Structural and Optical Characterization of CdO-ZnO Nanocomposites Deposited by Sol-Gel Method

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Abstract - *CdO-ZnO Nanocomposites thin films were synthesized by sol-gel method, using their respective acetates at 70°C. Samples were then characterized using; X-ray diffraction, scanning electron microscope and energy dispersive X-ray. XRD results confirmed the formation of CdO-ZnO nanoparticles. SEM images showed that pure ZnO nanoparticles have diameter in the range of ~90nm, pure CdO in range of ~80nm and the CdO coated ZnO nanoparticles in the range of ~140nm. The elemental analysis showed the stoichiometry composition of the samples. UV-Vis spectroscopy was done to get the optical properties of the nanoparticles. Fourier transform Infrared spectroscopy (FTIR) was performed to study the formation and reaction of –OH groups in the prepared samples*.

Key Words: Sol gel method, CdO-ZnO composite, Nanoparticles.

1.INTRODUCTION

Currently semiconductor materials are very popular in research activities across the world. The semiconductor particles have shown to exhibit size-dependent properties such as the scaling of their energy gap coupled with corresponding changes in the optical properties, moreover are considered as the front runners in the technologically important materials [1]. Nanostructured materials have received much attention in research because of their novel properties, which differ from those of their bulk materials [1]. Zinc Oxide (ZnO) is one of the few dominant nanomaterials for nanotechnology. ZnO has a wide direct band gap (3.37eV) [2] and relative large excitation binding energy (60 meV) compared to thermal energy (26meV) [2]. A wide band gap has many benefits like enabling high temperature and power operations, reducing electronic noise, making sustenance in large electric fields possible and raising breakdown voltages. By proper alloying with MgO or CdO, the band gap can be tuned in the range of 3-4 eV [3]. ZnO is also called as II-VI semiconductor, because Zn belongs to II group, and O_2 belongs to VI group in the periodic table. ZnO exhibits the most splendid and abundant configurations of nanostructures [4] that one material can form, due to its unique properties and potential for application in solar cells. ZnO is applied in electronic and photo-luminescence devices, chemical sensors and several other applications. ZnO has a hierarchical structure which is known for the high surface to volume ratio, they are of great physical or chemical importance in gas-sensor and photo-catalysis [4].

Zinc oxide has received much attention because of its unique piezoelectric properties which is suitable for surface acoustic wave devices, optical fibers and opto- electronic devices. Due to the high optical band gap [5, 6] ZnO films have been used as window layers in copper indium diselenide based hetero junction solar cells to enhance the short circuit current [7]. Another important advantage of ZnO is its chemical stability in the presence of hydrogen plasma which is applied in amorphous silicon solar cell fabrication by plasma enhanced chemical vapor deposition [4].

Cadmium oxide is a well-known II-VI semiconductor with a direct band gap of 2.2eV (520nm) and has developed various applications such as its use in solar cells, transparent electrodes, photodiodes, and sensors [8]. There are numerous reported methods for the preparation of the CdO nanoparticles, but most of these methods only describe the film formation of CdO. The synthesis of the particles as a free standing powder is yet to be extensively done [9]. Researchers have reported formation of nanobelts at high temperature from a number of metal oxides, like CdO [10], CdO nanowires [11]. Recently, the formation of CdO nanoparticles using thermal treatment of cadmium acetate has been described [11]. Coupling of different semiconductor oxides can reduce the band gap, extending the absorbance range to visible region leading to electron-hole pair separation under irradiation and consequently, achieving a higher photocatalytic activity among various elements [8]. Cadmium (Cd) incorporation into ZnO serves the purpose of band gap narrowing efficiently because of the smaller band gap of CdO as compared to ZnO. Further, the low dimensional structures of ZnO-CdO also show very good gas sensing properties and increased conductivity due to their high surface to volume ratio [11, 12].

The main aim of the study was to synthesize Pure ZnO, CdO and CdO coated ZnO nanoparticles using sol-gel method and to characterize them using XRD, EDX, SEM, FTIR and UV-Vis Spectrophotometer. The study provides knowledge on understanding crystal structure of the semiconductor particles which exhibit size-dependent properties like tuning of the energy gap and corresponding change in the optical properties.

