated silica particles. TEM is shown in the Figure I.11

\[\text{Fig. I.11: Transmission electron micrograph of SiO}_2@\text{ZnO (a and b) and bare SiO}_2\text{ spheres. Images a and b are of same sample with different magnifications. [I.107]}\]
An interesting study has been performed recently by Andelman et al [I.108]. They have studied the effect of particle morphology on photoluminescence of ZnO particles. Depending on the solvent used three different morphologies have been synthesized: triangular, rods, and spheres. Figure 1.12 (a-c) shows TEM images of these morphologies and (d) gives the PL spectra for these particles.

**Fig: 1.12:** Transmission electron micrographs of different morphologies of ZnO nanoparticles, (a) rods, (b) triangles, and (c) spheres. Effect of morphology on the PL is shown in (d). [I.108]
Photoluminescence investigations show that green luminescence observed in case of ZnO nanoparticles is strongly dependant on the particle morphology.

Synthesis of ZnO nanoparticles using various techniques like spray pyrolysis, using RF plasma, electrophoretic deposition, electrochemical synthesis etc. have also been reported [1.109-1.112].

1.5 Doped ZnO nanoparticles

Due to the vast applications zinc oxide is considered an important material. It has been doped with various transition metals and rare earth elements to change and study its properties.

Zinc oxide nanoparticles doped with Sb have been reported by Zeng et al [1.113]. Nanoparticles were synthesized by vapor condensation method using Zn-Sb alloy as a starting material. Synthesis was carried out in oxygen – argon atmosphere. Nanoparticles with the size ~ 60 nm have been reported. The particles have regular hexagonal shape, which authors claim is due to the Sb incorporated into ZnO lattice.

![Graph](image)

Fig. 1.13: Gas sensitivity of In doped ZnO to different volatile organic compounds as a function of temperature. 4.58 at % In is doped. [1.114]
Doping of Sb into ZnO leads to increase in the optical reflectivity and electrical resistivity in comparison to undoped ZnO nanoparticles. Zhu et al [1.114] have reported indium doped ZnO nanoparticles and studied its gas sensitivity.

Particles were synthesized by induction and laser heating of Zn-In alloy in presence of O₂-Ar gas mixture. The particles have been tested for their sensitivity towards volatile organic compounds (VOC) like benzene, acetone, ethyl alcohol etc. Results are plotted in Figure 1.13. It shows that with 4.58% In doping ZnO is showing highest sensitivity towards VOC at ~ 420 °C.

Fe doped ZnO nanoparticles have been synthesized and characterized by Yogo et al [1.115]. They have reported that shift in the absorption edge up to 600 nm could be observed in case of Fe doped ZnO nanoparticles.

Sulfur doped ZnO nanowires have been reported by Geng et al. [1.116]. The nanowires have been investigated using XRD, EDAX and PL. PL results show that luminescence is dependent on the sulfur doping percentage in ZnO. A blue shift and increase in the intensity of visible luminescence was observed as S doping percentage was increased, Figure 1.14.

![Figure 1.14](image)

**Fig. 1.14:** Effect of Sulfur doping on the PL of ZnO nanowires. (a) 5.4%, (b) 1.47%, (c) 1.41% and (d) 0% sulfur in ZnO. [1.116]
Zinc oxide nanoparticles doped with rare earth elements have been investigated by many groups. As zinc oxide is a well known phosphor material and rare earth ions are known to have an intense and narrow emission in the visible region. It was thought to be interesting to incorporate rare earth ions into ZnO lattice.

Park et al [1.117] have synthesized ZnO – EuCl₃ phosphor. Synthesis was carried by sintering ZnO and EuCl₃ in the temperature range of 1000 – 1200 °C. The powders were investigated using XRD and photoluminescence. Figure I.15 shows the PL spectra recorded for powder sintered in vacuum with various doping concentrations.

