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*General Introduction*
1.1. Nanotechnology and Nanomaterial

1.1.1. Introduction

Nanotechnology deals with materials or structures in nanometer scale ($10^{-9}$ m) typically ranging from 1-100 nm. Nanoparticles are particles with at least one dimension less than 100 nm [1]. The Greek word nano (means dwarf) is one thousandth of a micron and is roughly the length occupied by around 10 atoms stacked in a straight line. The term nanoparticle is sometimes referred to as nanopowder, nanocrystal or nanocluster. Nanostructures refer to textured materials or systems with at least one dimension on the nanoscale [2]. In recent years, nanosized particles or the nanomaterials have created significant scientific and technological interest due to their unique physical and chemical properties. The properties of nonmaterials are significantly different from those of atoms and bulk materials. This is mainly due to the nanometer size of the materials which render them: (i) large fraction of surface atoms, (ii) high surface energy, (iii) spatial confinement, and (iv) reduced imperfections, which do not exist in the corresponding bulk materials [3-7]. Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large fraction of atoms of the materials to be on the surface or interfacial atoms, resulting in more surface dependent material properties. Especially when the sizes of nanomaterials are comparable to Debye length, the entire material will be affected by the surface properties of nanomaterials [8, 9]. This in turn may enhance or modify the properties of the bulk materials. The global enthusiasm on nanotechnology is inspired by Physics Nobel Laureate Dr. Richard Feynman’s speech in 1959 on 29th December at the annual American Physical Society meeting on the campus of Caltech when he delivered a lecture titled “There’s Plenty of Room at the Bottom”, suggesting the possibility of manipulating things at atomic level [10]. This is generally considered to be the origin of nanotechnology. However, the real burst of nanotechnology didn't come until the early 1990s.

In Figure 1.1, the relationship between the volume and the surface area, a cube of 1 cm$^3$ is used as an example. The surface area of one 1 cm$^3$ cube is 6 cm$^2$. If
the cubicle is cut into eight smaller cubes, the surface area increases to 12 cm². Similarly, the surface area increases to 18 cm² if there are 27 cubes while the volume remains the same. From this example, it is obvious that nanostructures have a huge surface-to-volume ratio which far exceeds their bulk counterparts. It is this high surface-to-volume ratio that accounts for many promising applications given by nanostructure materials.

Figure 1.1 Relationship between the volume and the surface area.

Nanotechnology is a new field or a new scientific domain. Similar to quantum mechanics, on nanometer scale, materials or structures may possess new physical properties or exhibit new physical phenomena. Some of these properties are already known. For example, band gap of semiconductors can be tuned by varying material dimension. There may be many more unique physical properties not known to us yet. These new physical properties or phenomena will not only satisfy everlasting human curiosity, but also promise new advancement in technology. Nanotechnology has developed a bridge among all the fields of science and technology. The recent availability of revolutionary instruments like Scanning Probe Microscope (STM and AFM), High resolution Transmission Electron Microscope (HRTEM), Field Emission Scanning Electron Microscope (FESEM), Laser Raman Spectrometer etc., that approaches and allows the investigation of material properties with a resolution close to atomic level. It is strongly connected to such technological advances, the pioneering studies that have revealed new physical properties of matter at an intermediate level between atomic/molecular and bulk. Materials and structures with low dimensions have excellent properties which enable them to play a crucial role in the rapid progress of the fields of
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Science. With these amazing properties, nanostructures have become the backbone of research in all the fields of natural sciences.

Further, nanotechnology was also expanded extensively to other fields due to the novel properties of nanomaterials discovered and to be discovered. For example, nanowires can be potentially used in nanophotonics, laser [11], nanoelectronics [12], solar cells [13], resonators [14] and high sensitivity sensors [15]. Nanoparticles can be potentially used in catalysts [16], functional coatings, nanoelectronics [17], energy storage [18], drug delivery [19] and biomedicines [20]. Nanostructured thin films can be used in light emitting devices, displays and high efficiency photovoltaics. These are only a limited part of the fast developing nanotechnology, yet numerous of other potential applications of nanomaterials have already been or will be discovered.

By demonstrating its potential capability to improve human lives and contribute to the economic growth, nanotechnology is expected to have a high impact in research as well as everyday life. As a result, researchers are working hard to discover more and more nanomaterials and nanostructures with novel properties. Zinc oxide (ZnO) nanostructures have turned out to be one of the most promising categories in the field.

1.1.2. Nanostructures

According to the dimensions of nanostructures, nanostructure materials are classified as [21]:

(i) Zero dimensional (0D) - all three dimensions \((x, y, z)\) at nanometric scale. For example - nanoparticles.

(ii) One dimensional (1D) - two dimensions \((x, y)\) at nanometric scale and one dimension \((L)\) is not in nano. For example - nanorods and nanotubes.

(iii) Two dimensional (2D) - one dimension \((t)\) at nanometric scale and other two dimensions \((L_x, L_y)\) are not in nano. For example - nano thin films.

(iv) Three dimensional (3D)- all the three dimensions \((L_x, L_y, L_z)\) are not in nanometric scale. For example - nanocrystalline and nanocomposited materials.

Figure 1.2 shows the different nanostructures.

