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Effect of Cadmium Sulfide and Zinc Oxide Nanoparticles for Oxygen Sensor Applications

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ABSTRACT: *Zinc (ZnO) doped cadmium sulfide (CdS) nanoparticles were synthesized by chemical precipitation method. Structural, morphological and optical properties of ZnO/CdS nanoparticles were evaluated through comprehensive characterization technique.The XRD pattern identified that nature of hexagonal structure for ZnO doped CdS. ZnO doped CdS lead to decrease the crystallite size in the range of 2-1.4 nm. UV-VIS absorption spectra for the ZnO/CdS reveals that the optical absorption increases (370-390 nm) and corresponding optical energy band gap(3.35 to 3.17eV). The surface morphology of ZnO/CdS nanoparticles showed the compact nanocrystalline structure. Electrochemical impedance spectroscopy studies showed that the charge transfer resistance is lowered as annealing temperature at 573 K.*

Keywords: *Bandgap,Chemical precipitation method, Nanoparticle,TEM, XRD.*

I. INTRODUCTION

Semiconductor nano particles have attracted great interest in both theoretical research and technological applications. Size dependence of band gap in these nano particles is due to quantum confinement effect [1].The effect of high large surface on nano particles results high adsorption capacity and catalytic activity. Size-dependent nanoscale properties and its potential application were employed in different fields like non-linear optics, photo electrochemical cells, heterogeneous photo catalysis, optical switching and single electron transistors [2]**.**

However, the size distribution and the crystallinity of nano particles are generally poor because of low synthetic temperature and surface detects. Recently, many articles have introduced advanced low-temperature synthesis and colloidal growth. In order to yield quantum dots nano crystal with a sufficiently narrow size distribution and a facile annealing process is introduced to enhance the quantum efficiency [3].Several authors have prepared CdS with different (F, Pt, Pb, Zn, Al, Co, In, Sn, etc.) elements to meet several applications such as thin film solar cells, electrochemical cells and gas sensor. These semiconductors offer a great opportunity to integrate the magnetic, electrical and optical advantages when compared to a single semiconductor material [4].

Cadmium Sulfide (CdS) is one of the widely studied materials [5]**.** It is a group II-VI semiconductor with wide band gap energy of 2.4 eV and is widely investigated in important applications including electroluminescent, non linear optical devices, flat-panel displays and doping LED. Many studies have focused on CdS nanoparticles with different nano structure such as nanoparticles, nanowires and nanobelts [6].In 20th century, few reports are available in the literature on cubic to hexagonal phase transformation in CdS.CdS generally shows dimorphism of (i) zinc blende type (cubic form) and wurtzite type(hexagonal form)at relativelylow temperatures, and (ii) Wurtzite type at relatively high temperatures. The complete transformation has been observed from cubic to hexagonal phase around 873 K [7].

ZnO is II–VI semiconductor with a band gap 3.37 eV and high exciton binding energy 60 meV and it attracted applications, such as a transparent conductive contact, thin-film gas sensor, varistor, solar cell, luminescent material, surface electro acoustic wave device, heterojunction laser diode and UV laser. The integration of various semiconductors such as Cadmium Sulfide (CdS) and Zinc Oxide (ZnO) continued to show promising developing technologies ranging from senor to photovoltaic's device [8]**.** In order to enhance the photocatalytic activity of ZnO under visible light, it was combined with visible sensitizers such as CdS, CdO and CdTe. Among these sensitizers, CdS–ZnO heterojunction facilitated interband charge transfer from CdS to ZnO. The observed lifetime of the photo generated carriers in ZnO/CdS nano composite was higher than pure ZnO or CdS [9].

Recently, transition metal ions-doped II-VI nanoparticles have attracted keen interest because transition metal ions were incorporated into II-VI nanoparticles among researcher which improved the optical properties of nanoparticles. Many efforts were made on equal valence charge doping, for example, transition metals

Zn[10]**.** This study focused on the synthesis of ZnO doped CdS. The structural, optical and morphological of these materials were investigated as a function of annealing temperature.

II. EXPERIMENTAL

In the present study, cadmium sulfate ($CdSO_4$; Sigma Aldrich; (AR), sodium sulfide (Na_2SxH_2O; LobaChemie, Mumbai, India), zinc acetate (Zn $(CH_3COO)_2$. H_2O; LobaChemie, Mumbai, India) and de-ionized water were used to prepare ZnO/CdS nanoparticles without any further purification.