![PL spectra for ZnO-EuCl₃ powder sintered in vacuum with various doping percentages. (a) 0.01, (b) 0.015, (c) 0.025, (d) 0.07 and (e) 0.1 mol/mol. [1.117]](image)

From the Figure it is clear that for higher doping percentages sharp emission lines due to $^5D_j (j = 0,1) \rightarrow ^7F_j (j = 0,1,...,6)$ transition of Eu³⁺ ions were most intense.
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and visible emission due to ZnO host has been totally quenched. In the XRD peaks due to Eu₂O₃ could be seen along with that for hexagonal wurtzite ZnO.

Schmidt et al [1.118] have reported the study of Er³⁺ fluorescence in II-VI semiconductor cluster environment. ZnO nanoparticles doped with Er³⁺ were synthesized by hydrolysis and condensation of Zn-O-Er precursor at room temperature. Zn-O-Er precursor was prepared by refluxing ethanolic solution of zinc and erbium salts. The sample was investigated for its near IR fluorescence properties. Figure I.16 shows the spectra for Zn-O-Eu precursor and ZnO nanoparticles doped with Er³⁺.

Fig. I.16: NIR fluorescence spectra for Zn-O-Er precursor and ZnO:Er³⁺. [1.118]

Intensity of fluorescence has increased by two orders of magnitude after hydrolysis and condensation of Zn-O-Er precursor into ZnO.

Upconversion properties in the luminescence of Er³⁺ doped ZnO nanocrystals were studied by Wang et al. [1.119]. Upconversion means when the particles were excited with radiation with lower energy, emission at higher energy was observed. Doped nanoparticles were prepared by hydrolyzing the Zn-O-Er precursor with LiOH. Room temperature Stoke’s emission of Er³⁺ in ZnO was studied for the samples annealed at various temperatures. Temperature dependence of Stoke’s emission was
also investigated. When the particles were excited with an 808 nm laser, blue, green and red upconversion emission of Er\(^{3+}\) in ZnO nanocrystals were observed. Four band appearing at 405, 530, 550 and 660 nm depicted in Figure I.17 were assigned to the transitions \( ^{2}H_{9/2} \rightarrow ^{4}I_{15/2} \), \( ^{2}H_{11/2} \rightarrow ^{4}I_{15/2} \), \( ^{4}S_{3/2} \rightarrow ^{4}I_{15/2} \) and \( ^{4}I_{9/2} \rightarrow ^{4}I_{15/2} \) respectively. It was observed that upconverted intensity of green luminescence increases remarkably with annealing.

![Figure I.17: Upconversion luminescence spectra of Er\(^{3+}\) in ZnO nanocrystals annealed at (a) 400 and (b) 700 °C. [I,119]](image)

The upconversion process was assigned to the excited state absorption (ESA) and energy transfer upconversion (ETU) processes in ZnO:Er\(^{3+}\). The processes were discussed in detail.

Liu et al [1.120] have reported the terbium doped ZnO nanoparticles. Increase in the intensity of emission due to Tb\(^{3+}\) ions as the doping percentage was increased at the expense of the emission from host ZnO indicates that relaxation of carriers from excited states of ZnO to the rare earth dopants took place.
Europium doped zinc oxide nanoparticles were synthesized by Bhargava et al [1.121] using micellar microemulsion process. The process first forms a nanocrystalline hydroxide compound of ZnO and Eu which was converted to ZnO:Eu by heating it at 350 °C. Luminescence due to Eu$^{2+}$ was observed at 590 nm.

Dy$^{3+}$ doped ZnO nano crystals were synthesized using combustion method by Gu et al [1.122]. Zinc nitrate, dysprosium nitrate, lithium chloride and urea were used for the synthesis. Particles of the size ~ 20 nm were synthesized. Investigations were carried out using XRD, TEM, FTIR and PL. Luminescence spectrum is given in Figure I.18.