[3]
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Classification of nanostructures

The materials showing quantum mechanical phenomenon when size of bulk material reduces to nanometer range and it is referred to as the quantum size effect (QSE). In nanometer range of a material, the physical properties come to be very sensitive to the shape and size of the material. To understand this fact, the theoretical explanation on how energy states for conduction electrons and their distribution is related to shape and size of the material is given below [21].

In a 3D system, carriers are free to move in all three dimensions and hence, a bulk material is termed as a 3D system. The energy of the conduction electron can be written as [22-24]

\[ E = \frac{\hbar^2 k_x^2}{2m^*} + \frac{\hbar^2 k_y^2}{2m^*} + \frac{\hbar^2 k_z^2}{2m^*} \]

and the density of states (DOS) as

\[ \mathcal{D}(E) = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E} \]

In a 2D system, carriers are free to move in two dimensions and confined in one dimension. Quantum well is termed as a 2D system, and energy of the conduction electrons can be written as

\[ E_{n_z} = \frac{\hbar^2}{8m^*} \left( \frac{n_z^2}{L_z^2} \right) + \frac{\hbar^2 k_x^2}{2m^*} + \frac{\hbar^2 k_y^2}{2m^*} \]

where \( n_z \) is called the sub-band index. Here, carriers are confined along \( z \)-dimension with thickness \( L_z \) and free in \( x \)- and \( y \)-dimensions.

Similarly, the density of states (DOS) can be written as
and more than one confined states in a 2D system, the DOS at a given energy is the sum over all sub-bands below that particular energy. Hence, DOS for \( n \) number of confined energy states is given by
\[
D(E) = \frac{1}{2\pi} \left( \frac{2m^*}{\hbar^2} \right)^2 \sum_{i=1}^{n} d_i \Theta(E - E_i)
\]
where \( d_i \) the degeneracy factor and by definition, the Heaviside step function \( \Theta(x) = 0 \), for \( x < 0 \) and \( \Theta(x) = 1 \), for \( x > 0 \).

In a 1D system, carriers are confined in two dimensions but free to move in one dimension. Quantum wire is termed as a 1D system, and the energy of the conduction electrons can be written as
\[
E_{n_y n_z} = \frac{\hbar^2}{8m^*} \left( \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) + \frac{\hbar^2 k_x^2}{2m^*}
\]
where the energy levels depend on two quantum numbers \( n_y \) and \( n_z \). Here, \( L_y \) and \( L_z \) are lengths of the rectangular wire in \( y \)- and \( z \)-dimensions, respectively. Hence, DOS for such a 1D system is given by
\[
D(E) = \left( \frac{2m^*}{\hbar^2} \right)^2 \frac{1}{\pi \sqrt{E}}
\]
and more than one confined states in 1D system, DOS at a given energy level is the sum over all sub-bands below that particular energy level. Hence, DOS for \( n \) number of confined energy states is given as
\[
D(E) = \frac{1}{\pi} \left( \frac{2m^*}{\hbar^2} \right)^2 \sum_{i=1}^{n} \frac{d_i}{\sqrt{(E - E_i)}} \Theta(E - E_i)
\]

In a 0D system, carriers are confined in all the three dimensions. Quantum dot is termed as a 0D system, and the energy of the conduction electrons are entirely discrete and can be written as
\[
E_{n_x n_y n_z} = \frac{\hbar^2}{8m^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)
\]
where the energy states depend on three quantum numbers \( n_x, n_y \) and \( n_z \). Here, \( L_x \), \( L_y \) and \( L_z \) are the dimensions in \( x \)-, \( y \)-, and \( z \)-dimensions, respectively.
### Table 1.1

<table>
<thead>
<tr>
<th>Type</th>
<th>Density of States $D(E) = dN(E)/dE$</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>3D (Bulk)</strong></td>
<td>$D(E) = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E}$</td>
<td>3</td>
</tr>
<tr>
<td><strong>2D (Q. Well)</strong></td>
<td>$D(E) = \frac{1}{2\pi} \left( \frac{2m^*}{\hbar^2} \right) \sum_{i=1}^{n} d_i \Theta(E - E_i)$</td>
<td>2</td>
</tr>
<tr>
<td><strong>1D (Q. Wire)</strong></td>
<td>$D(E) = \frac{1}{\pi} \left( \frac{2m^*}{\hbar^2} \right) \frac{1}{\sqrt{(E - E_i)}} \Theta(E - E_i)$</td>
<td>1</td>
</tr>
<tr>
<td><strong>0D (Q. Dot)</strong></td>
<td>$D(E) = 2 \sum_{i=1}^{n} d_i \delta(E - E_i)$</td>
<td>0</td>
</tr>
</tbody>
</table>

(Q. Well = Quantum Well, Q. Wire = Quantum Wire, and Q. Dot = Quantum Dot)

**Figure 1.3** Density of states for 3D, 2D, 1D and 0D systems [21].
If there are $n$ confined states in 0D system, then DOS can be represented as $n$ $\delta$-functions and is given by

$$D(E) = 2 \sum_{i=1}^{n} d_i \delta(E - E_i)$$

where the delta function, $\delta(x) = 0$ (zero), for $x \neq 0$, and $\delta(x) = \infty$ (infinity), for $x = 0$, and integrates to a unit area.

The comparisons of $D(E)$ for electrons confined in 3D, 2D, 1D, and 0D systems are given in Table 1.1 and Figure 1.3 shows plots of the energy dependence and $D(E)$ for the nanostructures listed in Table 1.1.

