CHAPTER-7
Synthesis and Optical Properties of Cd-ZnO Nanoparticles and Dye-Sensitized Cd-ZnO Films

ZnO is a versatile IIb group semiconductor with numerous applications ranging from optoelectronics to chemical sensors due to its distinctive optical, electronic, and chemical properties. To further widen its useable wavelength range and improve the efficiency of ZnO-based devices, band-gap engineering by alloying is an effective technique. Cadmium oxide (CdO) is also a II b compound semiconductor with a narrower band-gap of 2.3 eV. By adding proper amount of Cd to ZnO, the band-gap of ZnO can be shifted to blue or even green light spectral range while keeping the crystalline structure and lattice parameter close to ZnO [1]. Cadmium oxide, is a known n-type semiconductor with a direct band gap of 2.3 - 2.5 eV and an indirect band gap of 1.36 - 1.98 eV. Cadmium oxide nanostructures are applied in solar cells, gas sensors, transparent electrodes and photodiodes, catalysts, photocatalysts and optoelectronic devices [2]. The numerous structures of cadmium oxide in nanoscale have been reported such as nanoparticles [3], nanowires [4], thin films, nanoneedles, nanotubes [5], nanorods, nanocrystals [6]. There are several techniques to prepare these materials such as sonochemical [7], microemulsion [8], hydrothermal/solvothermal method [9] and mechanochemical process [10]. Mechanochemical procedure is the act of grinding associated to the chemical reaction in solid state. Mechanical alloying, the type of solid state reaction, was introduced by Benjamin in 1960s for the first time and then, it was developed as
mechanochemical process to synthesize nanomaterials by McCormick. In fact, this process is a simple and useful route so that can be a beneficial technique to prepare various nanomaterials in industry. Many efforts have been carried out to improve the reaction conditions and attain the efficient parameters [11-13]. Hence, investigations on the synthesis and modification of nanosized ZnO have attracted tremendous attentions.

Different synthetic methods have been devised, including sol-gel technique, microemulsion synthesis, mechanochemical processing, spray pyrolysis and drying, thermal decomposition of organic precursor, RF plasma synthesis, supercritical-water processing, selfassembling, hydrothermal processing, vapor transport process, sonochemical or microwave-assisted synthesis, direct precipitation and homogeneous precipitation [14]. Meanwhile, there are reports that band gap of this material can change in a wide range from 1.1 to 3.3 eV due to mixing with appropriate materials. One of the effective approaches to tailor the optical properties of this material for various practical applications is the doping with selective elements. By choosing suitable rare earth doping, one can modify even the visible emission of ZnO. As well known, doping in semiconductor with selective elements offers an effective method to adjust their electrical, optical, and magnetic properties, which is crucial for their practical application. Although a considerable amount of research was done on nanostructure doping, it still remains a challenge to achieve efficient carrier density in ZnO semiconductors [15].

Typical ZnO based varistor is a very complex chemical system containing several dopants, such as Bi, Pr, Mn, Co, Cu, Sb, V, Cr and Cd. The electrical properties of ZnO are related closely to the composition and microstructure. So it is important to understand the effects of the individual additives in a fundamental manner. There are some reports
on the above doping elements in the ZnO varistor or thin film, but the effects of some doping elements on the grain and grain boundary of ZnO still remain unclear, because the doping effects have been studied in quite different systems under different experimental conditions, and the effect of individual dopant might be complicated by other dopants in ZnO with multi-components. Therefore, it is necessary to investigate the various dopants independently in a systemic way to understand the role of each dopant in the optical properties of ZnO. Recently, Han et. al. have studied the effects of Al and Mn doping on the electrical conductivity of ZnO in detail. In the present experiment simple Cd-ZnO systems were used to investigate the effect of cadmium dopant on the electrical conductivity of ZnO. In this chapter, simple one-step solid-state reaction in presence of PEG 400 $[\text{H-(O-CH}_2\text{-CH}_2\text{n-OH)}]$ has been carried out to synthesize ZnO and Cd-ZnO nanoparticles. The process was carried out at room temperature. Band gap energies of all the synthesized nanoparticles were calculated.