![Emission spectrum of 2% Dy$^{3+}$ doped ZnO nanocrystals. [1.122]](image)

The emission lines observed at 480 and 575 nm were attributed to the transitions $^{4}F_{9/2} \rightarrow ^{6}H_{15/2}$ and $^{4}F_{9/2} \rightarrow ^{6}H_{13/2}$ respectively. It was shown that by doping Li$^{+}$ into ZnO:Dy$^{3+}$ nanoparticles the luminescence intensity was increased by ~ 10 times.
Investigations on the luminescence of Eu\(^{3+}\) doped ZnO nano powders were reported by Li et al. [1.123]. The samples were prepared by high temperature calcinations method. Characteristic lines due to Eu\(^{3+}\) at 590 and 615 nm corresponding to \(^5D_0 \rightarrow ^7F_1\) and \(^5D_0 \rightarrow ^7F_2\) transitions respectively. Increase in the intensity of the luminescence due to Eu\(^{3+}\) with increasing doping percentage was recorded as shown in the Figure 1.19.

![Figure 1.19: Emission spectra for ZnO:Eu nanoparticles with different Eu concentrations. [1.123]](image)

All the references given till now about the rare earth doped nanocrystals have reported successful incorporation of rare earth ions into ZnO, though no direct evidence has been given for the same.

Bol et al [1.124] in their paper on the incorporation of trivalent rare earth ions into II-VI semiconductor materials have argued that it is not possible at all to incorporate rare earth ions into semiconductor lattice. In the report they have synthesized various rare earth doped II-VI semiconductor nanocrystals such as ZnS:Eu, CdS:Eu, ZnS:Tb and ZnS:Er using variety of synthesis techniques like chemical precipitation and inverse micelle technique. Luminescence properties were studied to investigate whether rare earth ions are really incorporated in to host
material. Heating of the samples at high temperatures (~ 800 °C) was carried out to forcefully diffuse rare earth ions into the host.

All the PL excitation and emission spectra were studied carefully and they came to the conclusion that it is not possible to dope rare earth ions into II-VI semiconductors effectively.

Thus there are exactly contradictory reports on the incorporation of rare earth ions into II-VI semiconductor nanocrystals indicating that there is a need to have a direct proof to know whether ions are really at the substitutional site, interstitial site or are not at all incorporated into the host and are present outside the particle. This is the main motivation, along with the fact that ZnO:Eu is an important system for its use in luminescence devices, behind the study of europium doped ZnO nanoparticles. Our work on this system will be discussed in the Chapter IV.

After the successful synthesis of (In, Mn)As and (Ga, Mn)As, diluted magnetic semiconductors have been studied extensively for their applications in semiconductor spin electronics (spintronics) [1.125]. There have been many reports, experimental [49a-(2-4)] as well as theoretical [1.126- 1.130], in which high Tc DMSs have been proposed. In the report by Dietl et al. he has shown that p type ZnO can be an interesting high Tc DMS if it is doped with transition metal ions, particularly Mn. This has tremendously increased interest in zinc oxide based diluted magnetic semiconductors.

Transition metal doped ZnO thin films have been reported by many groups [1.31-1.135]. It has also been tried in many other morphologies like rods [1.136], belts [1.137], tetrapods [1.138] etc. We are interested in transition metal doped ZnO nanoparticles. So in the coming section we will discuss some of the work carried out mostly on this system.

Theoretical study on the transition metal doped ZnO nanostructures have been performed by Sato et al [1.139]. The study was based on the first principle calculations. Electronic structure and magnetism of ZnO nanoparticles doped with V, Cr, Fe, Co, Ni and Mn have been studied extensively. It has been concluded that high Tc DMS can be obtained by doping ZnO with V, Cr, Fe, Co and Ni. It has also been reported that by electron doping Tc can be raised for these systems.
The authors have published similar paper [I.140] on semiconductor spintronics materials. In this report they have studied different semiconductor materials like ZnO, ZnSe, ZnS, ZnTe etc. with various transition elements doped in them. The investigation were again done based on first principles calculations. It has been shown that Mn doped ZnO changes its magnetic state from spin glass to the ferromagnetic state as the hole concentration was increased. It has also been shown that DMS based on Fe, Co and Ni doped ZnO show stable ferromagnetic states as shown in Fig. I.20.

