CHAPTER VIII

STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF SnO$_2$-CdS NANOCOMPOSITES

8.1 Introduction

Nanocomposites are a genus of materials in which one or more phases with nanoscale dimensions (0-D, 1-D, and 2-D) are embedded in a metal, ceramic, or polymer matrix. The universal idea behind the addition of the nanoscale second phase is to create a synergy between the various constituents, such that fresh and innovative thoughts, capable of meeting or transcending design expectations can be achieved. The properties of nanocomposites rely on a range of variables, particularly the matrix material, which can exhibit nanoscale dimensions, degree of dispersion, size, shape, and orientation of the nanoscale second phase and interactions between the matrix and the second phase.

The nanoscale reinforcing phase can be grouped into three categories namely, nanoparticles (0-D), nanotubes (1-D), and nanoplates (2-D). In the case of nanoparticles, the particle size and distribution are a priority. Depending on the type of nanoparticles added, the mechanical, electrical, optical, and thermal properties of metal nanocomposites can be altered [1]. Inorganic nanostructures are becoming quintessential systems for demonstrating novel phenomena at nanoscale, leading towards a spectrum of applications [2–8].

Tin oxide, a wide band gap material (3.6 eV) at 300 K and n-type semiconductor, possesses high conductivity due to intrinsic defects like Oxygen deficiencies, yet in its stoichiometric form it is a good insulator. It was also explained by Kilic and Zunger that the defects form readily in SnO$_2$ because the formation energy of oxygen vacancies and interstitials are very low. It is known to exhibit a low electrical resistance with high optical transparency in the visible range of the electromagnetic spectrum. Although they are transparent in the visible range, they are highly reflective for infrared light. It is this property that makes it useful as an energy conserving material. Metal oxide systems made up of SnO$_2$ are of tremendous significance owning to high chemical stability and good flexibility in fabrication. Tin oxide has been extensively used as gas sensors, photocatalysts, and energy storage and anticoating as per statistics [9–13]. The application of these nanomaterials may be restricted by their own physical and chemical characteristics like bandgap, electrical, optical properties, gas sensitivity and chemical stability. However a great deal of research is
necessary to improve the properties of these oxides. It is reasonable to suggest modification of SnO$_2$ nanostructures. CdS is a direct band gap (~2.42 eV) semiconducting material with an exciton binding energy of 28 meV [14]. It has budding applications in optoelectronics, solar cells, X-ray detectors and photoconductive devices [15–22].

Much attention has been given to cadmium sulphide as it has been known to exhibit a sharp peak in the photoconductivity excitation spectrum that is usually explained to be due to band to band transition, i.e. excitation of electrons directly from the valence band to conduction band, from absorption measurements. The study of photoconductivity properties is considered to be a substantial tool for providing information regarding the nature of the phosphors. Since last decades the photoconductivity properties of inorganic nanoparticles have become subject of intensive study [23–37] not only because of fundamental interests in the nature of the electronic excitations but also due to their applications in a range of optical and electronic devices.

8.2 Materials

To synthesize SnO$_2$-CdS nanocomposites, the following materials were used. Tin chloride dihydrate (SnCl$_2$.H$_2$O), sodium hydroxide (NaOH), cadmium nitrate (Cd(NO$_3$)$_2$) and Thiourea (CH$_4$N$_2$S) of analytical grade were supplied by Merck and were used as received without further purification.

8.3 Experimental

The two base material pure Tin Oxide (SnO$_2$), pure Cadmium Sulphide (CdS) are taken in the powder form. These proportions are ground properly in order to get a homogeneous mixture. The mixture is then annealed in a crucible in a muffle furnace at 500 °C for 3 hrs. The heated material is then cooled down to room temperature and again ground, in order to get a microcrystalline form. For the firing process, the muffle furnace was used. Samples were prepared by the similar procedure by just changing the molar ratios of the base materials as [25:75], [50:50] and [75:25] respectively.

8.4 Characterization Techniques

After drying, the synthesized samples are characterized by several techniques. The crystal structure and Micro structure analysis were carried out using X-Ray Diffraction (XRD) and Scanning Electron Microscopy [SEM] respectively. The X-ray power diffraction
(XRD) analysis was conducted using the Siefert 3003T/T X-Ray diffractometer with CuKα ($\lambda = 1.5406$ Å) radiation in the 2θ range 20°-70° to identify the structural phase composition. The sample morphology was examined using a FEI Quanta FEG 200 Scanning Electron Microscope equipped with an Energy Dispersive X-Ray Analyser (EDAX) detector. The optical absorption spectra of the samples were recorded using a double beam Perkin Elmer (model Lambda 35) spectrophotometer in the range 190-1100 nm and their band gaps were calculated. The samples were subjected to Infrared Spectroscopic studies in the range of 400-4000 cm$^{-1}$ using, FTIR–Perkin Elmer model Spectrum RX 1. The electrical and photoconducting properties of the samples were measured by the HIOKI 3532-50 LCR Hitester and Keithley electrometer.