7. RESULTS AND DISCUSSIONS

7.1 XRD ANALYSIS

The XRD patterns of ZnO nanoparticles are shown in Fig. 7.1. All the diffraction peaks could be indexed to hexagonal ZnO (JCPDS card no.75-0576). Diffraction lines of ZnO were broadened, and extent of broadening was found to be dependent on Miller indices of the corresponding sets of crystal planes. The powders showed the crystalline nature with peaks corresponding to $(100)$, $(002)$ and $(101)$ planes. Doping with the Cd ions leads to an expansion of the lattice depending on the doping level. The diffraction peak $(002)$ was narrower than $(100)$ peak, and in turn $(100)$ peak was narrower than $(101)$ peak. This clearly indicated the presence of asymmetry in the crystallite shape and the small
shift in peaks (1 0 0) and (0 0 2) of Cd-ZnO (Fig. 7.1b) towards higher diffraction angle. This shows the height of c-axis of the crystal is smaller than the basal diameter (crystal axis, \( a_1, a_2 \)) [16, 17, 18]. The lattice parameters for undoped ZnO nanoparticles were calculated from the XRD data. The lattice constants \( a \) and \( c \) were found to be 0.32395 nm and 0.51949 nm, respectively (Fig. 1a). As for Cd-ZnO, the lattice constant \( a \) increases to 0.32403 nm, and \( c \) decreases to 0.51918 nm (Fig. 7.1b). The basal diameter of a-axis (crystal axis, \( a_0, a_2 \)) of the crystal is bigger than the height of c-axis. From the calculations, it has been observed that the lattice parameter a-axis value of Cd-ZnO increases. This increase in the lattice parameter a value clearly indicates that the smaller Zn ions (ionic radius 0.74 Å) are substituted by the larger Cd ions (ionic radius 0.97 Å) in the hexagonal wurtzite ZnO structure and hence there is an increase in the lattice parameter values. This revealed that, there is a perceptible change in lattice parameter \( c \), but apparent increase in lattice parameter \( a \). This indicated clearly that the Cd doping distorted the a-axis of ZnO, which in turn caused the expansion of unit cell volume. The reason for this increment is attributed to the substitution of Zn atoms by Cd atoms [19]. This was confirmed by EDAX measurement. However, the substitution of Cd does not affect the structure of ZnO. The increase in lattice constants after doping is due to the substitution of smaller Zn\(^{2+}\) ion by bigger Cd\(^{2+}\) ion. Fig. 7.1c and 7.1d depicts XRD patterns of Cd-ZnO annealed at 450 °C and 550 °C respectively. The diffractogram of the sample obtained at 450 °C exhibits broader peaks than those of the sample annealed at 550 °C indicated that at low temperature Cd-ZnO is obtained in small crystals. As the annealing temperature increases from 450 to 550 °C, the peak intensity of Cd-ZnO nanoparticles increases with a decrease in the full width at half maximum (FWHM),
which indicates a possible change in the grain size. This can be seen from the inset view of Fig. 7.1. However, the peak intensity of the annealed samples at 550 °C (Fig. 7.1d) was found to be increased compared to those annealed at 350 °C and 450 °C (Fig. 7.1b and 7.1c). The increase in peak intensity at higher annealing temperature is attributed to the increase in crystallinity [20].

![XRD pattern of powder sample prepared at room temperature](image)

Figure 7.1: XRD pattern of powder sample prepared at room temperature (a) ZnO annealed at 350 °C, (b) Cd-ZnO annealed at 350 °C, (c) Cd-ZnO annealed at 450 °C, (d) Cd-ZnO annealed at 550 °C.

7.2 FESEM/EDAX ANALYSIS

Figure 7.2 shows the FESEM images and EDAX patterns of ZnO, Cd-ZnO and CdO, respectively. From Fig. 7.2A and 7.2B it can be seen that the size of ZnO and Cd-ZnO nanoparticles annealed at 350 °C are in the range of 17-35 nm and 30-65 nm,
respectively. As the annealing temperature increases from 450 to 550 °C, the crystal size of Cd-ZnO also found to be increased (Fig. 7.2C and 7.2D). This is because of the increase in the supersaturation of the reaction products, which accelerates the crystal core forming reaction within a short time. Under these conditions the controlling step of the reaction is transferred from grain growth to crystal nucleus formation. With the temperature continuing to rise, the phenomenon of "nuclear-aggregation" caused by the rapid formation of crystal nucleus is obvious that result in forming aggregate among the crystal nucleus [21, 22]. The rate of particle aggregation is a major factor that controls the morphology and structure (crystalline) of the final product [23-24]. Fig. 3A shows the EDAX spectrum of ZnO. The pattern shows the presence of only Zinc and Oxygen and hence indicates the purity of ZnO nanostructures. The EDAX spectrum of Cd-ZnO (Fig. 7.2F) shows an evidence for the presence of Cadmium, Zinc and Oxygen. The sulphar peak appeared in the spectra are due to the impurity in the carbon tape pasted on copper grids used for the measurement. FESEM micrograph (Fig. 7.2G) shows that the CdO crystals obtained at 350 °C have homogeneous size and morphology (140-175 nm). Fig. 7.2H shows the elemental composition and confirms the presence of Cadmium and Oxygen.

