CHAPTER 4
Characterization of Material

Quantum dots of metal oxide semiconductors exhibit many interesting electronic, optoelectronic and optical properties \([1-36]\). These properties become more interesting when the size of the quantum dots becomes very small (less than 1000 nm). To explore these properties of our synthesized metal oxide semiconductors quantum dots, the following characterizations have been carried out, which is my contribution to this chapter.

(i) UV-Visible Spectroscopy

(ii) X-ray diffraction study (XRD)

(iii) High Resolution Transmission Electron Microscopy (HRTEM)

In this chapter, the characterizations of the samples by the above mentioned techniques have been explained. The average crystallite size of the quantum dots is estimated by XRD, and HRTEM studies. The variation of band gap that occurs due to variation of size of the quantum dots has been explored by optical absorption spectroscopy.

4.1. UV-Visible spectroscopy

Ultraviolet-visible (UV-VIS) spectroscopy involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum,
molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy. Fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

The instrument used in ultraviolet-visible spectroscopy is called a UV-VIS spectrophotometer. This instrument measures the intensity (I) of light transmitted through the sample and compares it to the intensity (I_o) of light incident on the sample. The ratio of the intensity (I) of transmitted light through the sample to the intensity (I_o) of incident light on the sample is defined as transmittance which is usually denoted by “T”. That is, transmittance T = (I / I_o) and is expressed as percentage (%T). %T=Tx100 \[30\]

The absorbance, A is is related to the transmittance by the following realation:

\[ A = - \log (\%T) \] ................................ (4.1)

Optical absorbance (A) is an important way to explore the different energy states in semiconductor material. This study \[10-12\] is based on the fact that, if two possible energy states E_1 and E_2 exist in a system as shown in Figure 4.1, then electronic transition from band E_1 to E_2 can takes place when appropriate energy E_2 – E_1 = E is absorbed and the frequency of radiation has the simple form of

\[ \nu = \frac{E}{h} \text{ Hz} \]

or, \( E = h \nu \text{ joules.} \) .................(4.2)
That is, absorption wavelength or edge can be written as

$$\lambda_a = \frac{hc}{E}$$

Where ‘\(\lambda_a\)’ is the absorption edge, ‘h’ is the Planck’s constant and ‘c’ is the velocity of light.

For semiconductors, if \(E_1\) be the valance band, \(E_2\) be the conduction band energy and \(E\) be the band gap energy, then according to the above relation,
we have

\[ \lambda_a = \frac{hc}{E} \]

\[ E = \frac{hc}{\lambda_a} \] \hspace{1cm} (4.3)

Where ‘\( \lambda_a \)’ is the absorption edge, ‘h’ is the Planck’s constant and ‘c’ is the velocity of light.

By obtaining the value of absorption edge ‘\( \lambda_a \)’ of the samples from their respective absorption spectra, the band gap \( E \) of the specimen (for bulk as well as for quantum dot) can be calculated by the relation (4.3). After estimating the band gaps (of bulk and quantum dots) the radius of quantum dots can be obtained by using the following theoretical model known as “Hyperbolic band model”\(^{[7,8]}\).

\[ R = \sqrt[3]{\frac{2\pi^2 h^2 E_{gb}}{m^* (E_{gn}^2 - E_{gb}^2)}} \]

Where, \( R \) is the quantum dot radius, \( E_{gb} \) is the bulk band gap, \( E_{gn} \) is the quantum dot band gap, \( h \) is Planck’s constant, \( m^* \) is the effective mass of electron of the specimen. From radius \( (R) \), diameter of quantum dots can be calculated as \( D = 2R \).