ZnO-doped CdS nanoparticles were prepared by the chemical precipitation method at room temperature using cadmium sulfate ($CdSO_4$), zinc acetate (Zn $(CH_3COO)_2.H_2O$ and sodium sulfide (Na_2S). Initially, 0.1 M of cadmium sulfate ($CdSO_4$) and 0.1 M of sodium sulphide (Na_2S) was dissolved directly in 25 ml of de-ionized water at room temperature and stirred for 10 min. Then, both solutions were mixed slowly under constant stirring for 20 min. Then, 0.1 M of Zinc Acetate ($C_4H_6O_4Zn.2H_2O$) solution was prepared and added slowly dropwise to Cd-S mixed solution under stirring and yellow colour wet precipitation was obtained instantly. The obtained precipitation was dried in hot air oven at 373 K for 48 h. Finally, yellow colouredZnO/CdSnano powders were obtained and the powder samples were annealed at 573 K for 1 h.

III. CHARACTERISATION

The structural properties of the CdS sample was determined by X-ray diffractometer (XRD, X'Pert Pro; PANalytical, Netherlands) using Cu Kα as a radiation source (λ=1·5406 Å) which operated at 30 kV and 15 mA. The samples were scanned in the (2θ) range from 10 to 80°. The average crystallite sizes of all the samples were calculated from 2θ position of FWHM by Scherrer's formula.The optical properties of the prepared thin films were determined based on their optical spectra, obtained using a UV-visible spectrometer (V-570; JASCO, Japan) in the wavelength range from 200-900 nm. X-ray fluorescence spectrometry (XRF, EDX-720, and Shimadzu, Japan) was employed to identify the concentration of the elements presented in nano powder by using qualitative and quantitative measurements.The surface morphology of CdS nano particles was inspected using a scanning electron microscope (SEM, JSM-6390LV; JEOL, Tokyo, Japan) with an accelerating voltage of 20 kV. Electrochemical impedance spectroscopy (EIS) measurements were performed using MetrohmAutolab (PGSTAT302, The Netherlands) at room temperature. The sample powders obtained from the earlier-mentioned synthesis processes was employed to prepare pellets (i.e., a pellet of 10 mm diameter and 2 mm thickness) using a uniaxial pressure (Hydraulic pellet press, SRNO 833) at 20 MPa. The pellets were heated at 373 K for 2 h to decompose the in-between compounds and tested at room temperature for constant level of relative humidity.The TEM (CM200; Philips, USA) was operated at 120 kV and provided information about the individual nanoparticles up to high magnitude of 1,000,000X with a better resolution of less than 1 nm.

IV. RESULTS AND DISCUSSION

The X-ray diffraction pattern for ZnO/CdS nanoparticles is shown in Fig. 1. The diffraction peaks at 31.68°, 34.59°, 36.66° and 56.6° corresponding to hexagonal phase structure of ZnO. The lattice parameters was calculated and found to be a = 3.249Å and c = 5.206 Å [JCPDS No. 36-1451]. Further, peak position was observed at 24.96°, 26.49°, 28.20°, 36.66° and 43.82° and it exhibited hexagonal phase of CdS. The lattice parameter was a = 4.140Å and c = 6.71 Å [JCPDS No. 41-1049]. It was clear from XRD patterns that exhibited peak related to (100), (101), (102) and (110) reflections of the hexagonal structure at room temperature [11]**.**Whereas the particles annealed at 573 K exhibited the main peak (002) crystal plane as the preferential orientation and intensity influenced strong annealing temperature.

Further, it was found that the average crystallite size decreases in the annealing temperature at 573K for ZnO/CdS nanoparticles. The average crystallite size (D) was found to be within the range of 2-1.4nm (Table. 1). ZnO-doped CdS annealing temperature which grain size decreased slightly when compared to the pure ZnO/CdS nanoparticles [10, 12].

Table. 1. The ZnO/CdS nanoparticles of Wave length (nm) and Energy band gap (eV).

S.No	Samples	Grain size from XRD (nm)	Wave length (nm)	Energy Bandgap (eV)
1.	ZnO/CdS- As-prepared	2.0	370	3.35
2.	ZnO/CdS-573 K	1.4	390	3.17

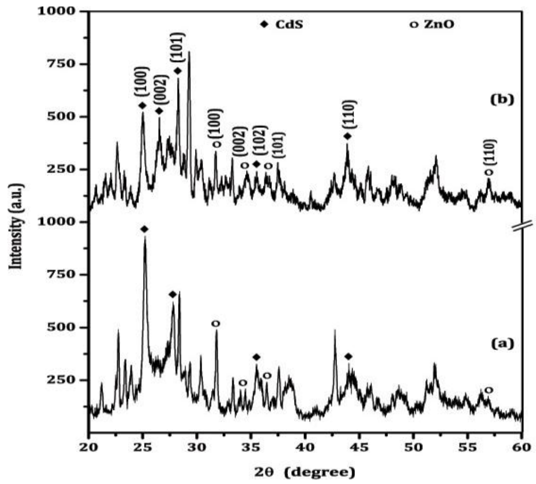


Fig. 1. XRD pattern of ZnO/CdS nanoparticlesa) ZnO/ CdS - As prepared, b) ZnO/ CdS - 573 K