8.5 Results and Discussion

8.5.1 X-Ray Diffraction Analysis

The phase and composition of the nanocomposites were identified by powder X-ray diffraction. The typical XRD pattern is shown in Figure 8.1 from which the crystal phase of the product was determined to be the nanocomposite of SnO$_2$-CdS. All the strong diffraction peaks can be indexed as a mixture of tetragonal SnO$_2$ and the hexagonal CdS, which is well consistent with the JCPDS, file Nos.88-0287 and 75-1545, respectively. The corresponding Miller indexes are clearly observed in the spectrum for SnO$_2$ and CdS respectively. As the content of tin oxide is increased, the intensity of the diffraction peaks of SnO$_2$ increases and the diffraction peaks of tin oxide alone were clearly observed. The lattice constants for each molar ratio were thereby calculated and tabulated (Table 8.1). Using Scherrer’s equation the crystalline size was estimated from the peak width and recorded.

$$d = \frac{k\lambda}{\beta\cos\theta}$$

k is the shape factor equal to 0.89, $\lambda$ is the X-ray wavelength for CuKα radiation (1.5406Å), $\theta$ is the Bragg diffraction angle and $\beta$ is the Full Width at Half Maximum (FWHM) of the observed peak. The dislocation density and lattice strain are also calculated and tabulated.
Figure 8.1: XRD pattern of the SnO$_2$-CdS nanocomposite for the three different molar ratios.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>a (Å)</td>
<td>4.767</td>
<td>4.74±0.002</td>
<td>4.735±0.001</td>
<td>4.730±0.005</td>
</tr>
<tr>
<td>c(Å)</td>
<td>3.186</td>
<td>3.185±0.005</td>
<td>3.184±0.004</td>
<td>3.183±0.004</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>71.51</td>
<td>71.45</td>
<td>71.42</td>
<td>71.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>CdS [75-1545]</th>
<th>Hexagonal</th>
<th>Hexagonal</th>
<th>Hexagonal</th>
<th>Hexagonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>a = b(Å)</td>
<td>4.15</td>
<td>4.135±0.002</td>
<td>4.138±0.001</td>
<td>4.134±0.004</td>
<td></td>
</tr>
<tr>
<td>c(Å)</td>
<td>6.737</td>
<td>6.710±0.005</td>
<td>6.722±0.008</td>
<td>6.725±0.005</td>
<td></td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>100.48</td>
<td>99.30</td>
<td>100.15</td>
<td>100.21</td>
<td></td>
</tr>
</tbody>
</table>

(a) Calculated lattice parameters for SnO$_2$ and CdS
<table>
<thead>
<tr>
<th>XRD peaks of</th>
<th>Ratio</th>
<th>$2\theta$</th>
<th>hkl</th>
<th>$\beta$</th>
<th>$d$ (nm)</th>
<th>$\varepsilon$ ($\times 10^{-3}$)</th>
<th>$\delta \times 10^{15}$ (lines/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>25:75</td>
<td>26.85</td>
<td>100</td>
<td>0.2166</td>
<td>39.39</td>
<td>0.69</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>26.65</td>
<td>100</td>
<td>0.2198</td>
<td>38.8</td>
<td>1.28</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>75:25</td>
<td>26.65</td>
<td>100</td>
<td>0.1964</td>
<td>43.43</td>
<td>0.8</td>
<td>0.72</td>
</tr>
<tr>
<td>CdS</td>
<td>25:75</td>
<td>28.05</td>
<td>101</td>
<td>0.3657</td>
<td>23.41</td>
<td>1.29</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>28.18</td>
<td>101</td>
<td>0.3151</td>
<td>27.16</td>
<td>0.76</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>75:25</td>
<td>28.08</td>
<td>101</td>
<td>0.3445</td>
<td>19.24</td>
<td>1.02</td>
<td>1.19</td>
</tr>
</tbody>
</table>

(b) Crystallite size, average strain and dislocation density calculated from XRD for SnO$_2$ and CdS

Table 8.1: Tabulation of the Lattice parameters and other calculated data from XRD analysis for the nanocomposite of SnO$_2$-CdS for different molar ratios.