![Ferromagnetic state](image)

**Fig. I.20:** Stability of ferromagnetic states in ZnO based DMS. [I.140]

Similar kind of study was done by Feng [I.141] on the electronic structure and ferromagnetism on Cu and Mn doped ZnO.

Transition metal doped zinc oxide nanoparticles have been reported by many groups [I.121, I.142-I.148] synthesized using chemical routs. A novel route was demonstrated by Cong et al [I.149] to synthesize Mn doped ZnO nanoparticles in which rheological phase reaction precursor method was used. It was demonstrated that ZnO particles doped with 5% Mn shows ferromagnetism at room temperature. The magnetization data is shown in the Figure I.21.
Vishwanatha et al [1.145] have synthesized colloidal Mn doped ZnO nanoparticles.

Fig. I.20: Magnetization of Zn$_{1-x}$Mn$_x$O with various doping percentages. [I.149]

Fig. I.21: EPR spectra for Mn doped ZnO nanoparticles. [I.145]
Particles were capped with PVP to obtain stability. Samples were investigated for structural and magnetic properties. Variation in the band gap could be observed with different doping percentages. From the electron paramagnetic resonance (shown in Figure 1.21) and X-ray absorption spectroscopy results it was concluded that Mn\(^{2+}\) ions are present at substitutional site in the interior as well as near the surface region of the particles.

Deka et al [I.150] have reported lightly cobalt doped ZnO nanocrystals synthesized by an auto combustion method. Particle size measured from TEM is ~ 5 to 10 nm. However bigger particles also could be seen in the micrograph. Magnetic measurements show that samples are ferromagnetic. Temperature dependant magnetization data shows that there is an increase in the Tc with doping percentage which was attributed to the presence of localized spins in the substituted Co\(^{2+}\). The temperature dependant magnetization data is shown in Figure 1.22.

![Figure 1.22: Temperature dependant magnetization of Co doped ZnO nanoparticles with 10% and 5% Co doping. [I.150]](image)

Ferromagnetism in the Ni\(^{2+}\) doped ZnO aggregates was reported by Radovanovic et al [I.151]. High Tc ferromagnetism could be observed in the samples.
Appearance of ferromagnetism in aggregates was attributed to the increase in domain volumes and the generation of defects at interfaces between nanocrystals.

The topic, transition metal doped ZnO, has gained more interest when Sharma et al [1.152] published an article in “Nature Materials” reporting the finding of ferromagnetism above room temperature in dilute Mn doped zinc oxide transparent thin films and ZnO:Mn pellets. Thin films were synthesized using laser ablation. Pellets were made by pressing the powder and the sintering was performed at various temperatures. Magnetization data was recorded at room temperature shown in the Figure 1.23. It was observed that sample with as low as 2% Mn doping shows ferromagnetism at room temperature. Effect of sintering temperature on the magnetization was studied; result is given in Figure 1.23.

![Fig. 1.23: Room temperature hysteresis loop for 2% Mn doped ZnO pellets sintered at different temperatures. [1.152]](image)

Electron energy loss spectroscopy measurements were performed which confirm that Mn is sitting at the substitutional position and has valency of $2^+$. 
Another paper came up in the same journal challenging the conclusions in the above discussed article. The paper was published by Kundaliya et al. [1.153] who investigated the origin of ferromagnetism in the ZnO:Mn system discussed by Sharma et al. [1.152]. Kundaliya et al have synthesized samples with the same method discussed in reference [1.152]. Investigation on the origin on dependence of magnetization on sintering temperature was carried out by thermo gravimetric analysis (TGA). ZnO:Mn sample was compared with MnO₂. The results, shown in Figure 1.24, indicate that ZnO:Mn sample shows same behaviour as that of MnO₂ which suggests that the Curie temperature reported by Sharma et al is in fact the temperature at which phase change occurred; from magnetic to nonmagnetic.