UV-Vis absorbance spectrum of ZnO/CdS powder is show in Fig. 2. A strong peak was observed at 370 and 390 nm (Fig. 2(a) and Fig. 2(b)) due to annealing temperature at 573 K.It revealed that, during annealing, the absorption edge undergoes a slight shift towards the higher wavelengths. ZnO/CdS only absorbed the light of the wavelength less than ≈ 400 nm corresponding to grain size of ≈ 2 nm. It was expected that doping with ZnO reduced the nanoparticle size. However, ZnO/CdS nanoparticles increased with annealing temperature in the light absorption to visible-light region. [10,11].Optical band gap was calculated through the absorption coefficient which signifies the blue shift in direct band gap from 3.35 to 3.17 eV respectively (Table. 1) [13]. Theoptical band gap was calculated using the Maxplank energy equation [14].The particle sizes got decreased by increasing the band gap values due to the quantum size effect [15].

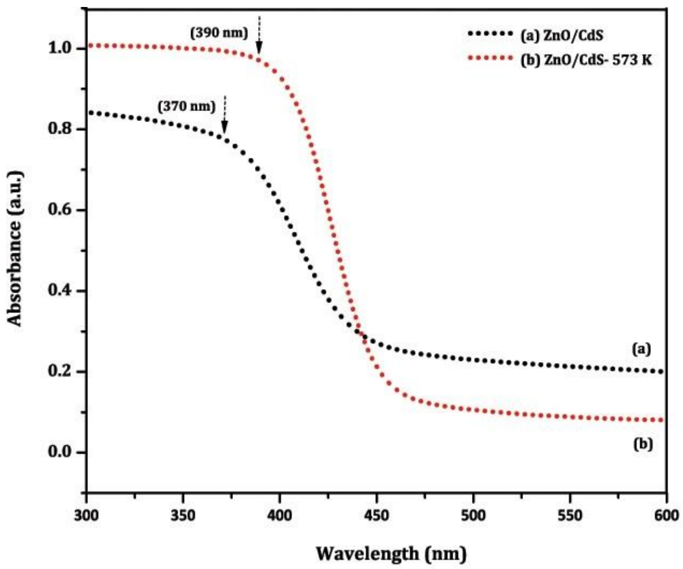


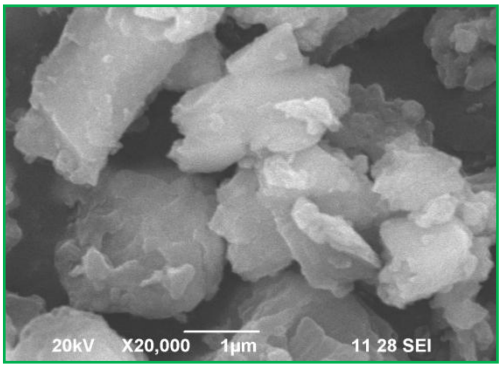
Fig. 2. Optical absorption spectra of ZnO/CdS nanoparticles

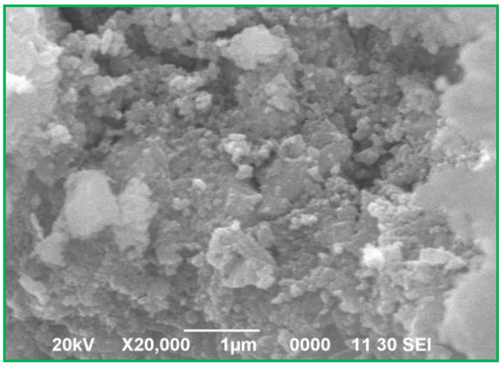
Table 2 shows XRF measurements for ZnO/CdSnanopowder and the presence of Cadmium (Cd), Zinc (Zn) and Sulfur (S) before and after annealing temperature along with trace element is confirmed.