This diameter is the size of quantum dot \(^{[3,6]}\). The bulk band gap \( E_{gb} \) and quantum dots band gap \( E_{gn} \) can be calculated from their respective absorption spectra by using the relation (4.3). \( h \) is the planck’s constant \((6.6 \times 10^{-34} \text{ Joule-Sec})\) and \( c \) is the velocity of light \((3.10 \times 10^8 \text{ m/s})\). \( m^* \) is the effective mass of electron of the specimen. Effective mass for, ZnO, SnO\(_2\) and Fe\(_2\)O\(_3\) is \( 2.45 \times 10^{-31} \text{ Kg} \), \( 2.51 \times 10^{-31} \text{ Kg} \) and \( 2.49 \times 10^{-31} \text{ Kg} \) respectively \(^{[6,31,32,33,34]}\).
4.2 X-ray diffraction study (XRD)

X-ray diffraction study is an important tool for finding different crystal parameters like crystallite size, d-spacing, diffraction planes, structure, phase, and lattice constants, etc. The intensities and the angles of diffracted X-ray beams are related to atomic arrangement of the crystal.

![X-ray diffraction diagram](image)

**Fig.4.3.** X-ray diffraction by sample.  **Fig.4.4.** A typical X-ray diffractometer.

In this study, X-ray diffractometer detects the X-ray, diffracted by crystal and gives the diffractogram, which is a plot between intensity and diffraction angle. Intensity is given in terms of arbitrary units (A.U) and the angle is in degrees. Figure 4.5 shows a schematic of pattern of such X-ray diffractogram.

![XRD pattern diagram](image)

**Fig 4.5.** Schematic of XRD pattern.
Next we explain how X-ray diffractogram is used in finding various crystal parameters of the quantum dots, prepared in our laboratory.

4.2.1. Sample identification

To identify any specimen, the diffraction angles produced by a particular sample are compared with the standard diffraction angles of the same material. A good match between experimental and standard values of diffraction angles is required to identify the specimen. The most commonly used database for the identification of crystal structures is ICDD (International Center Diffraction Data) system.

4.2.2. Crystallite (grain) size estimations

A crystallite is a single crystal in a polycrystalline aggregate. X-ray diffractogram is extensively used to calculate the average crystallite size (D) using Debye-Scherrer equation \(^9\). The equation is written as

\[
D = \frac{0.9\lambda}{W\cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldas
middle point of the peak is A. Two more points P and Q are taken on the plot collinear to point A. Two perpendiculars from points P and Q are drawn on the abscissa, which is cut by the perpendicular lines at point R and S. The segment RS is the full width at half maximum (FWHM) in degrees. Finally, this is converted into radians, which is the required FWHM (W).

![Schematic of Single XRD peak.](image)

**Fig.4.6. Schematic of Single XRD peak.**

**II. Diffraction angle or glancing angle (\( \theta \)) and X-ray wavelength**

In the diffractogram, the angle axis is calibrated in terms of “\(2\theta / \text{degree}\)”. From this, glancing angle “\( \theta \)” can be obtained. The X-ray wavelength “\( \lambda \)” used in the X-ray diffractometer is 1.541 Angstrom.

In practice, the experimental data obtained from XRD study of any specific specimen may slightly differ from the standard values due to the following reasons.

1. Calibration error
2. Instrumental error
3. Sudden power fluctuation during experiment

4. External noises.

The X-ray diffraction (XRD) analyses of quantum dot samples are carried out using a PAN analytical X’Pert Pro X-ray Diffractometer with Cu Kα radiation as an X-ray source at 40 kV and 30 mA in a scanning angle (2θ) ranging from 20° to 70° with scan speed 0.001°s⁻¹. Various XRD data have been calculated using X’Pert High Score software.

Using ICDD (International Center Diffraction Data) sample parameters (Size, lattice constants, crystal planes etc.) are obtained very easily now a days.

4.3 High Resolution Transmission Electron Microscopy (HRTEM):

HRTEM opens a new door to nano-science research by providing pictorial view of nanoparticles with very high magnification of 800000X or more. This study, gives the information about size, shape and surface morphology of any specimen. High Resolution Transmission electron microscopy (HRTEM) is a microscopic technique whereby a beam of electrons is transmitted through the specimen. An image is formed from the electrons, transmitted through the specimen which is magnified and focused by an objective lens and appears on an imaging screen, a fluorescent screen is used in most HRTEMs and also the image is recorded by a sensor such as a CCD camera. Normally, HRTEM are interfaced with computer.
Fig. 4.7. a. Photograph of HRTEM instrument

Fig. 4.7. b. Labeled image of HRTEM instrument

Photograph of HRTEM instrument and Labeled image of HRTEM are shown in Fig 4.7.a and Fig 4.7.b respectively. Different parts of HRTEM are explained below:

**Electron gun**-The HRTEM consists of an electron emission source, which is normally a tungsten filament, It is also called Electron gun.