**1.1.3. Exciton, Bohr Radius and Quantum Confinement Regime**

For a semiconductor after applying some energy (thermal or electrical), the electron lies in the conduction band and the hole in the valence band. The bound state of an electron-hole pair is called an exciton and it requires minimum energy to excite it. The electron-hole pair is bounded together by the Coulomb interaction to form a hydrogen-type atom, called a Mott-Wannier type of exciton. A strongly bound exciton is called a Frenkel exciton, which is similar to a long-lived excited state of an atom or a molecule [21]. In semiconductor and in nanostructures, all the excitons are of the Mott-Wannier type. The Bohr radius of the exciton is given by

$$a_B = \frac{\hbar^2}{\mu e^2} \varepsilon$$

where $\varepsilon$ is the dielectric constant and $\mu$ is the effective mass and is given as

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

where $m_e^*$ and $m_h^*$ are effective mass of electron and hole respectively, which are less than that of rest mass of electron ($m_o$). Bohr radius of ZnO, $a_B \sim 2$ nm.

When the physical size of a given structure is nearly equal to that of the normal electron orbit then we can say the system is quantum confined, and the phenomenon is called quantum confinement. Thus, quantum confinement occurs when the dimension of a nanocrystal ($D$) is made very small so that its physical
dimension becomes comparable to the size of an exciton in bulk crystal \( i.e., \) the Bohr exciton radius \( (a_B) \), leading to significant changes in the optical and electronic properties.

The Bohr exciton radius can be taken as a meter-stick to judge the extent of confinement experienced by a nanostructure. There are three types of confinement regimes [25]:

- **Weak confinement regime:** \( R >> a_B \) the dimension of the system \( (R) \) is much larger than exciton Bohr radius and \( R >> (a_e, a_h) \). Where, \( a_e \) and \( a_h \) are the Bohr radius of the electron and hole respectively.
- **Strong confinement regime:** \( R << a_B \), the dimension of the system \( (R) \) is much smaller than exciton Bohr radius and \( R << (a_e, a_h) \).
- **Intermediate confinement regime:** \( R \approx a_B \) and \( R < a_e \) but \( R > a_h \).

### 1.2. Structure and Properties of ZnO

#### 1.2.1. Crystal Structure of ZnO

![ZnO structure](image)

**Figure 1.4** The zinc blende (left) and rock salt (right) phases of ZnO [27].

Zinc oxide (ZnO) is a II-VI semiconducting material. It has three crystal structures: cubic zinc blende \( (B3) \), cubic rocksalt \( (B1) \) and hexagonal wurtzite \( (B4) \) structure. The hexagonal wurtzite structure is the most commonly and stabilized
ZnO phase at ambient pressure, and temperature. Zinc blende ZnO is stable only by growth on cubic structures [26-28], whereas rocksalt structure is a high-pressure metastable phase forming at ~10 GPa, and cannot be epitaxially stabilized [29]. Figure 1.4 shows the crystal structures of zinc blende and rock salt phases of ZnO.

Figure 1.5 The hexagonal wurtzite structure of ZnO.

ZnO is crystallised preferentially in the stable hexagonal wurtzite structure belongs to the space group $C_{6v}^4$ in the Schoenflies notation and $P6_3mc$ in the Hermann–Mauguin notation at room temperature and normal atmospheric pressure as shown in Figure 1.5. It has lattice parameters $a = 0.32495$ nm and $c = 0.52069$ nm, the values of $c/a$ was determined in the range of 1.593-1.6035 [30]. The electro negativity values of $O^{2-}$ and $Zn^{2+}$ are 3.44 and 1.65 respectively, which is responsible for the strong ionic bonding between $Zn^{2+}$ and $O^{2-}$. The zinc blende and wurtzite-type structures are covalently bonded with $sp^3$ hybridization. In wurtzite structure each oxygen ion is surrounded tetrahedrally by four zinc ions and vice versa, stacked alternatively along the $c$-axis. This kind of tetrahedral arrangement of $O^{2-}$ and $Zn^{2+}$ in ZnO will form a non-central symmetric structure composed of two interpenetrating hexagonal closed packed (hcp) sub-lattices of zinc and oxygen that are displaced with respect to each other by an amount of
0.375 along the hexagonal axis [31]. This is responsible for the piezoelectricity, spontaneous polarization and it also plays a vital role in crystal growth, defect generation and etching.

The commonly observed face termination of wurtzite ZnO exist different chemical activity, stability and the variation of surface energies in each faces as given below [32-34].

Basal crystal faces:
(i) Polar Zn terminated (0001)
   $c$ - axis oriented with surface energy $1.6 \text{ J/m}^2$
(ii) Polar O terminated (000-1)
    $c$ - axis oriented with surface energy $1.6 \text{ J/m}^2$

Prismatic crystal faces:
(iii) Non-polar (11-20)
    $a$ - axis oriented with surface energy $2.0 \text{ J/m}^2$
(iv) Non-polar (10-10)
    $m$ - axis oriented with surface energy $3.4 \text{ J/m}^2$

Mixed faces:
(v) Mix-polar (11-21)
    $r$ - axis oriented with surface energy value not reported

These characters play an important role in the growth process of ZnO nanostructures.