2. Materials and Methods

The chemical reagents used in this work were Zinc acetate dihydrate, Cadmium acetate dihydrate, ethanol, mono ethanol amine and distilled water. All reagents were analytical grade and used as supplied.

2.1 Synthesis of ZnO

The ZnO nanoparticles were prepared by dissolving 100 ml of 0.2M Zinc acetate dihydrate in 200ml ethanol. This solution was stirred vigorously at 70^{o}C for 12 hours by a magnetic stirrer. The precipitate obtained was filtered and washed thoroughly with deionized water. The precipitate was dried in an oven at 100^{0}C and ground to a fine powder using motor (4). The powder obtained was calcined at 500^{0}C for 4 hours.

2.2 Synthesis of CdO

0.1M $CdCl_2$ (20ml) was dissolved in 0.1M NaOH (100ml) stirred continuously for 3 hours, precipitation was done and the precipitate was washed in methanol then allowed to dry. Calcium hydroxide was formed which was heated in an oven at 250^{0}C for 5 hours to get CdO [8].

2.3 ZnO-CdO nanocomposites

The synthesized ZnO and CdO nanoparticles were mixed at varying ratios for the study

2.4 Characterization

The morphological study was carried out by Scanning electron microscopy (SEM) on a ZEISS EVO 18 equipment. The chemical composition of samples was analyzed through an energy dispersive x-ray (EDX) spectrometer attached to the SEM equipment. Structural characterization of the nanoparticles was examined by X-Ray diffraction (XRD) using a Philips Diffractometer (40KV, Cu K_α radiation with λ =1.5406A^o). Molecular analysis was done by FTIR spectroscopy. Optical characterization was done using a Perkin Elma Lambda 35 UV-VIS spectrophotometer equipped with an integrating sphere.

3. Results and Discussion

3.1 Structural properties

Figure 1 shows an XRD spectrum of pure ZnO and CdO nanoparticles, showing the respective peaks. The peaks for ZnO nanoparticles indicate a hexagonal wurtzite structure from standard JCPDS files [13]. From the XRD data it can be confirmed that, pure ZnO and CdO nanoparticles are in single phases. These results were in agreement with results obtained in ref [5] and [13]. XRD was done for checking the phase formation, and crystallite size.

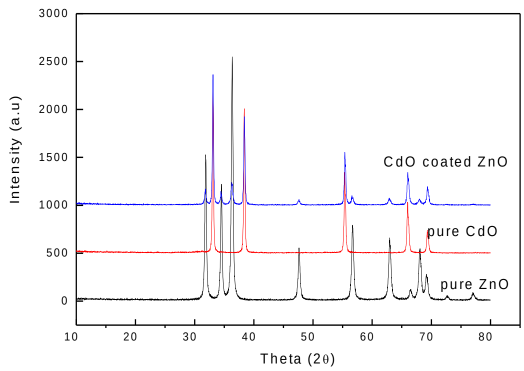
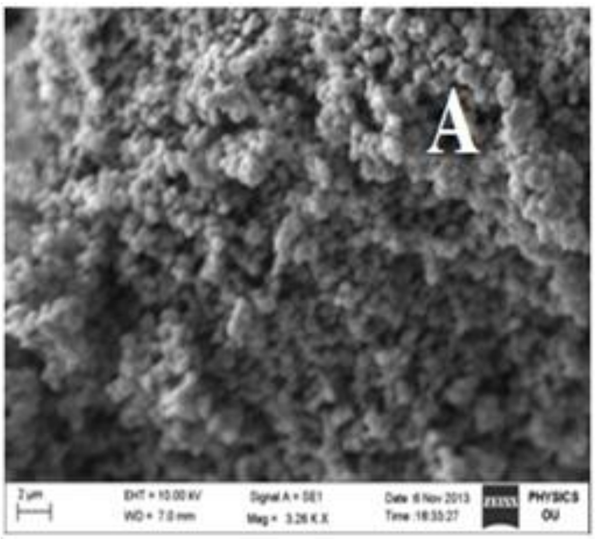


Fig. 1 XRD spectrum of the pure ZnO, CdO and CdO-ZnO composite

From the diffraction patterns it was seen that, most peaks observed are matching with hexagonal wurtzite structure of ZnO and some matched with CdO indexed to cubic structure. Some extra peaks are also observed because of the composite ZnO-CdO. Some new planes are formed by combining different structures.