**High Voltage Source**- By connecting electron gun to a high voltage source (typically ~100–300 kV) the gun is provided sufficient current and it begins to emit electrons by field electron emission into the vacuum.

**Anode** –The emitted electrons are collected by the anode.

**Rotary pump and Turbo pump**-The vacuum system for evacuating HRTEM to an operating pressure level (typically of the order of $10^{-4}$ Pa.) consists of several stages.. Initially, a low or roughing vacuum is achieved with a rotary vane
pump setting a sufficiently low pressure to allow the operation of a turbo pump establishing high vacuum level necessary for operations.

**Different lenses** - The lenses of HRTEM allow for beam convergence, with the angle of convergence as a variable parameter, giving the HRTEM the ability to change magnification simply by modifying the amount of current that flows through the coil. Typically HRTEM consists of four stages of lensing. The stages are the condenser lenses, the objective lenses, the intermediate lenses and the projector lenses.

**Specimen Tray** - Specimen tray contains the specimen or sample.

**Fluorescent Screen** - Imaging systems in HRTEM consist of a phosphor screen, which may be made of fine (10–100 μm) particulate zinc sulfide, for direct observation of sample image by the operator.

**Control box** - It is used for optimizing resolution, magnification factor and other associated parameters as per requirement.

**Optical Binocular** - It is incorporated for manual observation / monitoring of the qualitative aspect of the images to execute necessary control/adjustment/tuning of the device to have the desired pictorial view.

### 4.4. Conductivity Test

To test the conductivity of the samples, whether p-type or n-type, a simple method called ‘thermoelectric effect’ have been used \(^{[16]}\). A measurement of the sign of the voltage across a semiconductor specimen, one end of which is heated, is a rough and ready way to tell if the specimen is n-type or p-type. For p-type semiconductor, the sign is positive (+ve), and negative (-ve) for n-type semiconductor. In this work, the
conductivity of all the prepared samples are tested by the method. The tests show that the samples (ZnO, SnO$_2$ and Fe$_2$O$_3$) possess n-type conductivity $^{[19,35,36]}$. The results are verified by “Hall effect” also.

4.5. Characterization of samples

In the next consecutive sections, the characterizations of our prepared semiconductor metal oxide quantum dots are discussed in details.

4.5.1. Zinc oxide (ZnO) quantum dots embedded in PVA (Polyvinyl Alcohol) matrix

ZnO specimen$^{[29]}$ has been characterized by UV/VIS optical absorption spectroscopy (Perkin Elmer Lamda 35 1.24), X-ray diffraction study (Bruker AXS, X-ray source: Cu K$_\alpha$) and high resolution transmission electron microscopy (HRTEM) (JEM 2100, Jeol).

I. Optical absorption spectroscopy

![Absorption edge of quantum dot](image)

![Absorption edge of bulk](image)

**Fig. 4.8.** Optical spectra of ZnO  a: quantum dot, b: bulk
In the optical absorbance spectra shown in Figure 4.8, “a” denotes the spectrum of ZnO quantum dot while “b” denotes that of bulk. It is seen that the band edge absorption in quantum dot is strongly blue shifted at 215 nm with respect to bulk specimen which possesses the absorption edge at around 390 nm. For estimating particle size from blue shift, a theoretical model [7,8] has been proposed, known as hyperbolic band model that is written as

\[ R = \sqrt{\frac{2\pi^2 \hbar^2 E_{gb}}{m^* (E_{gn}^2 - E_{gb}^2)}} \] ........ (4.5)

Where, R is the quantum dot radius, \( E_{gb} \) is the bulk band gap, \( E_{gn} \) is the quantum dot band gap, \( \hbar \) is Planck’s constant, \( m^* \) is the effective mass of electron of the specimen. The bulk band gaps at room temperature and the effective mass[^6,^7] of electron of ZnO is listed in the Table 4.1.