1.2.2. Electronic Band Structure of ZnO

Band gap is the characteristic property of the semiconductors and the electrical, optical, and other properties of semiconductors depend strongly on its band gap. At absolute zero temperature in semiconductors, the valance band is completely filled and conduction band is leaving empty. When the temperature is increased, electrons from the valance band are thermalized and get excited through the conduction band leaving holes at the top of the valence band. The band gap ($E_g$) of a semiconductor is defined as the energy difference between the top of the valence band ($E_v$) to bottom of the conduction band ($E_c$) and is given by $E_g = E_c - E_v$. Therefore, the band structure of semiconductors gives understanding
of the electron states in the conduction band and the hole states in the valance band [35].

![Energy level diagrams of semiconductors](image)

**Figure 1.6** Energy level diagrams of (a) direct and (b) indirect band gap semiconductors.

There are two different types of band gap in semiconductors [21, 36]:

(a) **Direct band gap semiconductor:**

The minimum of the conduction band (CB) and maximum of the valence band (VB) occurs at the same \( k \)-point in the Brillouin zone. For example- ZnO, ZnS, ZnSe, CdS, CdSe, CdTe, PbS, PbSe, and PbTe.

(b) **Indirect band gap semiconductor:**

The minimum of the conduction band (CB) and maximum of the valence band (VB) occurs at different \( k \)-point in the Brillouin zone. For example- Ge, Si, AlAs, AlSb, and GaP.

ZnO is a direct band gap compound II-VI semiconductor material. The electronic configurations of Zn and O are \( 1s^22s^22p^63s^23p^63d^{10}4s^2 \) and \( 1s^22s^22p^4 \) respectively. Therefore, valance orbital of Zn is \( 4s \) and that of O is \( 2p \), which results the lowest CB and uppermost VB formation due to the antibonding level of Zn (Zn\(^{2+}\) 4s) and bonding level of O (O\(^{2-}\) 2p) respectively. Hence, the CB of ZnO is s-like.
and that of VB is *p*-like [35]. Since ZnO is called a direct bandgap semiconductor, the top of the VB and bottom of the CB are both at the same center point \( \Gamma \) in the Brillouin zone (i.e. at \( k = 0 \)), as clear from Figure 1.7 [35, 37]. It is already mentioned that, the bottom of the CB is formed in the empty \( 4s \) states of Zn\(^{2+} \) or the antibonding \( sp^3 \) hybrid states, which has \( \Gamma_1 \) symmetry without including of spin and symmetry \( \Gamma_1 \otimes \Gamma_7 = \Gamma_7 \) with spin [37]. The VB of ZnO is split into two states \( \Gamma_5 \) and \( \Gamma_1 \) without spin which is formed in the occupied \( 2p \) orbital under the influence of the hexagonal crystal field, whereas under the influence of the crystal field with spin gives a further splitting into three two-fold-degenerate sub-VB of symmetries \( (\Gamma_1 \oplus \Gamma_5) \otimes \Gamma_7 = \Gamma_7 \oplus \Gamma_9 \oplus \Gamma_7 \), as shown in Figure 1.7. In all wurtzite-type semiconductors, the combined influence of the crystal field and the spin-orbit coupling gives rise to three two-fold degenerate VB, labeled from higher to lower energies as A \((\Gamma_7)\), B \((\Gamma_5)\) and C \((\Gamma_7)\).

![Figure 1.7](image)

**Figure 1.7** Valence band and conduction band of ZnO [37].

Figure 1.7 shows how the ZnO valance band splits experimentally to three subbands A, B, and C in the vicinity of the bandgap of the ZnO due to the interaction of the crystal field and spin-orbit coupling. There is \( \Gamma_7 \) symmetry in the A, C
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subbands while B subband has $\Gamma_9$ symmetry. The transitions from A and B subbands to the conduction band are dipole spin flip and can be allowed only when $E \perp c$ and from C sub-band to conduction band can be only when $E \parallel c$ [37, 38].

1.2.3. Basic Physical Properties of ZnO

At room temperature, some of the basic physical parameters are listed in the Table 1.2 [31, 39].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constants at 300 K</td>
<td>$a = 0.32495$ nm, $c = 0.52069$ nm</td>
</tr>
<tr>
<td></td>
<td>$c/a = 1.602$ (ideal hexagonal structure shows 1.633)</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g cm$^{-3}$</td>
</tr>
<tr>
<td>Molecular mass</td>
<td>81.389 g mol$^{-1}$</td>
</tr>
<tr>
<td>Melting point</td>
<td>2250 K (~1975 °C)</td>
</tr>
<tr>
<td>Stable crystal</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008, 2.029</td>
</tr>
<tr>
<td>Bandgap energy at 300 K</td>
<td>3.3 eV</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6-1.2 W cm$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Thermal expansion coefficient at 300 K</td>
<td>$\alpha_a = 4.31 \times 10^{-6}$ K$^{-1}$ and $\alpha_c = 2.49 \times 10^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>$C_p = 40.3$ J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>$m_e = 0.24 m_0$</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>$m_h = 0.59 m_0$</td>
</tr>
</tbody>
</table>

1.3. Synthesis of ZnO nanostructures

There are two types of processes for synthesis of nanostructures—‘bottom-up’ and ‘top-down’ [10].

