SYNTHESIS OF CdO-ZnO NANOCOMPOSITES PARTICLES BY SOL-GEL METHOD

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ABSTRACT

Cadmium Oxide-Zinc Oxide (CdO-ZnO) nanoparticles powder have been synthesized by sol-gel method. The samples were characterized by X-ray diffraction, UV-Visible absorption and scanning electron Microscopy SEM. The X-ray analysis shows that the obtained powder is polycrystalline and the crystalline size in the range of 8-23nm. The SEM micrographs show particles with spherical shape. The optical band gap values of CdO-ZnO nanoparticles were calculated to be about 2.99eV -3.10 eV in the temperature 600^0 C, comparing with that of the bulk ZnO 3.37eV, by optical absorption measurement.

INTRODUCTION

The synthesis of nano structures of semiconductors in a nano powder form has been a rapidly growing area of research due to their important optical, physical and chemical properties [1].

Nanostructures based on zinc oxide and cadmium oxide are particularly interesting because of their n-type conductivity which makes these materials more suitable for modern technologies. ZnO and CdO have promising applications in catalysis, gas sensors, solar cells, paint pigments [2] etc. Zinc Oxide (ZnO) has a wide direct band gap (3.37eV) and a relatively large excitation binding energy (60MeV) compared to thermal energy (26MeV) [3]. It is also known to be a II-VI semiconductor; because Zn belongs to group II while O_2 belong to group VI in the periodic table. ZnO is a first metal oxide to be used as chemical sensors. Modifying it with CdO in a composite growth will significantly improve its sensing capability [4] for CO, NO, and CH_4 as reported by Ferro et al [5,12]. Cadmium oxide (CdO) is a well known semi conductor which has a direct band gap of 2.3 eV and indirect band gap of 1.98eV [6]. The composite growth of the two semiconductor oxides would reduce the band gap of ZnO, and could help to prevent the electron-hole recombination, enhance the absorption of solar light and increase the photocatalytic activity of ZnO [7,14]. Reduction in band gap reduces the distance between the

conduction band and the valence band making it easier for electrons to access conduction band. The generation of charge carriers is the basis of photovoltaic production of energy. The formation of composites of CdO and ZnO is an efficient band gap narrowing technique because of the narrow band gap in CdO (2.3eV) as compared to ZnO (3.37eV) [6]. The growth of ZnO-CdO composites produces a supper lattice which is a characteristic of ZnO based light emitters and detectors. In this present study, we demonstrate a simple chemical method (sol-gel) for synthesis of CdO-ZnO nanocomposites nanoparticles.

Experimental Work

The ZnO-CdO nanocomposites were synthesized by using sol-gel method. Zinc acetate and cadmium acetate were used as sources of zinc and cadmium respectively. The gel solution was prepared by dissolving varied weights (varied between 0.5-4.0g) of $Zn(CH_3COO)_2$ and $Cd(CH_3COO)_2$ respectively, in a mixture of 40 ml ethanol and water respectively in a 250 ml beaker under constant stirring for 8 minutes. To this solution, 6g of polyvinyl alcohol (PVA) was added under constant stirring until a clear homogenous transparent viscous solution was obtained. Water and ethanol served as solvents and polyvinyl alcohol (PVA) was used to make the gel network rigid where the dispersed ions cannot alter their positions. The solution was heated at 353K in an oven to evaporate the solvent and obtained a homogenous gel. The gel was then transferred into a furnace pan and annealed at 873K for 7 hours. During the pyrolysis process, the PVA polymeric network was slowly burnt through the outer surface to form CdO-ZnO nanocomposites nanocrystals. The obtained samples were crushed to prepare a fine powder.

Results and Discussion

X-ray diffraction (XRD) Studies of CdO-ZnO

X-ray diffraction technique is used for the determination of crystal structure and lattice parameters along with structural changes and identification of phases of the prepared particles.

Fig. 1 depicts the XRD of the CdO-ZnO composite nano particles synthesized for different concentrations and annealed at 873 K using Cadmium acetate and Zinc acetate as precursors. The XRD measurements were carried out using a *Philip PW1830* x-ray diffractometer with *CuKα* radiation (*λ=1.5406*) in the range 20 to 80^{o} in 2θ.