<table>
<thead>
<tr>
<th>Name of the samples</th>
<th>Bulk Band gap</th>
<th>Values of effective mass</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.20 eV</td>
<td>2.45 x 10^{-31} Kg</td>
<td>wurzite</td>
</tr>
</tbody>
</table>

**Table 4.1. Bulk band gap and effective masses of ZnO**

The data obtained from the analysis are put in Table 4.2.

<table>
<thead>
<tr>
<th>Absorption edge in quantum dot</th>
<th>Energy gap in quantum dot</th>
<th>Bulk absorption edge</th>
<th>Bulk band gap</th>
<th>Enhancement in band gap due to size quantization</th>
<th>Quantum dot size (Diameter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>215 nm</td>
<td>5.8 eV</td>
<td>390 nm</td>
<td>3.18 eV</td>
<td>2.62 eV</td>
<td>11 nm</td>
</tr>
</tbody>
</table>

**Table 4.2. Data of ZnO/PVA specimen revealed from optical absorption spectroscopy.**
II. X-ray diffraction study

From X-ray diffraction study (Figure 4.9) average particle size (crystallite size) is calculated by using Debye-Scherrer formula \[ D = \frac{0.9\lambda}{WCos\theta} \], ‘\( \lambda \)’ is wave length of X-ray (0.1541 nm), ‘W’ is FWHM (full width at half maxima), ‘\( \theta \)’ (theta) is the glancing angle and ‘D’ is particle diameter (crystallite size). Considering all the peaks (2\( \theta \) in degree) in the X-ray diffractogram, the average crystallite (quantum dot) size has been assessed and found to be 11 nm. Further, by analyzing the X-ray diffractogram with the help of ICDD (International Center Diffraction Data) it has been revealed that ZnO quantum dots are wurzite in structure.

Fig 4.9: XRD Spectra of ZnO Quantum dots embedded in PVA
III. High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM photograph of ZnO quantum dots$^{[29]}$ is shown in Figure 4.10 which provides the surface morphological view of the particles. The sample size and shapes are put in the Table 4.3.

![HRTEM Photographs of ZnO](image)

**Fig.4.10. HRTEM Photographs of ZnO**

<table>
<thead>
<tr>
<th>Average particle size</th>
<th>Particle Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 nm</td>
<td>Elliptical</td>
</tr>
</tbody>
</table>

**Table. 4.3. Data of ZnO/PVA sample obtained from HRTEM study**

All these characterizations infer that sizes of ZnO quantum dots are within 11 nm.

4.5.2 Zinc oxide (ZnO) quantum dots embedded in PVP (Polyvinyl Pyrrolidone) matrix

ZnO specimen$^{[28]}$ has been characterized by UV/VIS optical absorption spectroscopy (Perkin Elmer Lamda 35 1.24), X-ray diffraction study (Bruker AXS, X-ray source:
Cu Kα) and high resolution transmission electron microscopy (HRTEM) (JEM 2100, Jeol).

II. Optical absorption spectroscopy

![Optical Spectra](image)

**Fig. 4.11. Optical spectra of ZnO embedded on PVP a: quantum dot, b: bulk**

In the optical absorbance spectra shown in Figure 4.11, “a” denotes the spectrum of ZnO quantum dot\(^{[28]}\) while “b” denotes that of bulk. It is seen that the band edge absorption in quantum dot is strongly blue shifted at 210 nm with respect to bulk specimen which possesses the absorption edge at around 390 nm. For estimating particle size from blue shift, a theoretical model \(^{[7,8]}\) has been proposed, known as hyperbolic band model that is written as

\[
R = \sqrt{\frac{2\pi^2 \hbar^2 E_{gb}}{m^* (E_{gn}^2 - E_{gb}^2)}} \quad \ldots \ldots \quad (4.6)
\]

Where, R is the quantum dot radius, \(E_{gb}\) is the bulk band gap, \(E_{gn}\) is the quantum dot band gap, \(h\) is planck’s constant, \(m^*\) is the effective mass of electron of the
specimen. The bulk band gaps at room temperature and the effective mass \(^{[6,7]}\) of electron of ZnO is listed in the Table 4.4.