Table. 2. XRF chemical analysis for ZnO/CdS nanoparticle

ZnO/CdS As -prepared		**ZnO/CdS - 573 K**	
Elements	***Weight %***	***Elements***	***Weight %***
Cd	54.17	Cd	69.176
S	22.853	S	15.333
Zn	20.423	Zn	13.769
K	2.499	K	1.722
Cu	0.055		

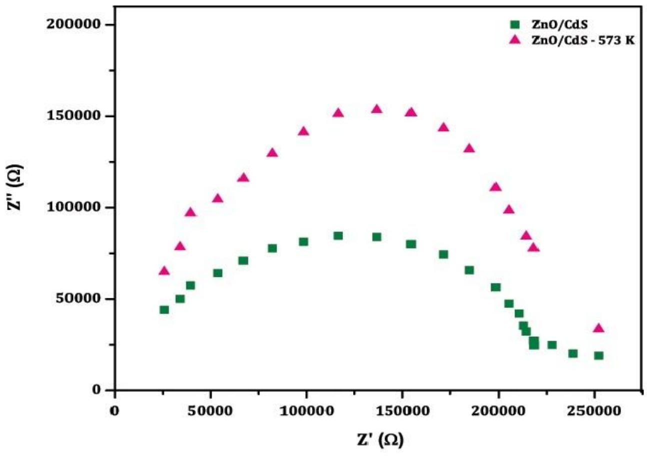
The surface morphology of ZnO/CdS nanoparticle isshownin Fig.3. It clearly indicates that the formation of aggregate nano clusters surface morphology of ZnO-CdS nanoparticles is similar to that of CdS [15].





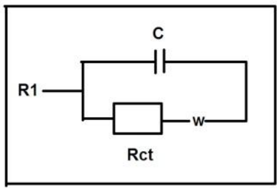
(a) ZnO / CdS - As prepared (b) ZnO/ CdS -573 K

Fig. 3. SEM image for ZnO/CdS nanoparticles



a)

The electro chemical impedance spectroscopy was efficient tool for the investigation of surface modified electrodes. Fig. 4 (a) shows the impedance Nyquist plots and its equivalent circuit for annealing temperature. The observed semicircle shaped curve at high frequency shows a characteristic an interfacial electron transfer. The diameter of semicircle was establish to be increased in the order of ZnO/CdS(As prepared) >ZnO/CdS–573K, these results signifying that low charge transfer resistance in the same order. This behavior mainly controlled by the interfacial electron transfer within the entire range of the applied frequencies. The impedance spectra was analyzed by using an equivalent circuit, the charge transfer resistance (R_{ct}), solution resistance (R_s), capacitance (C) and Warburg impedance (W) showed in Fig. 4 (b).



b)

Fig. 4. Electrochemical impedance analysis of ZnO/CdS nanoparticles

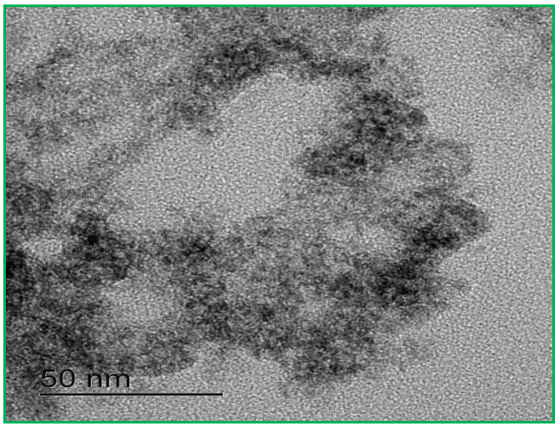
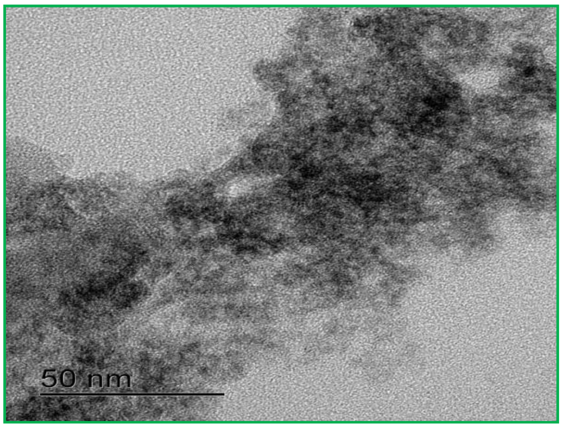


Fig. 5 (a) and (b) shows TEM images for as prepared and annealing temperature showed that it occurs mostly in spherical shape with narrow size distribution. The primary particle size and morphology were also obtained from TEM image.



(a) ZnO/CdS-As Prepared (b) ZnO/CdS – 573 K

Fig. 5. TEM images of the ZnO/CdS nanoparticles

V. CONCLUSION

ZnO/CdS nanoparticles have been prepared by chemical precipitation method.The structural characterization of ZnO doped CdS were carried out through XRD, UV-Vis studies. The synthesized ZnO/CdS nanostructure revealed hexagonal structure and their evaluated average crystallite size was 2-1.4 nm with an increase in bandgap from 3.35 to 3.17 eV at annealing temperature 573 K.It was found that doping with ZnO reduced the nanoparticle size. This revealed that strong quantum confinement effect was present in the prepared ZnO/CdS nanoparticles.

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