It was observed that all the samples were polycrystalline with peaks of ZnO identified, having hexagonal wurtzite structure with lattice constants *a = 3.24982* and *c = 5.20661* corresponding to those of the ZnO patterns from the JCPDS data card (powder Diffraction file card No. 00-036 – 1451). On the other hand, CdO peaks were also identified in the samples having cubic sodium chloride (NaCl) rock-salt structure, with octahedral cation and anion centers rocksalt cubic structure and lattice constant *a = 4.675*.

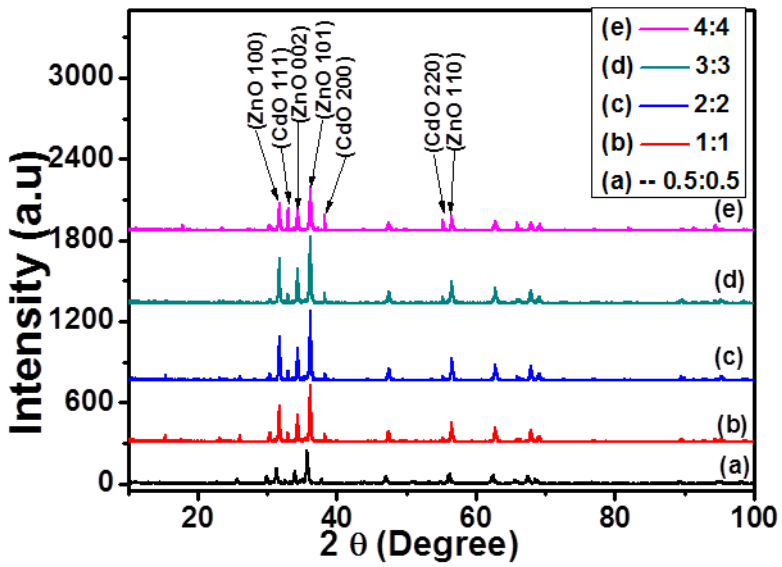

Fig.1 XRD of CdO-ZnO nanocomposites from cadmium acetate and zinc acetate for different masses

From XRD patterns, it is clear that the ZnO peaks showed strong preferential growth of high intensities in the (101) crystal plane for all the samples. However, other orientations corresponding to (002) (100) (102) at corresponding 2θ values of 36.3, 34.4, 31.8, 47.6

respectively are present with very low relative intensities compared with (101) plane. The strong diffraction peaks for CdO, Fig. 1 were seen at 2θ values of 33.1, 38.4, 55.1, 65.8,corresponding to the (111), (200), (220), and planes which can be index to cubic pattern of CdO (JCPDS card No. 65 – 2908). The diffraction peaks of ZnO and CdO were randomly distributed indicating a uniform composite growth of the particles. Average particle sizes (D) were estimated along the most prominent diffraction peaks using Debye-Scherrer (Eqn. 1)

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad 1$$

where θ is Braggs diffraction angle K is a constant (0.94), λ is the X-ray wavelength (λ = 1.54056), and β is full width at half maximum (FWHM).. The estimated average particle sizes of ZnO and CdO nanoparticles were found to be in the range of 8 to 24 nm. No characteristic peaks for other impurities were detected, confirming that the products obtained are phase pure.

It was observed that the estimated crystallite sizes of CdO-ZnO prepared showed strong response to precursor concentration, increasing with increasing concentration. However, a gradual decrease in crystallite sizes was observed after the 2.0 g mass ratio which later appeared almost constant as the concentration was increased to 4.0 g. This may be assigned to agglomeration of particles during growth process as the concentration was increased. However at higher concentrations, the ionic congestion at the interface might have introduced some crystallographic defects which lower the crystalline quality of the particle as observed [8]. According to Li-Jing et al [9] uncontrolled agglomeration can offset nano effects to a certain extent. Karami [4] also stated that the optimum condition for synthesis of uniform nanostructured CdO/ZnO composite with high response slope and wide dynamic range for sensors application will be at 2 g weight of the precursors. Fig. 2 and Table 1 show the variation of crystallite size with mass of CdO-ZnO nanocomposites.