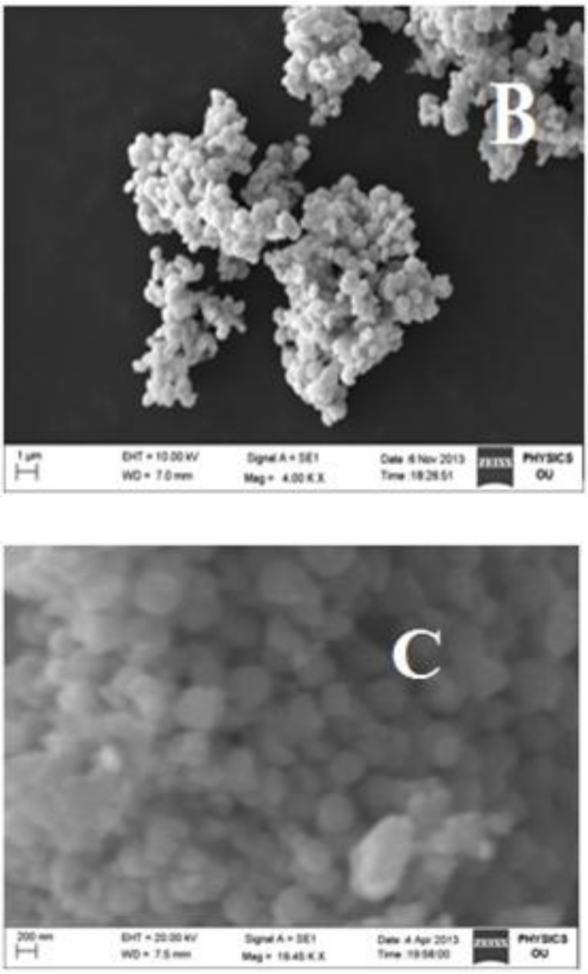


Fig. 2 A, B, C the SEM micrographs for pure ZnO, CdO and CdO-ZnO composite nanoparticles respectively

Fig 2 shows the SEM micrograms of pure ZnO, pure CdO and CdO-ZnO composite respectively. SEM images show that pure CdO nanoparticles are clear spherical shape with size range of ≈50 nm. This agrees well with reported works [14], pure ZnO nanoparticles range of ≈90 nm and CdO-ZnO composite heterojunction nanoparticles in the range of 140 nm. Aggregation of heterojunction nanoparticles were formed. Similar results were observed previously [5, 15]. From SEM images, it is clear that the pure CdO particle size is 75nm. Figure 2A, shows the SEM images for pure ZnO, figure 2B for pure CdO,while figure 2C shows the ZnO-CdO composite nanoparticles. From this there is an appreciabe increase in the crystal size of ZnO nanoparticles in the composite.

Figure 3 shows EDX micrographs of the nanoparticles, stoichiometric ratio estimated from EDX indicates the formation of high purity nanoparticles. From this EDX analysis the elemental ratios of constituents are indicated. The pure ZnO, pure CdO and CdO-ZnO composite nanoparticles were formed. They were in good agreement with results obtained in [16]