8.5.2 Williamson Hall analysis

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Compound</th>
<th>Scherrer’s Method</th>
<th>W-H Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$D_{avg}$ (nm)</td>
<td>$D$ (nm)</td>
</tr>
<tr>
<td>25:75</td>
<td>SnO$_2$</td>
<td>39.39</td>
<td>36.60</td>
</tr>
<tr>
<td></td>
<td>CdS</td>
<td>23.41</td>
<td>26.81</td>
</tr>
<tr>
<td>50:50</td>
<td>SnO$_2$</td>
<td>43.43</td>
<td>44.63</td>
</tr>
<tr>
<td></td>
<td>CdS</td>
<td>33.28</td>
<td>34.86</td>
</tr>
<tr>
<td>75:25</td>
<td>SnO$_2$</td>
<td>27.16</td>
<td>30.85</td>
</tr>
<tr>
<td></td>
<td>CdS</td>
<td>19.24</td>
<td>20.34</td>
</tr>
</tbody>
</table>

Table 8.2: Comparison of the Geometric parameters obtained from the Scherrer formula and W-H plot from the nanocomposite of SnO$_2$-CdS for different molar ratios.

The crystallite size and lattice strain are the two main properties that are usually extracted from the peak width analysis. In different ways Bragg peaks are affected by the crystallite size and lattice strain, which increase the peak width and intensity, shifting the $2\theta$
peak position accordingly. In order to obtain these parameters the Williamson-Hall and Scherrer methods were applied.

W-H analysis is a simplified integral breadth method where, both size induced and strain induced broadening are deconvoluted by considering the peak width as a function of 2θ [38]. The strain-induced broadening in powders due to crystal imperfection and distortion are related by using the formula

\[ t = \frac{0.9 \lambda}{\beta_c \cos \theta} \Rightarrow \beta_c = \frac{0.9 \lambda}{t \cos \theta} \]

\[ \beta_{\text{nr}} = 4 \varepsilon \tan \theta \]

\[ \beta_{\text{nr}} = \frac{0.9 \lambda}{t \cos \theta} + 4 \varepsilon \tan \theta \]

\[ \Rightarrow \beta_{\text{nr}} \cos \theta = \frac{0.9 \lambda}{t} + 4 \varepsilon \sin \theta \]

So if we plot \( \beta \cos \theta \) against \( 4 \sin \theta \) we get a straight line with gradient and intercept 0.9/t. Thus the strain and particle size are calculated from the slope and y-intercept of the fitted line respectively. Table 8.2 gives the comparison of the data obtained from the Scherrer’s formula and the Williamson-Hall plot

8.5.3 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

Typical Scanning Electron Microscopy (SEM) images of the SnO\(_2\)-CdS composition are presented in Figures 8.2 (a), (b) and (c). Applications in the field of nanoscience are encompassed by the impressive range of morphological variations. This has strongly driven the development of electron microscopy which demands not only increased resolution but also in-depth information about the sample. FESEM is a higher and more efficient tool than SEM whose observations can elucidate well defined and complicated morphologies. From the panoramic FESEM images, the as-prepared samples contain numerous thin flake-like structures, arranged in different directions in all three molar ratios. The micrographs on careful observation also demonstrated that the arrangements of the flakes are in aggregated form. The architecture of the composites does not alter much as the molar ratio is varied.
(a) SnO$_2$ - CdS (25:75)

(b) SnO$_2$ - CdS (50:50)
Figure 8.2: SEM images of SnO$_2$-CdS nanocomposite with three different molar ratios

![SEM images of SnO$_2$-CdS nanocomposite](image)

Figure 8.3: Histogram for the EDAX analysis (atomic weight %) for the nanocomposite of SnO$_2$-CdS for the three different molar ratios.

![EDAX histogram](image)

Energy Dispersive X-ray (EDX) spectroscopy was used to confirm the elemental composition for regions of interest. The EDAX atomic percentage histogram is shown in Figure 8.3. It is clear that all four constituent elements (Sn, Cd, S and O) are homogeneously
distributed throughout the agglomerate. From the histogram, it is also clear that the samples are generally richer in sulphur than oxygen content.