7.3 UV-VIS SPECTRAL STUDIES

Figure 7.3A shows the UV-Visible absorption spectra of ZnO and Cd-ZnO samples annealed at different temperatures. The band gaps are found to be 3.38 eV for ZnO (Fig. 7.3a) and 3.34 eV (Fig. 7.3b) for Cu-ZnO. The small shift in band gap is attributed to the doping of Cd with ZnO [25, 26]. Fig. 7.3B is the enlarged view of Fig. 7.3A.
Figure 7.2: FESEM images of pure samples as-prepared and annealed (A) ZnO nanoparticles at 350 °C, (B) Cd-ZnO at 350 °C, (C) Cd-ZnO at 450 °C, (D) Cd-ZnO at 550 °C. EDAX spectra of pure samples as-prepared (E) ZnO nanoparticles at 350 °C, (F) Cd-ZnO at 350 °C. FESEM images of pure samples as-prepared and annealed (G) CdO nanoparticles at 350 °C, (H) EDAX spectra of pure CdO.
With increase in the annealing temperature from 350 to 550 °C (Fig. 7.3b -7.3d), the optical absorption edge was slightly shifted towards longer wavelength (3.38 to 3.26 eV), which may be attributed to the improvement in morphological and crystallinity of the samples at higher annealing temperature [27, 28]. The optical band gap \( E_g \) of ZnO and Cd-ZnO was calculated by using the formula, \( E_g = \frac{hc}{\lambda} \) [20]. The presence of Cd in the doped sample has been shown in the EDAX spectrum, which suggested relatively high dispersion of Cd component in the samples. The crystallinity of Cd-ZnO improved when the temperature increased from 350 to 550 °C (Fig. 7.3b - 7.3d). It is obvious that the conduction type of Cd-ZnO was dependent on the temperature. The shift in the band gap attributed to the effect of temperature on the crystallinity of Cd doped samples. Upon increasing the temperature, the peak showed a red shift that indicates the narrowing of the band gap due to Cd incorporation. On the other hand, as the crystallinity increases, the \( E_g \) value was shifted from 3.38 to 3.26 eV. The change in the optical band gap of Cd doped sample upon increase in temperature was due to the change of crystallinity at higher annealing temperature [29]. In Fig. 7.3C as-prepared CdO crystals show a broad absorption peak with the band gap of 2.77eV, which confirms the semiconducting character of CdO nanoparticles. It has shown to be an industrially important material that can be widely used for the applications such as solar energy conversion [33].

7.4 FT-IR ANALYSIS

FT-IR spectra of ZnO and Cd-ZnO nanoparticles are shown in Figure 7.4. The absorption peaks at 3508.44 and 1544.18 cm\(^{-1}\) are attributed to the O-H stretching vibration and its corresponding bending vibrations of the chemically adsorbed water molecules. The absorption band observed at 2359 cm\(^{-1}\) arises from the absorption of atmospheric CO\(_2\) on
Figure 7.3: (A) UV-Vis spectra of as-prepared doped and undoped nanoparticles annealed at different temperatures (a) ZnO at 350 °C, (b) Cd-ZnO at 350 °C, (c) Cd-ZnO at 450 °C, (d) Cd-ZnO at 550 °C, (B) Enlarge view of Fig 7.3A, (C) CuO at 350 °C.
the metallic cations. Peak at 1134.28 cm\(^{-1}\) may be due to the C-O group of the surfactant (PEG). The band around 450-500 cm\(^{-1}\) in both spectra are attributed to Zn-O stretching vibration (Figs. 7.4a and 7.4b) \[30\]. Similar features have been observed for Cd-ZnO sample (Fig. 7.4b). However a slight shift in the position of absorption band towards higher frequency has been observed for Cd-ZnO. The shift in band position (497-473 cm\(^{-1}\)) can be related to the change in the bond length that takes place upon substitution of Zn with Cu \[32\]. The IR spectra of the modified samples did not show any band corresponding to the transition metal (Cd). It might be due to the reason that the content of incorporated metal is slight; therefore the intensity of the band related to Cd-O-Zn is very low \[31\].