<table>
<thead>
<tr>
<th>Name of the samples</th>
<th>Bulk Band gap</th>
<th>Values of effective mass</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.20 eV</td>
<td>2.45 \times 10^{-31} Kg</td>
<td>wurzite</td>
</tr>
</tbody>
</table>

**Table 4.4. Bulk band gap and effective masses of ZnO**

The data obtained from the analysis are put in Table 4.5.

<table>
<thead>
<tr>
<th>Absorption edge in quantum dot</th>
<th>Energy gap in quantum dot</th>
<th>Bulk absorption edge</th>
<th>Bulk band gap</th>
<th>Enhancement in band gap due to size quantization</th>
<th>Quantum dot size (Diameter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>210 nm</td>
<td>5.9 eV</td>
<td>390 nm</td>
<td>3.18 eV</td>
<td>2.72 eV</td>
<td>10.6 nm</td>
</tr>
</tbody>
</table>

**Table 4.5. Data of ZnO/PVP specimen revealed from optical absorption spectroscopy.**

**II. X-ray diffraction study**

From X-ray diffraction study (Figure 4.12) average particle size (crystallite size) is calculated by using Debye-Scherrer formula\(^{[9]}\)

\[
D = \frac{0.9\lambda}{W\cos\theta}
\]

‘\(\lambda\)’ is wave length of X-ray (0.1541 nm), ‘\(W\)’ is FWHM (full width at half maxima), ‘\(\theta\)’ (theta) is the glancing angle and ‘\(D\)’ is particle diameter (crystallite size). Considering all the peaks\(^{[2]}\) (20 in degree) in the X-ray diffractogram, the average crystallite (quantum dot) size has been assessed and found to be 9 nm. Further, by analyzing the X-ray diffractogram with the help of ICDD (International Center Diffraction Data) it has been revealed that ZnO quantum dots are “wurzite” in structure.
III. High Resolution Transmission Electron Microscopy (HRTEM):

HRTEM images of PVP film (4.13.i.a) and ZnO quantum dots (4.13.i.b) are shown in Figure 4.13. It is evident in the HRTEM image (4.13.i.b) that ZnO crystallites (quantum dots) are circular in shape with sizes within 10 nm. Fig (4.13.ii) shows the Scanning Electron Microscope (SEM) image of ZnO quantum dot surface\textsuperscript{[28]}. ZnO sample sizes assessed from these three studies are well matching, which is a distinct advantage over earlier reports\textsuperscript{[2,3]}. All these characterizations infer that sizes of ZnO quantum dots (diameter) are within 10.6 nm.
4.5.3 Tin oxide (SnO$_2$) quantum dots embedded in PVP matrix

SnO$_2$ specimen$^{[22]}$ has been characterized by UV/VIS optical absorption spectroscopy (Perkin Elmer Lamda 35 1.24), X-ray diffraction study (Bruker AXS, X-ray source: Cu K$_\alpha$) and high resolution transmission electron microscopy (HRTEM) (JEM 2100, Jeol).

I. Optical absorption spectroscopy

In the optical absorbance spectra shown in Figure 4.14, denotes the spectrum of SnO$_2$ quantum dot (prepared sample)$^{[22]}$. It is seen that the band edge absorption in quantum dot is strongly blue shifted at 220 nm with respect to bulk specimen which possesses the absorption edge at around 340 nm. Blue shift is a distinct signature of quantum dot formation$^{[1,2,4]}$. For estimating particle size from blue shift, a theoretical model$^{[6,7]}$ has been proposed, known as hyperbolic band model$^{[5]}$ as indicated in the next page (Eq. no. 4.7).