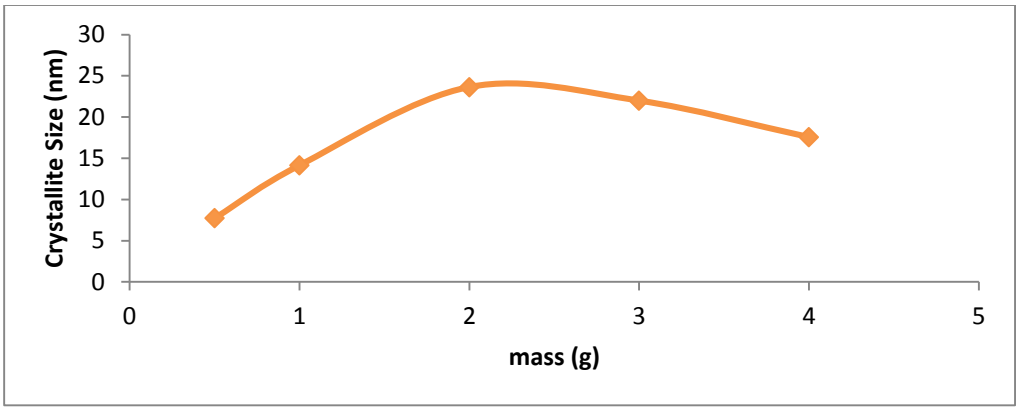

Fig. 2 Variation of crystallite size (nm) with mass (g)

Concentration (g)	Size (nm)
0.5	7.73
1.0	14.14
2.0	23.63
3.0	21.98
4.0	17.56

Table 1 Variation of mass with Crystallite size for Cadmium acetate and Zinc acetate precursors.

The average highest intensity of the peaks was also observed at 2.0g of the calcined products. It was also noted that the growth in cadmium acetate and zinc acetate has a bigger crystallite size than the growth with cadmium nitrate and zinc nitrate.

Surface Morphology

The surface morphology of the synthesized dried powder was studied using SEM as illustrated in Fig. 3The CdO-ZnO nanocomposites synthesized using cadmium acetate and zinc acetate show the micrographs of the particles with spherical shape for 0.5g concentration. The micrographs of the concentration at 1.0g show regular spherical shape. The image shows spherical of coupled semiconductor along with more pronounce spherical shape particles at the concentration of 2.0g. The morphology of the spherical aggregated in chain-like at 3.0g and 4.0g with more

agglomerations at 4.0g. It is observed that in each case the micrographs at 2.0g have particles with randomly distributed spherical shape could be an optimal concentration for gas sensing.

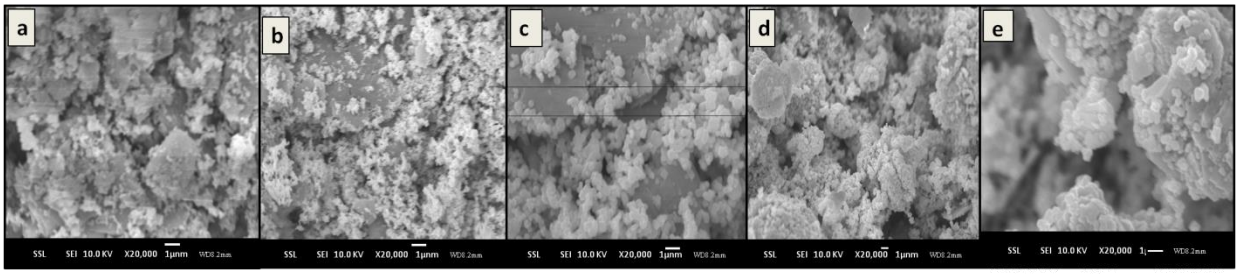

Fig. 3 Shows SEM micrograph of CdO -ZnO at different mass ratios prepared from Cadmium acetate and Zinc acetate precursors (a) [0.5:0.5]g (b) [1:1]g (c) [2:2]g (d) [3:3]g (e) [4:4]g