In top-down methods, usually start with large subunits, bulk material, which is then broken down in a desired size using mechanical, chemical or other forms of energy. The majority of micro fabrication techniques for inorganic materials, including ball milling and lithography techniques fit this description.
There are disadvantages during the etching process in lithographic techniques; the processed patterns contain crystallographic damages in addition to the defects that can play a significant impact on physical and chemical properties of nanomaterials. Applications of nonmaterial prepared by these methods are few. This is because, as expected, particle size and morphology cannot be easily controlled and results would be non-reproducible.

Bottom-up approaches can be used to synthesize by self-assembly or some inorganic structures by starting with small subunits that are assembled with varying degrees of control, depending on which method is being used. Control over size distribution and morphology is possible, therefore these methods are preferable to top-down methods. Other advantages of bottom-up over top-down include simple processing steps which can be scaled up to synthesis reproducible monodisperse nanomaterials. In this approach promises a better chance to obtain nanostructures with less defects and imperfections.

Synthesis of ZnO nanostructures at various environments with effect of (a) pH variation, (b) temperature variation, (c) molar concentration variation of precursors, (d) amount of capping agent variation, and (e) Cu doped variation has been stated existing literature below.

<table>
<thead>
<tr>
<th>SI No.</th>
<th>Details of Synthesis</th>
<th>Inferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Synthesis of ZnO nanostructures using aqueous chemical growth were grown on Corning 7059 for various pH values by using equimolar (0.01 M) aqueous solution of Zn(NO₃)₂·6H₂O and HMTA as precursors in an aqueous chemical growth (ACG) method. Both the solution and the substrate were placed in Pyrex glass bottles having polypropylene autoclaveable screw caps and heated constantly at 95 °C for 1 h, 2 h and 5 h in a laboratory oven.</td>
<td>The pH of the solution significantly influences the shape of the ZnO nanostructures and hence, leading to a modification of the morphology from rod-like to prism-like and also flower-like structures [40].</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Solution pH was maintained by using 0.1 M NaOH solution and the prepared samples were washed with MilliQ water for eliminate residual salts and dried at same temperature (95°C).</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. In a simple wet chemical method, different morphologies of nanorods have been obtained using 0.02 mol Zn(NO$_3$)$_2$·6H$_2$O and 0.15 mol NH$_3$·H$_2$O as starting precursors in the presence of PEG (Mw=4000). The mixture was stirred vigorously at temperatures 60 °C, 70 °C and 80 °C respectively. The samples, named as sample60, sample70 and sample80 were washed several times with deionized water and alcohol, and then dried at 60 °C in air overnight. The pH of the solution samples prepared under pH=9.3 and pH=11.6 and experimental procedure was the same as sample70. Both the pH and temperature have been influenced in the formation of flower-shaped ZnO nanorod cluster and single nanorods through a very simple wet chemical method. The as synthesized nanorods exhibit blue emission at 466 nm and green-yellow at 542 nm for a large quantity of O vacancies, Zn vacancies and Zn interstitial defects [41].</td>
</tr>
<tr>
<td>3. In two-step chemical bath deposition method (CBD), ZnO nanorod arrays (ZNAs) were fabricated on Si substrates with different sizes in diameter. <strong>Substrates pre-treatment (spin coating):</strong> Zn (OOCCH$_3$)$_2$·2H$_2$O was dissolved in 5 mM pure ethanol solution and the solution was coated onto Si (100) substrates by a spin coater for 30s at the rate of 2000 rpm. The substrates were spin coated for four times, dried ZNAs with different average diameters have been controlled through changing growth time when pH and θ are fixed. In PL spectrum, it is indicated that low density of the deep level defects of Zn vacancies and green emission due to O vacancies centered around 520 nm [42].</td>
</tr>
</tbody>
</table>
in room temperature and then annealed in air at 250 °C for 30 min. Before final growth of ZnO nanorods, all substrates were pretreated twice for the above processes have been followed.

**CBD growth process:**

In a beaker, pre-treated Si substrates were immersed at an angle $\theta$ between substrate and beaker bottom in which a mixed equimolar (0.1M) aqueous solution of Zn (NO$_3$)$_2$.6H$_2$O and C$_6$H$_{12}$N$_4$. Then the beaker was kept at temperature 93 °C in an oven for different time. After growth, all substrates were removed from the solution, washed with deionized water and then dried at room temperature. The pH of the solution was adjusted with ammonia water of 2~4 mL which was depending on the Zn salt concentration and target pH.

4. Nano ZnO was prepared by sol-gel method. For the preparation of 0.2 M homogenous solution, 4.39 g (CH$_3$COOH)$_2$.Zn.2H$_2$O powder was dissolved in 100 mL methanol and was then sonicated at 750 Watt for 30 minutes. After that, 1.0 M NaOH solution was dropped into solution (CH$_3$COOH)$_2$.Zn.2H$_2$O until 5 pH variations were obtained: pH 7, pH 8, pH 9, pH 10, pH 11, and pH 12. The solution become milky white, and was

The pH condition in sol-gel reaction plays an important role to control the characteristics of nanoZnO produced. Precipitation time of ZnO increased over increasing pH and also size of the nanoparticles [43].
sonicated for another 30 minutes. It was then idled for several days to observe the precipitation of nano ZnO in the solution. The precipitation contains nano ZnO was obtained and was centrifuged at 3000 rpm for 30 minutes. The supernatant was treated in 80 °C oven to remove the remaining water. Finally, it was grinded with mortar to be shaped into powder.