![Absorption edge of quantum dot](image)

**Fig. 4.14: UV/VIS absorption spectra of SnO$_2$ a. quantum dots embedded on PVP**
\[ R = \sqrt[\frac{2\pi^2 h^2 E_{gb}}{m^*(E_{gn} - E_{gb}^2)}} \] ................................(4.7)

Where, \( R \) is the quantum dot radius, \( E_{gb} \) is the bulk band gap, \( E_{gn} \) is the quantum dot band gap, \( h \) is planck’s constant, \( m^* \) is the effective mass of electron of the specimen. The bulk band gaps at room temperature and the effective mass\(^{[6,7,31]} \) of electron of \( \text{SnO}_2 \) is listed in the Table 4.6.

<table>
<thead>
<tr>
<th>Name of the samples</th>
<th>Bulk Band gap</th>
<th>Values of effective mass ((m^*))</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SnO}_2 )</td>
<td>3.6 eV</td>
<td>2.51 x 10(^{-31}) Kg</td>
<td>Rutile structure</td>
</tr>
</tbody>
</table>

### Table 4.6. Bulk band gap and effective masses of \( \text{SnO}_2 \)

The data obtained from the analysis are put in Table 4.7.

<table>
<thead>
<tr>
<th>Absorption edge in quantum dot</th>
<th>Energy gap in quantum dot</th>
<th>Bulk absorption edge</th>
<th>Bulk band gap</th>
<th>Enhancement in band gap due to size quantization</th>
<th>Quantum dot size (Diameter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>220 nm</td>
<td>5.6 eV</td>
<td>340 nm</td>
<td>3.6 eV</td>
<td>2 eV</td>
<td>13 nm</td>
</tr>
</tbody>
</table>

### Table 4.7. Data of \( \text{SnO}_2/PVP \) specimen revealed from optical absorption spectroscopy

#### II. X-ray diffraction study

From X-ray diffraction study (Figure 4.15) average particle size (crystallite size) is calculated by using Debye-Scherrer formula\(^{[9]} \)

\[ D = \frac{0.9\lambda}{W\cos\theta} \]  

‘\( \lambda \)’ is wave length of X-ray (0.1541 nm), ‘\( W \)’ is FWHM (full width at half maxima), ‘\( \theta \)’ (theta) is the glancing angle and ‘\( D \)’ is particle diameter (crystallite size). Considering all the peaks\(^{[2]} \) (20 in degree) in the X-ray diffractogram, the average crystallite (quantum
dot) size has been assessed and found to be 12 nm. Further, by analyzing the X-ray diffractogram with the help of ICDD (International Center Diffraction Data) it has been revealed that SnO$_2$ quantum dots are rutile in structure.

![XRD spectra of SnO$_2$ quantum dots](image)

**Fig. 4.15: XRD spectra of SnO$_2$ quantum dots**

III. High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM images of PVP film (4.16.c) and SnO$_2$ quantum dots (4.16.a,b) are shown in Figure 4.16. It is evident in the HRTEM image (4.16.a) that SnO$_2$ crystallites (quantum dots) are circular in shape with sizes within 12 nm$^{[22]}$.

![HRTEM images of SnO$_2$ sample](image)

**Fig. 4.16: HRTEM images of SnO$_2$ sample**

SnO$_2$ sample sizes assessed from these three studies are well matching. This matching occurs due to the formation of well uniformed and circular shaped
quantum dots by using PVP matrix. All these characterizations infer that average size of SnO₂ quantum dots (diameter) are within 13 nm.

4.5.4 Iron oxide (Fe₂O₃) quantum dots embedded in PVP matrix

Fe₂O₃ specimen has been characterized by UV/VIS optical absorption spectroscopy (Perkin Elmer Lamda 35 1.24), X-ray diffraction study (Bruker AXS, X-ray source: Cu Kα) and high resolution transmission electron microscopy (HRTEM) (JEM 2100, Jeol).

I. Optical absorption spectroscopy

In the optical absorbance spectra shown in Figure 4.17, denotes the spectrum of Fe₂O₃ quantum dot (prepared sample). It is seen that the band edge absorption in quantum dot is strongly blue shifted at 360 nm with respect to bulk specimen which possesses the absorption edge at around 650 nm. For estimating particle size from blue shift, a theoretical model has been proposed, known as hyperbolic band model as indicated in the next page (Eq. no. 4.8).