**Figure 7.4**: FTIR spectra of as-prepared (a) ZnO at 350 °C, (b) Cd-ZnO at 350 °C
7.5 UV-Vis Spectral Studies of Dye-Sensitized Cd-ZnO

Figure 7.5: The optical absorption spectra of Cd-ZnO films before and after sensitization with Eosin B (EB).

Figure 7.5 Show the optical absorption spectra of Cd-ZnO films before and after sensitization with Eosin B (EB), Fast Sulphon Black F (Fig. 7.6) and Solochrome Black T (Fig. 7.7) at different concentrations. The electronic spectrum of Eosin B exhibits $\lambda_{\text{max}}$ at 532 nm (Fig. 7.5), which is red shifted and broadened when adsorbed on Cu-ZnO film in comparison with that of the other two dyes (Fig. 7.6 and 7.7). The $\lambda_{\text{max}}$ of Fast Sulphon Black F (FSF) and Solochrome Black T (SBT) are about 617 and 501 nm, respectively. The use of dyes, whether organic or inorganic complexes in DSSCs, raises some concern with regard to the long-term photostability. One of the ideas that are currently being
investigated is the use of inorganic semiconductor nanoparticles, such as Cu-ZnO, dye as a sensitizer. Its optical absorption can be modulated over a wide spectral range by sensitizing with dyes. There are two main ways in which the efficiency of DSSCs can be improved: extend the light-harvesting region into the visible region (Vis), and lowering the redox potential of the electrolyte to increase $V_{OC}$ (open circuit potential). One of the major factors that contribute to the high-energy conversion efficiency in DSSCs is generally attributed to the ultra-fast electron injection from dye to the Cu-ZnO conduction band and a much slower reverse process. The dynamics of electron injection at the dye-Cu-ZnO interface has been the subject of considerable recent investigations. Moreover, the absorption strength and the photogenerated carrier lifetime can be enhanced significantly. Some preliminary measurements at the band edge show that the sensitization of dyes on Cu-ZnO nanoparticles decreases the absorption edge for some extent. This implies that electrons are being transferred to the Cu-ZnO nanoparticles. The electron transfer process appears to saturate once a certain concentration ratio of dye is reached. The increase of absorption spectrum from 400 - 630 nm may be due to the change of energy level for the Cd-ZnO [48] and the shift is due to the change in the energy of the lowest unoccupied molecular orbital (LUMO) of the dye. Red-shift is also reliable with the decreased band gap of the adsorbed Eosin B compared to that of free Eosin B solution. The results exhibits Eosin B shows good light response compare to Azo-dyes. The difference in the absorption peak is due to the binding of Eosin B to the oxide surface and electron injection from exited state of dye to conduction band of semiconductors [13]. This difference, however, was not found in the case of FSF and SBT.
Results and Discussions

Chapter 7

320 400 480 560 640
Wavelength (\(\lambda\))

Figure 7.6: The optical absorption spectra of Cd-ZnO films before and after sensitization with Fast Sulphon Black F (FSF).

[Graph showing absorption spectra]

Figure 7.7: The optical absorption spectra of Cd-ZnO films before and after sensitization with Solochrome Black T (SBT).

[Graph showing absorption spectra]
7.6 CONCLUSION

➢ In summary, hexagonal undoped and Cd-doped ZnO nanoparticles have been synthesized using PEG 400 as surfactant. The effect of annealing temperature on the structure and optical properties were studied.

➢ The intensity of peaks was increased with increase in temperature. With increase in the annealing temperature the optical band gap edge shifts towards longer wavelength.

➢ The lattice parameters for undoped and doped ZnO nanoparticles were calculated from the XRD data. The lattice constants $a$ and $c$ have been changed.

➢ The Cd doping and degree of crystallinity are the probable causes for the band gap difference. The changes of the optical band gap of Cd doped samples were due to the change of crystallinity at higher temperature.

➢ As an electrode in DSSC, Cd-ZnO can improve the absorption of visible light (400 - 630 nm) and increase electrons injection from Eosin B to the conduction band of Cd-ZnO, resulting in the enhancement of efficiency for dye-sensitized solar cell.
REFERENCES