8.5.4 UV-Visible absorption study

![UV–Visible absorption spectra SnO<sub>2</sub>-CdS nanocomposites of three molar ratios](image)

Figure 8.4: UV–Vis absorption spectra SnO<sub>2</sub>-CdS nanocomposites of three molar ratios

Figure 8.4 shows the absorption spectra of the nanocomposite synthesized by hydrothermal method. The SnO<sub>2</sub>-CdS nanocomposite was subjected to ultraviolet-visible (UV-Vis) spectroscopy analysis in the wavelength range of 200 to 800 nm. The electronic band gap can thereby be calculated from the data that is obtained. The increase in the absorption at energies close to the band gap manifests itself as an absorption edge in the UV-Visible absorption spectra. The UV-Visible absorption spectra of the samples are shown in Figure 8.4. SnO<sub>2</sub> is observed to have absorption bands at 321 nm, 321 nm and 326 nm, and CdS, absorption edges at 501 nm, 502 nm, and 504 nm. The excitonic peaks of SnO<sub>2</sub> and that of CdS are found to be blue shifted with respect to their bulk, which could be attributed to the confinement effects. [30]. The excited wavelength was obtained from the absorption spectra ($\lambda_{ex}$). The band gap was thereby calculated using the formula $E_g = \frac{hc}{\lambda}$. The difference between the calculated band gap and the bulk band gap of the material was reported. The UV–Vis absorption spectra data of the nanocomposites are tabulated in Table 8.3.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard Band gap (eV)</th>
<th>$\lambda_{ex}$ (nm)</th>
<th>Band gap (eV)</th>
<th>Band gap difference (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25:75</td>
<td>SnO$_2$ 3.6 321</td>
<td></td>
<td>3.87</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>CdS 2.42 501</td>
<td></td>
<td>2.48</td>
<td>0.06</td>
</tr>
<tr>
<td>50:50</td>
<td>SnO$_2$ 3.6 321</td>
<td></td>
<td>3.87</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>CdS 2.42 502</td>
<td></td>
<td>3.48</td>
<td>0.06</td>
</tr>
<tr>
<td>75:25</td>
<td>SnO$_2$ 3.6 326</td>
<td></td>
<td>3.81</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>CdS 2.42 504</td>
<td></td>
<td>2.47</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 8.3: Band gap of SnO$_2$-CdS nano composite with three different molar ratios

8.5.5 Fourier Transform Infrared Spectroscopy

Spectroscopic investigations were carried out for all the samples of the SnO$_2$-CdS nanocomposites. The spectrographs are presented in Figure 8.5 and the wavelengths assigned are presented in Table 8.4.

Figure 8.5: FTIR spectra for the nanocomposite of SnO$_2$-CdS for different molar ratios
## Sample Wavenumber (cm⁻¹) Assignments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂:CdS 25:75</td>
<td>620.45</td>
<td>Cd-S bond- weak peak of CH –Stretching</td>
</tr>
<tr>
<td></td>
<td>1112.08 and 1407.39</td>
<td>S=O medium and Strong group of sulphate</td>
</tr>
<tr>
<td></td>
<td>1611.68</td>
<td>H-O-H bending vibration mode attributed to the absorption of water</td>
</tr>
<tr>
<td></td>
<td>3463.30</td>
<td>Broad band corresponding to the stretching mode of the OH group contributed by the water content in the sample.</td>
</tr>
<tr>
<td>SnO₂:CdS 50:50</td>
<td>617.03</td>
<td>Sn-O stretching mode</td>
</tr>
<tr>
<td></td>
<td>1110.32 and 1456.07</td>
<td>S=O Sulphate group</td>
</tr>
<tr>
<td></td>
<td>1615.39</td>
<td>Due to deformation vibrations of H₂O molecules</td>
</tr>
<tr>
<td></td>
<td>3442.02</td>
<td>Broad band corresponding to the stretching mode of the OH group contributed by the water content in the sample.</td>
</tr>
<tr>
<td>SnO₂:CdS 75:25</td>
<td>617.32</td>
<td>Sn-O stretching mode</td>
</tr>
<tr>
<td></td>
<td>1113.53</td>
<td>S-O sulphate</td>
</tr>
<tr>
<td></td>
<td>1617.21</td>
<td>Due to deformation vibrations of H₂O molecules</td>
</tr>
<tr>
<td></td>
<td>3435.91</td>
<td>Broad band corresponding to the stretching mode of the OH group contributed by the water content in the sample.</td>
</tr>
</tbody>
</table>

Table 8.4: Tabulation of the observance for the wavenumbers from the FTIR spectra for the composite of SnO₂-CdS for the different molar ratios.
8.5.6 Dielectric