5. ZnO nanorod arrays (ZNAs) were synthesized by a two-step chemical bath deposition method (CBD). Pre-treated Si substrates were immersed in a mixed equimolar (0.1M) aqueous solution of Zn(NO$_3$)$_2.6$H$_2$O and C$_6$H$_{12}$N$_4$. Then the beaker was kept at temperature 93 °C for 2 h in oven. After growth, two samples one is as grown and other sample was annealed at 500, 600, and 700 °C respectively for 1 h in air.

The crystal structure and optical properties show much better at an annealing temperature of 500 °C [44].

6. Synthesis of ZnO nanoparticles by a hydrothermal method at 120 °C using Zn(NO$_3$)$_2.6$H$_2$O was added slowly in a solution of PEG prepared in 50 ml distilled water. The mixed solution was simultaneously stirred and heated for 4 h continuously; which was followed by NH$_3$ drop by drop for a turbied white precipitation.

Crystallite sizes are found to be different for as prepared sample and that of annealed sample. The morphology of the annealed ZnO is rod shaped with hexagonal wurtzite phase [45].

7. ZnO nanoparticles synthesized by a chemical method. Equimolar (1 M) solutions of Zn(CH$_3$COO)$_2.2$H$_2$O and ZnO nanoparticles prepared by chemical method without using capping agent. After annealing, the
NaOH were prepared in de-ionized water. Regularly recorded by mixing 5 ml of each reactant of 1 M Zn(CH₃COO)₂·2H₂O and 1M NaOH for acidic nature (pH=5.9) and basic nature (pH=12.2) of the reactant solutions respectively. 50 ml of each reactant solutions was mixed for the preparation of 100 ml product solution. Finally the value of pH of product solution was found to be 7.32 and white precipitation of ZnO particles thus formed. The precipitate was washed with de-ionized water and dried in an oven at 100 °C for 12 h.

| 8. | Quantum dots (QDs) of ZnO were synthesized by sol-gel technique using Zn(CH₃COO)₂·2H₂O and NaOH as precursors. Solutions of 0.5 M NaOH and 0.08 M Zn(CH₃COO)₂·2H₂O in anhydrous ethanol at temperature 60 °C and at room temperature were prepared separately. In Zn²⁺ solution, PVP was dissolved and drop-wise 48 ml NaOH solution was added and stirred 30 minutes with 10 ml Zn²⁺ solution by a magnetic stirrer. After that, n-heptane was added with the mixture solution and the precipitation of ZnO QDs from the sol was collected with the help of centrifugation. It was then re-dispersed into de-ionized water and ethanol respectively. Finally, one part of precipitate was Annealing Effect has been observed both in structural and optical properties. When the annealing temperatures is increases, QDs of ZnO continually cluster and go bigger, results in the red shift of UV peak position. With increasing temperature, lots of oxygen atoms entered into Zn vacancies and hence the reason for the change of visible emission band [47]. | wurtzite phase of ZnO particles remains same; whereas fluorescence emissions are affected. UV-visible spectrum showed blue shift in ZnO nanoparticles [46]. |

[18]
dried for 6 h in air named as Sample A and other part of precipitate were annealed for 5 min at temperatures 200, 300, 400 and 600 °C respectively named as Sample B, C, D and E.

9. ZnO rods were synthesized on the substrate of bare glass using wet chemical method. Equi-amount of Zn(NO$_3$)$_2$.6H$_2$O and C$_6$H$_{12}$N$_4$ aqueous solution was mixed in a sealed glass vessel kept at 95°C. Cleaned substrate was immersed into the reactant solution. The concentration of the mixed solution was changed from 0.001-0.1 mol/L and the reaction time also changed from 0.5 to 4 h. The bare glass substrate covered with white layers; washed with DI water and dried at 95 °C. Reactant concentration plays an important role in the formation of ZnO rods. With increasing reaction concentration, the ratio of the length to diameter decreased and the orientation of rods varied from parallel at lower reaction concentration to perpendicular to the substrate when the concentration increased up to 0.1 mol/L [48].

10. ZnO nanoparticles were prepared by hydrothermal method. 0.1 M Zn(CH$_3$COO)$_2$.2H$_2$O stock solution was prepared in 50ml methanol under stirring. In order to get the pH value of reactants between 8 and 11, 25ml of NaOH (varying from 0.2 M to 0.5 M) solution prepared in methanol was added in the stock solution of Zn(CH$_3$COO)$_2$.2H$_2$O and stirred continuously. The prepared solutions were transferred into teflon lined sealed stainless steel autoclaves and maintained at various temperature in the range of 100 to 200 °C for 6 and 12 ZnO nanoparticles have the hexagonal wurtzite structure and the particle size increases with growth temperature and decreases with concentration of the precursors. For the synthesized ZnO nanoparticles, the green PL emission is observed due to the oxygen vacancy or Zn interstitial defects [49].
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**General Introduction**