4.5 Optical Studies

Optical studies of the nanocomposites were carried out using diffuse reflectance spectrometer operating at a wavelength range of 200nm to 800nm using a UV–VIS-NIR scanning spectrometer (Lamda 750, Perkin Elmer). UV-Vis Diffuse reflectance (UV-DR) studies, performed at room temperature (RT), have been employed to know the optical properties of the CdO-ZnO nanocomposites. To obtain E_g from UV-Vis absorption spectroscopy in dispersed samples, the Kubelka-Munk equation was used in finding the band gaps. The Kubelka-Munk equation is expressed as follows (2) [5,10,13]

$$f(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} \qquad 2$$

Where: **R** is the absolute reflectance of the sampled layer, **k** is the molar absorption coefficient and **s** is the scattering coefficient. Diffuse reflectance spectra of the samples are shown in Fig 4 (a-e). The reflectance spectra show a strong decrease after some certain wavelengths for the

different samples i.e. (a) 325nm (b) 360m (c) 370nm (d) 350nm (e) 360nm from the synthesis using cadmium acetate and zinc acetate precursors. This decrease is related to optical transitions occurring in the optical band gap.

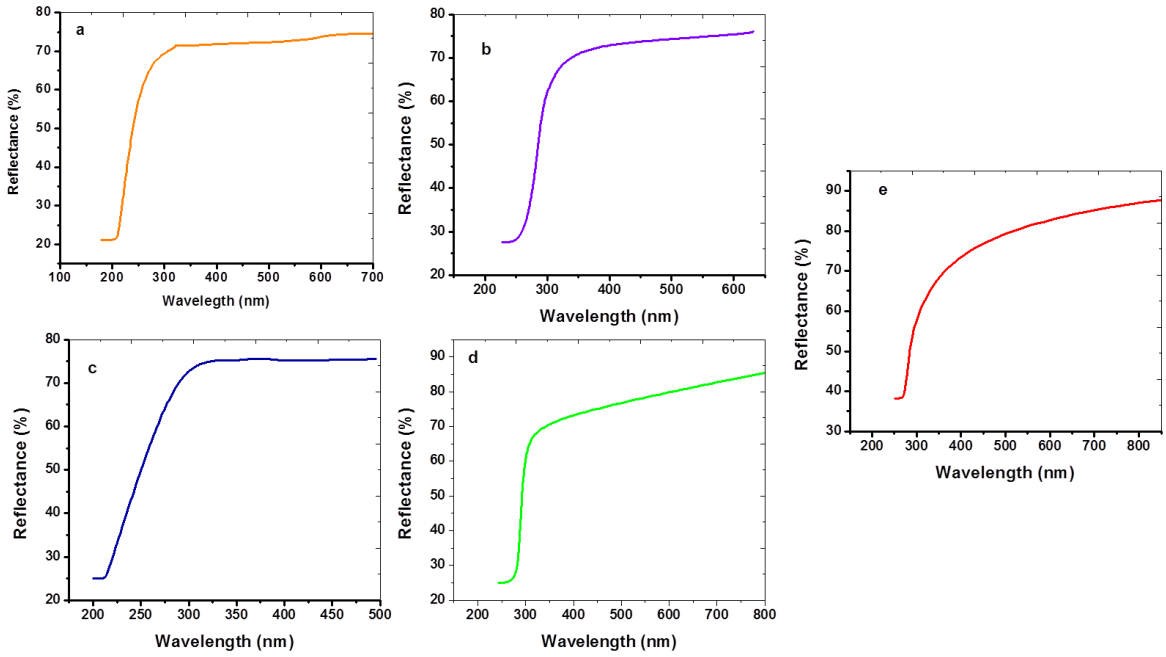

Fig 4 Reflectance spectra of CdO-ZnO composites synthesized from cadmium acetate and Zinc acetate for different mass ratios

The Kubelka-Munk theory is generally used for the analysis of diffuse reflectance spectra obtained from weakly absorbing samples, where F(R) is the Kubelka-Munk function which corresponds to the absorbance, R is the reflectance, K is the absorption coefficient, and S is the scattering coefficient thus we have [5,13]

$$(k/s * h\nu)^n = A(h\nu - E_g) \qquad 3$$

Where **A** is an energy-independent constant, $\mathbf{E_g}$ is the optical bandgap, and **n** is a constant which determines the type of optical transitions: for indirect allowed transition, n = 2 for direct allowed transition, n = 1/2.