The dielectric properties of materials are mainly due to contributions from the electronic, ionic, dipolar and space charge polarizations. Among these, the most important contribution to the polycrystalline materials in bulk form is from the electronic polarization, present in the optical range of frequencies. The dielectric constants of the SnO$_2$-CdS nanocomposites were measured using HIOKI 3532 LCR Hi TESTER in the frequency range from 50 Hz to 5 MHz. The samples were mounted between two electrodes. The capacitance of the parallel plate capacitor formed by the electrodes, with the sample as a dielectric medium was measured. The variation of capacitance was recorded in the frequency range 50Hz to 5MHz at different temperatures. The dielectric constant has higher values in the lower-frequency and it decreases at higher frequencies. The dielectric constant of SnO$_2$-CdS nanocomposite is high at lower frequencies due to the contribution of the electronic, ionic, dipolar and space charge polarizations, which depend on the frequencies. Space charge polarization is generally active at lower frequencies and indicates the purity and perfection of the nanoparticles. The dielectric loss arises when the polarization lags behind the applied AC field and is caused by the impurities and imperfections in the crystal lattice, which may be due to the space charge polarization. The low dielectric loss at high frequencies imply that the samples possess good optical quality with lesser defects. It is also observed that A.C conductivity increases with increase in temperature, indicating mobility of charge carriers responsible for hopping. As temperature increases, mobility of hopping ions increases thereby increasing conductivity. The A.C conductivity also increases with increasing frequency. The electrons which are involved in hopping are responsible for electronic polarization in SnO$_2$. 
8.5.6.1 Dielectric Constant for the nanocomposite of SnO$_2$-CdS

a) Dielectric constant of SnO$_2$-CdS (25:75)

b) Dielectric constant of SnO$_2$-CdS (50:50)
c) Dielectric constant of SnO$_2$-CdS (75:25)

Figure 8.6: Dielectric Constant plots for the nanocomposite of SnO$_2$-CdS for different molar ratios

8.5.6.2 Dielectric Loss for the nanocomposite of SnO$_2$-CdS

a) Dielectric loss of SnO$_2$-CdS (25:75)
b) Dielectric loss of SnO$_2$-CdS (50:50)

c) Dielectric loss of SnO$_2$-CdS (75:25)

Figure 8.7: Dielectric Loss plots for the nanocomposite of SnO$_2$-CdS for different molar ratios
8.5.6.3 A.C. Conductivity analysis for the nanocomposite of SnO$_2$-CdS

![Graph showing A.C. Conductivity of SnO$_2$-CdS (25:75)](image)

**a)** A.C. Conductivity of SnO$_2$-CdS (25:75)

![Graph showing A.C. Conductivity of SnO$_2$-CdS (50:50)](image)

**b)** A.C. Conductivity of SnO$_2$-CdS (50:50)
c) A.C. Conductivity of SnO$_2$-CdS (75:25)

Figure 8.8: A.C. Conductivity plots for the nanocomposite of SnO$_2$-CdS for different molar ratios

8.5.7 Photoconductivity

Figure 8.9 shows the I–V characteristics of the SnO$_2$-CdS nanocomposite. The I–V readings were taken in vacuum at room temperature, 350K and 390K, using a 100W halogen lamp. The I–V readings in the absence of halogen lamp is also shown for comparison. When the light was turned on, the conductivity immediately increased. In the presence of light, the photocurrent increases slowly with applied voltage and with further increase in voltage, the photocurrent increases rapidly. Photocurrent exhibits the existence of different kinds of conduction mechanism. The conduction processes can be explained in such a way that for low voltages the density of injected charge carrier is lower than the density of thermally generated charge carriers which in turn leads to the ohmic behavior. The photocurrent increases linearly with the increase in temperature. It is observed that with the increase in temperature there is rapid and incremental change in photocurrent.
a) Photoconductivity of SnO$_2$-CdS (25:75)

b) Photoconductivity of SnO$_2$-CdS (50:50)
c) Photoconductivity of SnO$_2$-CdS (75:25)

Figure 8.9: Photoconductivity plots for the nanocomposite of SnO$_2$-CdS for different molar ratios

8.6 Conclusion

To summarize, the metal oxide nanocomposite of SnO$_2$-CdS was prepared by the versatile hydrothermal method for three different molar ratios. Various characterizations were carried out to study the materials synthesized. The XRD pattern confirmed the crystallization of the tetragonal phase of SnO$_2$ and hexagonal phase of CdS. The presence of tin oxide and cadmium sulphide in the nanocomposite was however confirmed by the FTIR analysis and EDAX. Further calculations like crystallite size, lattice strain and dislocation density were also reported from both the Scherrer and Williamson-Hall calculations. The excitation wavelengths were noted for all three molar ratios and in all three cases a blue shift was observed. The HRSEM micrographs gave an insight of the morphology of the nanocomposites that were investigated systematically for the three molar ratios. The dielectric constant, dielectric loss and A.C conductivity of the Tin oxide-Cadmium sulphide nanocomposite were measured in the frequency range of 50Hz-5MHz at different temperatures. Effects of voltage and temperature on the photoconductivity of SnO$_2$-CdS in different compositions were studied.
References