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<td>h under autogenous pressure. At room temperature, white solid products were washed with methanol, filtered and then dried in air in an oven at 60 °C.</td>
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<td>11.</td>
<td>Monodisperse ZnO nanoparticles were synthesized by using PVP as the capping molecules. Colloidal solutions of ZnO were prepared in 2-propanol from the reactants ((\text{CH}_3\text{COO})_2\text{Zn}.2\text{H}_2\text{O}) and NaOH in the presence of PVP having a molar ratio Zn(II)/PVP = 5:3. The precipitates of ZnO nanoparticles were stored at room temperature for characterizations.</td>
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<td>12.</td>
<td>In a conical flask, 20 ml of (n)-pentanol containing 0.05 g of PVP (K30) was mixed with 0.8 ml aqueous solution of NaOH (0.15 mol) and stirred at room temperature for 30 minutes. After that, 0.6 ml of (\text{Zn(NO}_3\text{)}_2.6\text{H}_2\text{O}) (0.10 mol) containing ethanol solution was added and stirred for another 30 min. The whole solution was heated at 95 °C in an oven for one day. The obtained precipitate was washed with ethanol 3 times by centrifugation and ultrasonic, and prepared for characterization.</td>
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<td>13.</td>
<td>ZnO powder synthesized by precipitation method using (\text{Zn(CH}_3\text{COO)}_2.2\text{H}_2\text{O}) and PVP as starting materials. Various amounts of PVP ((1 \times 10^{-4} \text{ M}, 2 \times 10^{-4} \text{ M and } 3 \times 10^{-4})) were used. When the concentration of PVP was increased, the grain sizes of ZnO were decreases and correspondingly the optical band gap of ZnO powder also increased [52].</td>
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M) were added into previous \( \text{Zn(\text{CH}_3\text{COO})}_2\cdot2\text{H}_2\text{O} \) precursor solutions (0.1 M and 0.2 M, 50 ml) with continuous stirring. After that, 1.6 g NaOH was dissolved in 50 ml distilled water and was slowly added to the previous mixed precursor solutions; white precipitates were formed and stirred vigorously for one hour at ambient temperature. After filtering precipitates, rinsed with distilled water, drying at 60 °C and calcined at 600 °C for one hour.

14. ZnO nanoparticles synthesize by a cost effective simple chemical method at low temperature. In this method, \( \text{Zn(\text{CH}_3\text{COO})}_2\cdot2\text{H}_2\text{O} \), NaOH pellets, poly-vinylpyrrolidone (PVP) and citric acid (CA) were used and for preparation of aqueous solution double distilled water was used. A stoichiometric ratio of PVP is dissolved in 100 ml distilled water with the slow addition of \( \text{Zn(\text{CH}_3\text{COO})}_2\cdot2\text{H}_2\text{O} \) to the solution and the reaction mixture was stirred constantly for several minutes followed by the addition of NaOH in the molar ratio of \( \text{Zn}^{2+}/\text{OH} = 0.09 \), whence a turbid white precipitate were formed at about 10 min. The mixture is then put in a beaker sealed with an aluminium foil and then in a hot air oven maintained at 100°C. Capping molecules influenced the sizes of nanoparticles. UV-vis spectra showed that energy band gap increases for smaller particle, indicated strong particle size confinement [53].
temperature for 48 h, which is then cooled to room temperature naturally. The white precipitate deposited at the bottom is collected and washed with distilled water and ethanol to remove impurity ions. Eventually, ZnO samples were obtained by centrifugation and dehydration of the precipitate at 60°C. The above said process is repeated for the synthesis of ZnO nanoparticles with multicapping agents involving the mixture of PVP and CA with molar ratio of CA/PVP = 1:2 in weight.

| 15. | Different doping percentages of Cu doped ZnO nanoparticles were synthesized by hydrothermal method. Required amount of Zn(CH$_3$COO)$_2$.2H$_2$O, Cu(CH$_3$COO)$_2$.H$_2$O and 0.5 M oxalic acid were dissolved in double distilled water and stirred vigorously for 20 min. The product was put into sealed autoclave and maintained at pressure of 150 kPa for 3 h at temperature ~ 90 °C. The white precipitates were centrifuged, washed with double distilled water for several times and finally washed with ethanol to remove impurities in the final products. The precipitate was dried at 60 °C in air for 3 h and the white powders were then heated at 400 °C for 2 h, named as RCu1, R Cu2, R Cu3, R Cu5, R Cu8 and R Cu10 for 1%, 2%, Wurtzite structures of rod shape ZnO:Cu$^{2+}$ nanoparticles degrade gradually with increasing Cu concentration. The nanorods showed strong ferromagnetic behavior initially, and suppressed at higher percentage of Cu, whence paramagnetic nature was enhanced [54]. |
| 16. | Undoped and Cu doped ZnO nanoparticles (5, 10, 15, 20, 25 and 30 at %) were synthesized by co-precipitation method. Appropriate amount of ZnCl$_2$ and CuCl$_2$·2H$_2$O have been dissolved in distilled water and mixed carefully. To control the pH of the solution within range 7-8, aqueous ammonia has been added slowly to the previously prepared mixed solution. The precipitates were collected and washed with distilled water, and dried in oven for 3-4 h. Finally, the precipitates were annealed in Muffle furnace at 600 °C for 2 h. | It is reported that, effect of Cu doping on the structural and electrical properties has been observed and substitution limit of Cu in ZnO to be low 10 at %. Beyond this level, there was a secondary phase of CuO. There is a decrease in DC electrical resistivity as well as the activation energy with increasing Cu content [55]. |
| 17. | Cu-doped ZnO nanopowders (Zn$_{1-x}$Cu$_x$O, x = 0, 0.02, 0.04 and 0.06) have been synthesized by co-precipitation method. In 50 ml double distilled water, equimolar (1M) Zn(NO$_3$)$_2$·6H$_2$O and Cu(NO$_3$)$_2$·3H$_2$O were dissolved and stirred vigorously by a magnetic stirrer for 2 h. Separately in 50 ml distilled water, a buffer solution was prepared by dissolving 4 g NaOH and 10.6 g Na$_2$CO$_3$, maintained pH = 4.6 of the solution for better precipitation reaction. The white precipitates were achieved by drop wise addition of buffer solution to the initially prepared solution which was stirred constantly for 2 h at room | XRD analyses supported the Cu concentration limit is below 6 % (0.06) molar fraction and the average crystalline sizes decreases with increasing Cu content. FTIR spectra confirmed the presence of functional groups and chemical bonding with Cu. Substitution of Cu into ZnO lattice has been confirmed by PL spectra [56]. |
temperature. The white precipitates were filtered, washed with distilled water for several times, and dried in oven at 80 °C for 2h. The dried products were collected, ground by an agate mortar and were annealed at 500 °C under Ar atmosphere for 2 h followed by furnace cooling. The same procedure was followed for other samples preparation.