![Fig. 1.24: TGA data for MnO₂ (red) and ZnO + 2% MnO₂ mixture. [1.153]](image)

An extensive XRD analysis was also performed on the samples. In conclusion the authors have stated that the ferromagnetism observed in case of ZnO-Mn system is not due to the Mn incorporation into ZnO but it is due to the ferromagnetic phase of Mn₂₋ₓZnxO₃₋₅.
Thus transition metal doped ZnO for the application as a DMS and observed ferromagnetism is still an open question.

1.6 Zinc oxide complex nanostructures and microstructures

Due to the size and shape dependant physico-chemical properties, growing nano as well as micro crystalline particles of various materials with different geometries has gained tremendous interest in recent few years.

Zinc oxide, due to its various properties and applications is a key material which has been considered to be grown in variety of shapes. ZnO is a versatile functional material that has a diverse group of growth morphologies. It has been grown in the morphologies such as combs, rings, springs, rods, belts, tubes, cages, spheres etc.

Structurally, ZnO has three types of fast growth directions; 
\[
\langle 2\overline{1}0 \rangle \pm \left[ 2\overline{1}0 \right] \pm \left[ 1\overline{2}0 \right] \pm \left[ \overline{1}20 \right]; \quad \langle 01\overline{1}0 \rangle \pm \left[ 01\overline{1}0 \right] \pm \left[ 1\overline{1}0 \right] \pm \left[ \overline{1}00 \right] \quad \text{and} \quad \pm \left[ 0001 \right].
\]

By tuning the growth rate along these directions zinc oxide can be obtained in variety of morphologies. An important factor determining the growth is the relative surface activity of the various growth facets under given conditions. Figure 1.25 shows typical growth morphologies of 1-D ZnO nanostructures. [1.154]

Fig. 1.25: Typical growth morphologies of 1-D ZnO nanostructures and corresponding facets. [1.154]
Zinc oxide have been grown and studied in variety of morphologies. Nanorods of zinc oxide have been reported by many groups [1.155-1.159]. Their structural, optical properties have been studied extensively. Nanoneedles of ZnO, due to its field emission properties, have attracted much attention.

![Aligned ZnO nanoneedles as field emission probes.](image)

Many groups have synthesized ZnO nanoneedles [1.160-1.164]. Nanoneedles of ZnO which were reported for field emission applications [1.162] are shown in Figure I.26.

Nanobelts of ZnO were reported by many groups [1.165-1.167]. Complex structure like nanocomb of ZnO was reported by Wang et al [1.168]. Due to the differences in the surface energies of the different facets and the polar surfaces very thin nanobelts of ZnO tend to roll over and form rings and spirals. This was demonstrated by many groups [1.169-1.171]. Flowerlike structures of ZnO and its possible growth mechanism was studied by Zhang et al. [1.172]. Tetrapod structures of ZnO have been studied by many groups [1.173, 1.174]. Tian et al [1.175] have reported various complex morphologies of ZnO.

Among all these morphologies spheres of ZnO form an important group due to their applications in photonic band gap materials, other optical and sensing properties. There are few reports in which micro particles of zinc oxide with interesting morphologies have been studied.

Seeling et al. [1.176] 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. Authors have demonstrated the method to achieve the monodispersity using a two step method.