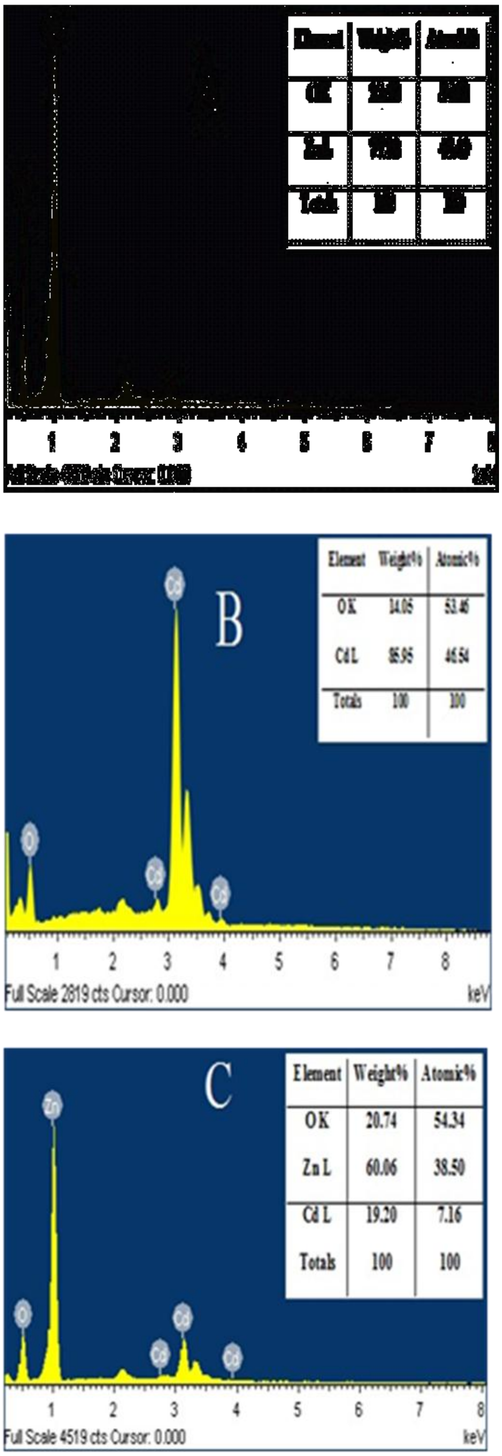


Fig. 3 EDX analysis of pure ZnO pure CdO and CdO-ZnO composite nanoparticles

The FTIR spectra of pure ZnO and CdO-ZnO composite nanoparticles was shown in figure 4 The absorption peaks from 1000cm^{-1} to 3000 cm^{-1} correspond to hydroxyl and carboxylate impurities in materials. In FTIR spectra very broad band centered at 3465cm^{-1}which can be ascribed to the O-H stretching mode of hydroxyl group. The peaks between 2850 cm^{-1}and 3000 cm^{-1} are due to C-H stretching vibration of alkane groups.

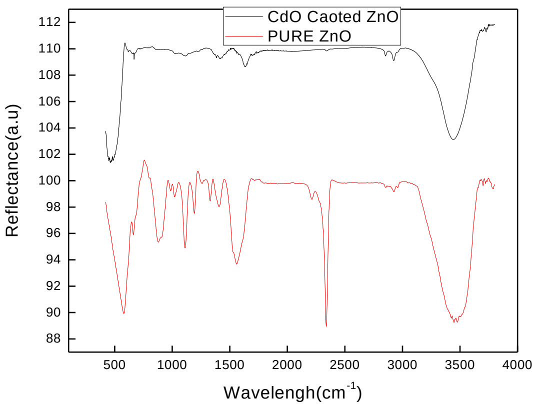
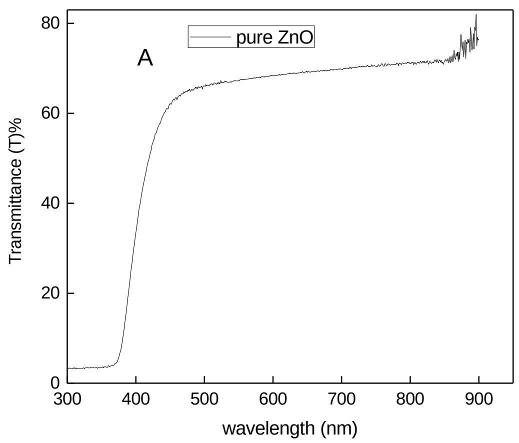
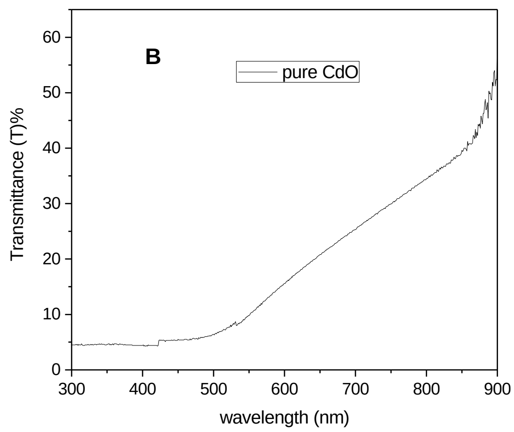