| 18. Cu doped ZnO nanoparticles were synthesized by co-precipitation method. Two solutions were prepared in 440 ml distilled water, one solution containing appropriate amount of ZnSO$_4$.7H$_2$O and CuSO$_4$.5H$_2$O (Sol A) and the other containing 44 mmol NaOH (Sol B). Sol A was then put into ultrasonic cleaner for 2 h at 50 °C using a 57 kHz operating frequency and was stirred using a magnetic stirrer at 80 °C. After that Sol B was added into Sol A until the mixed solution reached final pH=12 and was stirred constantly for 30 min. Finally, solution was aged for 18 h at room temperature and the solution was centrifuged. So obtained precipitate was washed several times with ethanol and distilled water, dried at 200 °C in a vacuum oven for 1h yielding Cu doped ZnO brown powder. |
| XRD measurement revealed that hexagonal wurtzite structure of Cu doped ZnO and the solubility limit of Cu in ZnO was ~ 11 at%. UV-vis spectra confirmed a clear red shift and all samples were exhibit ferromagnetic ordering at room temperature. From the infrared absorption spectra showed clear evidence of hydrogen incorporation in ZnO [57]. |
1.4. Applications of ZnO

ZnO is an important II-VI wide-band-gap (3.3 eV, at 300K) semiconductor material exhibits interesting properties including high exciton binding energy of 60 meV, strong adsorption ability and low growth temperature, which makes it a wide variety of interesting applications in photocatalysts, chemical sensors, piezoelectric transducers, transparent electrodes [58, 59], electroluminescent devices, ultraviolet laser diodes [60-63], photonic crystals [64], photodetectors [65], varistors [66] and solar cells [67]. Various processes have been applied to the synthesis of ZnO nanostructures, such as nanowires, nanorods [68, 69], nano-tubes [70], and nanobelts [71], which have been attracted intensive interest due to their potential applications in a variety of novel nano-devices, such as photodiodes, field-effect transistors, single-electron transistors [72] and chemical sensors [73-75]. ZnO coating on polyethylene naphthalate (PEN) reduces the diffusion of oxygen with PEN [76]. It can also be used on polycarbonate (PC) in outdoor applications, which protects PC from solar radiation and decreases the oxidation and photo-yellowing of PC [77]. Compared to gallium nitride (GaN), ZnO can be used for many of the same applications, as some of the properties of these two materials overlap for optoelectronic applications; however ZnO has some distinct advantages over GaN because of its high exciton binding energy (60 meV) which is much larger than that of GaN (~21-25 meV) [78]. It has been reported many authors that the changes induced by incorporation of transition metal ions into ZnO lattice. Copper (Cu) doped into the ZnO lattice has shown to improve properties such as photocatalytic activity, gas sensitivity and magnetic semiconductivity [79-81].

ZnO have emerged as promising candidates for active food packaging systems due to their antibacterial activity [82-84]. Titanium dioxide (TiO₂) can be used as a self-cleaning and self-sterilizing material to coat different tools, like wares in sanitary, food table and cooking [85, 86]. The antimicrobial effects of TiO₂ are totally dependent on irradiation of ultraviolet and/or visible light to it for its photocatalytic behavior. In food packaging industry this is a drawback because of the antimicrobial activity will only be effective in irradiated packages. This can be overcome using ZnO and act as a permeation barrier coating [87] and is Generally
Recognized as Safe material (GRAS) by the U.S. Food and Drug Administration (21CFR182.8991). However, ZnO in nanoscale can also play an important role in reducing pathogen contamination and extending the shelf-life of food products.

1.5. Aim of the Research Work

Zinc oxide (ZnO) is a fascinating material due to its various applications and exhibits attractive interesting properties as reported from numbers of literature survey. The main aims of the present study were:

- To synthesize of ZnO nanostructures by low temperature wet chemical method and characterize them.
- To synthesize of ZnO nanostructures and study the effects of (i) pH variation, (ii) temperature variation, (iii) molar variation of Zn source, (iv) wt% variation of capping agent and (v) Cu doped variation.
- We have studied the antibacterial effect of ZnO nanostructures and Cu doped ZnO nanostructures in different bacteria culture for application of synthesized nanostructures.

1.6. References


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