The intersection between the linear fit and the photon energy axis gives the value to *Eg*. The calculated band gap values are indicated in Fig.5. Band gap values obtained from synthesis using cadmium acetate and zinc acetate are (a) 3.10eV, (b) 3.09eV, (c) 2.99eV, (d) 3.04eV, (e) 3.09eV for the different mass ratio used.

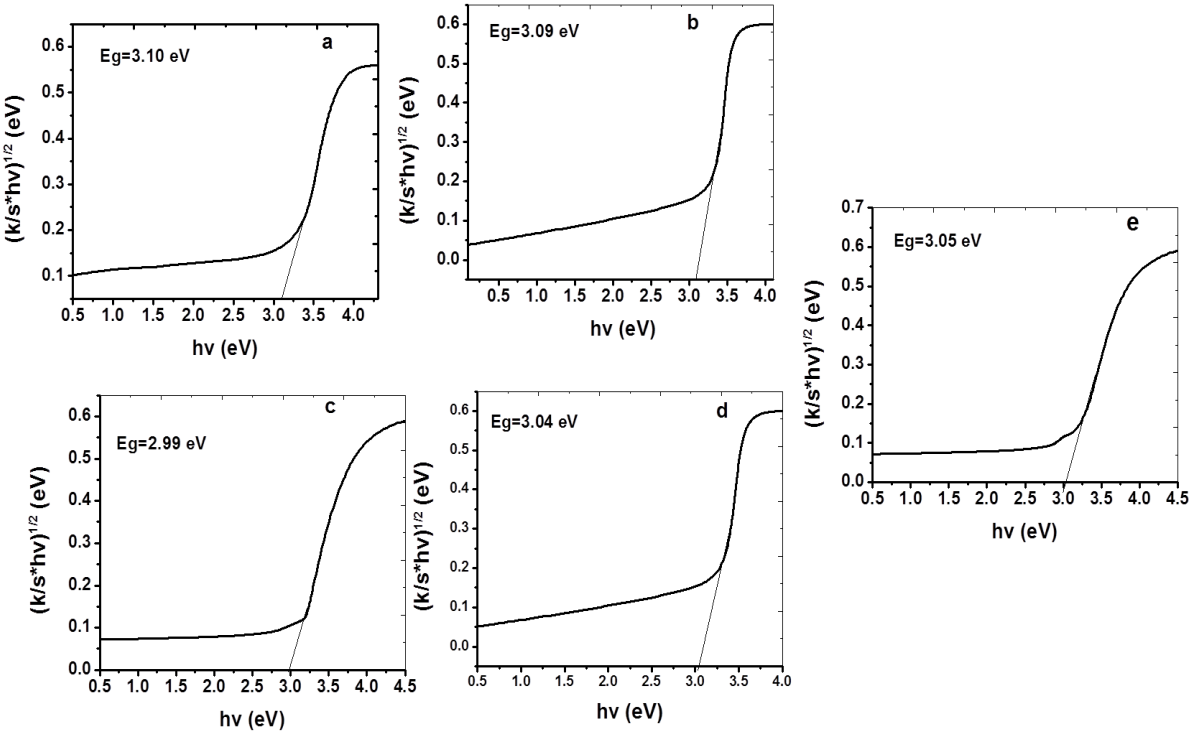

Fig. 5 Kubelka-Munk transformed reflectance spectra of ZnO and CdO-ZnO nanoparticles showing their band gap from cadmium acetate and zinc acetate

Conclusion

CdO-ZnO nanoparticles have been successfully synthesized by simple Sol-Gel method. The prepared ZnO nanoparticles were spherical in shape and were characterized using XRD, UV-Vis absorption and SEM techniques. The average particle size was found to be 9-24nm using Scherrer's equation. CdO-ZnO nanoparticales offer tremendous potential in future applications of electronic and magneto–electric devices. It may also be, applied for photocatalysis, gas sensing, biomedical device and sun screen applications. The method has a high yield and can be used for large scale synthesis of CdO-ZnO nano particles [11]

Phototalytic nanomaterials such as CdO-ZnO allow ultraviolet light to destroy pesticides, industrial solvents and germ, thus, they can be used for antibacterial activity and for water treatment. They can also be used for degradation of organic contaminants, gas sensors and in electronic

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