Fig. 4 FTIR spectra of pure ZnO and CdO-ZnO composite

The peaks observed at1600cm^{-1} and 850cm^{-1} is due to the asymmetrical and symmetrical stretching of the zinc carboxylate, respectively. The peaks from 450 to 650 cm^{-1} are due to metal oxide bonds [17]. The metal oxide peak is centered at 570 cm^{-1} in pure ZnO, actually the peak Centre corresponding to ZnO present between 450 cm^{-1}to 500 cm^{-1}, for our material the peak is slightly shifted towards higher wavelength side this is expected due to defects present in the material [18]. Most probable defect is zinc vacancies (VZn) interstitial zinc ions (Zni), oxygen anti-sites in ZnO. In case of CdO-ZnO composite nanoparticles the peaks centered at 448, 468 and 491cm^{-1} these correspond to CdO, ZnO and impurities present in CdO-ZnO material, respectively similar results were obtained by other researchers [15].

3.2 Optical Properties





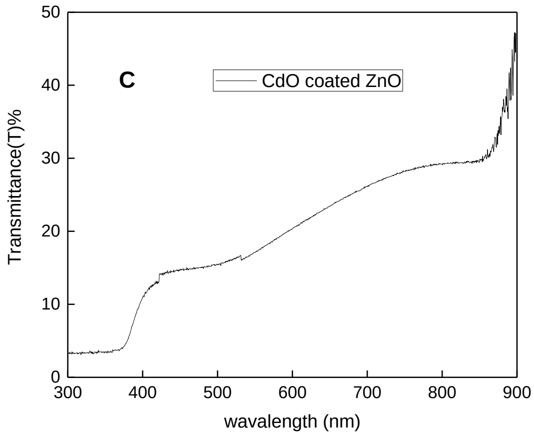


Fig. 5 A, B, C Transmittance spectra of pure ZnO, CdO and CdO-ZnO composite film

The optical transmittance was recorded at room temperature for various wavelengths (from 200nm to 900nm) by using UV-Vis optical spectrophotometer. Figure 5 show the graph of transmittance versus wavelength for pure ZnO, pure CdO and the ZnO-CdO nanocomposite. From figure A, the transparent spectrum of pure ZnO nanoparticles have high transparency above 60% in UV and visible range while a pure CdO nanoparticles have transmittance below 50% in visible range and for the nanocomposite (ZnO-CdO) the transmittance of composite nanoparticles is in between pure ZnO and pure CdO nanoparticles. This is comparable with results reported [16, 19, 20].

4. Conclusions

Pure ZnO, CdO and CdO-ZnO composite nanoparticles were synthesized by Sol-gel method at 70°C substrate temperature. Results, XRD; confirms that two phases are present in CdO-ZnO composite nanoparticles. One phase corresponding to ZnO and other second phase corresponding to CdO. The size of nanoparticles was estimated by SEM images. The size of a pure ZnO is 90nm, pure CdO is 80nm and CdO-ZnO composite nanoparticles is 140nm. The presence of hydroxyl and carboxylate impurities in the above materials and metal oxide bond was found by the use of FTIR. The optical properties were determined by use of UV-Vis Spectrophotometer and the spectrum show that the transmittance of the CdO-ZnO composite lies between that of pure ZnO and CdO.

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