![SEM micrographs of the monodispersed ZnO powders of various sizes.][1]

In Figure 1.27 SEM micrographs of ZnO particles are given. Particles are monodispersed and size of the particles was controlled by amount of supernatant added in the second step of the reaction. Particles were investigated for their photonic band gap property. It was demonstrated that the periodic arrays of the particles show photonic band gap in the fcc(111) direction at ~ 2.2d, where d is the particle diameter. Luminescence study was also carried out which revealed that ZnO spheres exhibit lasing action and periodic arrays have low lasing threshold than the random arrangements.

Mesoporous polyhedral cages of zinc oxide have been demonstrated by Gao et al. [I.177]. The material was synthesized using a solid-vapor deposition process in the horizontal tube furnace. Temperature used for the evaporation of ZnO was 1150 °C. Deposition was carried out in the Ar gas flow. Morphology of the structures was studied extensively and a possible growth model was reported which comprised of solidification of liquid droplets, surface oxidation and sublimation. Flower like structures were also reported by introduction of Sn as a catalyst.
Zinc oxide hollow spheres were synthesized using a non-template solution approach by Li et al. [1.178]. Coordination polymer, \[ \text{Zn}(4,4'-\text{bipy})(\text{NCS})_2 \] \_n was used as a reactant in this route. Structural characterization was done using XRD and morphology was studied using SEM as well as TEM techniques. Transmission electron microscopy images confirmed the hollow nature of the spheres which was also observed in some of the opened spheres using SEM. Possible role of coordination polymer in the formation of hollow spheres of ZnO has been reported.

Micrometer and submicrometer scale hollow zinc oxide dandelions made via modified Kirkendall process were reported by Liu et al. [1.179]. Synthesis process comprised of reaction of zinc nitrate, sodium hydroxide and zinc metallic powder in deionized water. The reaction was carried out in Teflon-lined stainless still autoclave. Temperature maintained was \( \sim 200 \) °C. SEM investigations carried out show ZnO dandelions which are made up of one dimensional nanorods. Images are shown in the Figure I.28.

Fig. I.28: FESEM images of ZnO dandelions. [I.179]
X-ray photoelectron spectroscopy analysis was carried out to know the chemical composition of synthesized dandelions.

Interesting structures called as hollow urchins were demonstrated by Shen et al. [1.180]. The urchins were synthesized by thermal evaporation of metallic zinc in the tube furnace on the silicon substrate. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, photoluminescence etc. techniques were employed to understand the structure, morphology and optical properties of the hollow urchins. It was found that the hollow urchins were made up of ZnO nanowires packed in high density which were grown epitaxially. It was also shown that these structures can be used in electronic and opto-electronic devices.

Application of ZnO spheres as random lasers was demonstrated by Wu et al. [1.181]. monodispersed ZnO spheres, pressed in a pellet, were used for this purpose. Experimental and theoretical study was carried out to investigate the lasing action in closely packed ZnO spheres. Figure 1.29 (i) shows emission spectra from a ZnO pellet with particle diameter of 617 nm. Spectra were recorded for the incident pumping intensity of (a) 6 MW/mm² and (b) 11 MW/mm².

![Fig. 1.29: Lasing action in ZnO spheres. (i) shows the emission spectra and (ii) gives the plot of incident pump intensity at lasing threshold against the ZnO sphere diameter. [1.181]](image)
Figure 1.29 (ii) gives the dependence of incident pump intensity at lasing threshold on the diameter of the spheres. A drastic decrease in the lasing threshold from 85 nm to 137 nm was attributed to the reduction of random lasers cavity size which is related to transport mean free path. Theoretical calculations were carried out to support the data. Synthesis of ZnO spheres and their application in the Dye-sensitized solar cells was reported by Chen et al. [1.182]

In summary, papers published in recent past few years, discussed above indicate that study of spherical particles and some novel morphologies of zinc oxide is an active area of research. One can obtain novel morphologies of ZnO due to some of its very unique properties, as discussed in the beginning of this section. This inspired us to synthesize ZnO spherical particles. We have used chemical route as it is inexpensive and simple. Results will be discussed in Chapter VI.
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