![Absorption edge of quantum dot](image)

**Fig. 4.17:** UV/VIS absorption spectra of Fe₂O₃ a. quantum dots embedded on PVP b. bulk
\[ R = \sqrt{\frac{2\pi^2\hbar^2E_{gb}}{m^* (E_{gn}^2 - E_{gb}^2)}} \quad \text{.........}(4.8) \]

Where, \( R \) is the quantum dot radius, \( E_{gb} \) is the bulk band gap, \( E_{gn} \) is the quantum dot band gap, \( \hbar \) is planck’s constant, \( m^* \) is the effective mass of electron of the specimen. The bulk band gaps at room temperature and the effective mass\(^{[6,7,33,34]}\) of electron of \( \text{Fe}_2\text{O}_3 \) is listed in the Table 4.8.

<table>
<thead>
<tr>
<th>Name of the samples</th>
<th>Bulk Band gap</th>
<th>Values of effective mass</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>2.2 eV</td>
<td>2.49 x 10(^{-31}) Kg</td>
<td>wurzite</td>
</tr>
</tbody>
</table>

**Table 4.8. Bulk band gap and effective masses of \( \text{Fe}_2\text{O}_3 \)**

The data obtained from the analysis are put in Table 4.9.

<table>
<thead>
<tr>
<th>Absorption edge in quantum dot</th>
<th>Energy gap in quantum dot</th>
<th>Bulk absorption edge</th>
<th>Bulk band gap</th>
<th>Enhancement in band gap due to size quantization</th>
<th>Quantum dot size (Diameter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>360 nm</td>
<td>3.4 eV</td>
<td>650 nm</td>
<td>2 eV</td>
<td>1.4 eV</td>
<td>15 nm</td>
</tr>
</tbody>
</table>

**Table.4.9. Data of \( \text{Fe}_2\text{O}_3/PVP \) specimen revealed from optical absorption spectroscopy**

II. X-ray diffraction study

From X-ray diffraction study (Figure 4.18) average particle size (crystallite size) is calculated by using Debye-Scherrer formula\(^{[9]}\)

\[ D = \frac{0.9\lambda}{WC\cos\theta} \]

\( \lambda \) is wave length of X-ray (0.1541 nm), \( W \) is FWHM (full width at half maxima), \( \theta \) (theta) is the glancing angle and \( D \) is particle diameter (crystallite size). Considering all the peaks\(^{[3]}\) (20 in degree) in the X-ray diffractogram, the average crystallite (quantum
dot) size has been assessed and found to be 14 nm. Further, by analyzing the X-ray diffractogram with the help of ICDD (International Center Diffraction Data) it has been revealed that Fe₂O₃ quantum dots are “wurzite” in structure.

Fig. 4.18: XRD spectra of Fe₂O₃ quantum dots

III. High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM images of Plane-view(4.19.a) and cross sectional view of (4.19.b) of Fe₂O₃ quantum dots are shown in Figure 4.19. It is evident in the HRTEM image (4.19.a) that Fe₂O₃ crystallites (quantum dots) are circular in shape with sizes within 15 nm. [23]

Fig. 4.19: HRTEM images of Fe₂O₃ sample
Fe₂O₃ sample sizes [23] assessed from these three studies are well matching. This matching occurs due to the formation of well uniformed and circular shaped quantum dots by using PVP matrix instead of PVA (polyvinyl alcohol) matrix [2]. All these characterizations infer that sizes of Fe₂O₃ quantum dots (diameter) are within 15 nm.

4.6 Conclusion:

The prepared quantum dots have been characterized by various techniques, namely UV/VIS spectrometry, XRD and HRTEM. The characterizations infer that ZnO quantum dots are within 11 nm and 10.6 nm on PVA and PVP respectively. Further, it has been inferred that ZnO quantum dots are uniformly arranged on PVP rather than on PVA. In case of SnO₂ quantum dots, the size is within 13 nm while the size of Fe₂O₃ is within 15 nm. the structures of ZnO, Fe₂O₃ the quantum dots are wurtzite while the structure of SnO₂ is rutile.
References:


