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A simple and low-cost route to homogenize CdS nanospheres for thin films applications

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Abstract

Homogenous shape and size of semiconducting nanoparticles play an important role on thin films deposition which determines the functionality and efficiency of electronics, optoelectronics, and photovoltaic devices. Although thin films of CdS nanospheres have been obtained using synthesis and deposition techniques such as chemical bath deposition, electrochemical deposition, solvothermal deposition, and sol-gel deposition, the non-uniform morphology of nanospheres reduces the quality of the deposited thin films affecting the desired performance of devices. In this study, vacuum condition was used in the synthesis process of CdS nanospheres to homogenize their size and shape. The synthesized CdS nanospheres were deposited as a thin film on ITO coated glasses using spin-coating technique. Characterization results show the formation of CdS nanospheres with homogeneous morphology and average size of 40 nm. In addition, results demonstrated an easy and low-cost approach to homogenize CdS nanospheres to obtain thin films suitable for semiconducting thin films applications.

Keywords: *CdS nanospheres, vacuum conditions, thin films, spin-coating.*

1. Introduction

In the last decade, biomedical, clean energy, electronics and optoelectronics industry have increased their attention in techniques used to synthetize and deposit semiconducting nanoparticles because of their feasibility to produce more efficient and cheaper thin film devices [1 - 3]. The interest in nanoparticles is by reason of their magnetic, electrical, optical, chemical and physical properties that are unique. In addition, the high demand of clean energy has promoted the increase of interest in versatile materials and cost effective synthesis techniques for thin film photovoltaic applications [4 - 7]. The functionality and efficiency of optoelectronics, photovoltaic and electronics devices based on thin film technologies depend strongly on the properties of the semiconductor materials. Specially, semiconducting materials comprising compounds of elements II and VI groups of the periodic table such as CdSe, CdS, ZnS, and PbS have demonstrated excellent properties for fabrication of low dimensional multilayer devices [8 - 11].

Heterostructures of cadmium sulfide (CdS), cadmium telluride (CdTe), cadmium selenide (CdSe) and their ternary mixed crystals with direct band gap are fabricated by low-temperature deposition techniques where the internal and external surfaces are intrinsically well passivated and are characterized by a low recombination velocity for the excess carriers [6, 7]. This property allows the use of these compound materials to build a multi-junction structure with a band-gap gradient aiding the collection of excess carriers and hence facilitating the development of optoelectronics and photovoltaic devices [11 - 12]. In particular, CdS is a binary compound used as window material in thin film optoelectronics and photovoltaic devices [13]. It has excellent properties as heterojunction material with CdSe and CdTe [14 - 17]. CdS is widely used as n-type semiconductor with a direct band gap of 2.42 eV and an appropriate optical absorption in the short wavelength range of the visible spectrum [18].

Heterojunctions of CdS, CdSe and CdTe have been obtained by deposition and synthesis techniques such as chemical bath deposition [9, 10], electrochemical deposition [11], solvothermal deposition [12, 13], sol-gel deposition [14, 15], and spin coating, among others [19]. Although these heterojunctions are being obtained by different techniques, the non-uniform morphology of nanospheres reduces the quality of the deposited thin films affecting the desired performance of devices. In this study, a non-aqueous precursor was used to obtain CdS nanospheres by colloidal solvothermal technique. The size and shape of the nanoparticles were homogenized using vacuum environment during the growing process [20]. The synthesized CdS nanospheres were deposited as a thin film on a substrate of soda-lime glass covered by ITO using spin coating technique under room temperature. The synthesized CdS nanospheres were characterized by morphological, chemical and optical techniques. The obtained result demonstrates that the proposed method allows synthesis of nanoparticles with homogeneous morphological and average size of 40 nm. The uniformity of deposited thin films demonstrates feasibility for low dimensional multilayer heterostructures that can be applied in electronics, optoelectronic, and photovoltaic devices [20 - 23].

2. Synthesis of the CdS nanospheres

The chemical reagent used to perform the synthesis of the CdS colloidal spheres are polyvinylpyrrolidone (PVP K30, MW=10,000), ethanol, acetone, ethylene glycol (EG), isopropyl alcohol, thiourea (TU), cadmium nitrate ($Cd(NO_3)_2 \cdot 3H_2O$), and deionized (DI) water. The amounts of each reagent used for the synthesis are 10.8 gr of $Cd(NO_3)_2 \cdot 3H_2O$, 2.66 gr of TU and 3.89 gr of PVP [24]. The reagents were dissolved in 350 ml of EG by constant stirring until the solution became homogeneous. To obtain the optimal heater time for the synthetizes of the CdS nanospheres having homogenous morphology and size, seven samples of the initial solution were separated. Further after, each samples was heated at 140 ºC under a vacuum of 40 Torr for different times. The sample one was heater for 30 min, the sample two for 40 min, and so on until sample seven was hater for 90 min. Fig. 1 shows the obtained solutions after cooling at room temperature.

The CdS nanoparticles were precipitated with acetone in a ratio of 5:1 (colloidal solution: acetone) and centrifuged at 6000 rpm for 20 min. The obtained precipitated yellow was washed several times with DI water and isopropyl alcohol to eliminate all residual reagents. Further after, the precipitate nanoparticles were placed in a desiccator under room temperature condition to dry them completely. Spheres with diameter between 40 and 100 nm were obtained by tuning the heating times between 30 to 90 min. According to this result, the use of vacuum condition during heating time ensures similar size and morphology of the CdS nanospheres.

Fig. 1 Solutions heated at 140 °C for times varying from 30 to 90 min with increments of 10 min. The control (non-heated) sample is also shown.

3. Deposition of he CdS nanspheres

Thin films were deposited on ITO coated soda-lime glass substrates from TechInstro, with dimensions of 25 mm × 25 mm × 0.7 mm, resistivity of 10 Ω·m and transmittance > 90 %. The material for the thin film deposition was prepared by mixing 50 % of CdS nanospheres, 40% of EG, and 10 % of IPA. The film deposition was performed using spin coating technique at 7200 RPM for 30 seconds. Three deposition cycles were performed on each substrate. After each deposition, to reduce stress, passivate dangling bonds and improve crystalline structure the samples were annealed at 140 °C [8, 19, 25 - 26]. Hence, substrates with one, two and three deposition-cycles were analyzed.

4. Characterization techniques

Frontier FT-IR Spectrometer from Perkin Elmer was used to obtain infrared spectra. Scanning Electron Microscope JEOL JSM-6010LA and field emission microscope Lyra3XMU from TESCAN were used for imaging and X-ray analysis. The optical properties were analyzed with a UV-Vis 2600 Shimadzu spectrometer. Raman light scattering measurements were carried out using Perkin Elmer Raman station 400F with 785 nm laser and a max output power of 250 mW. A Scanning Empyrean X-ray Diffraction System from PANalitical Empyrean equipment was used for the identification of crystalline phases of deposited materials.

4. Results and discussions

Figure 2 shows the FTIR spectrum of the colloidal solution with the synthesized CdS nanospheres. In Fig. 2 is observed the characteristic bands of C-H at 1406 and 2938 cm^{-1} and of O-H at 3304 cm^{-1} which correspond to ethylene glycol (EG). In addition, it is observed the Cd-S bond stretching vibration band at 634 cm^{-1} and two intense peak at 1034 cm^{-1} and 1080 cm^{-1} corresponding to the presence of sulfur.

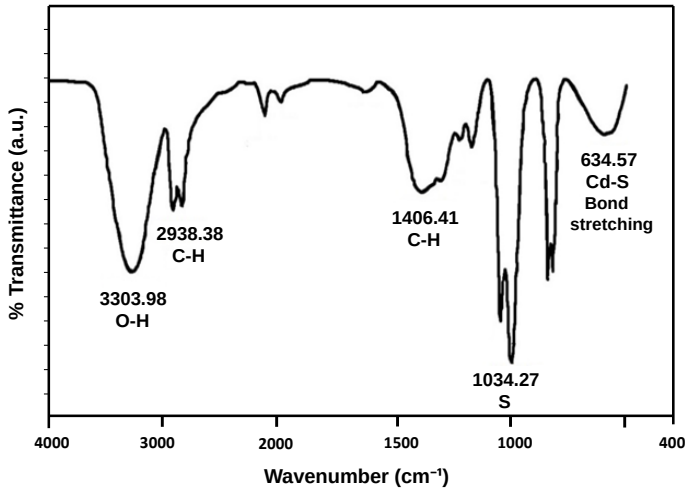
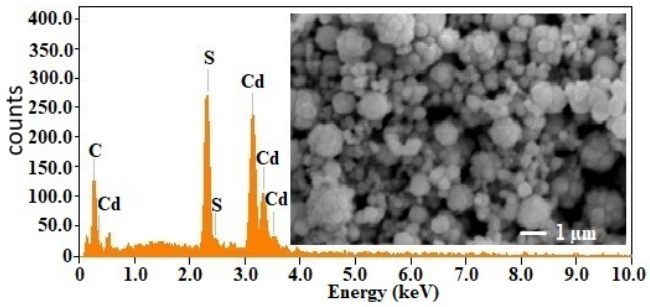
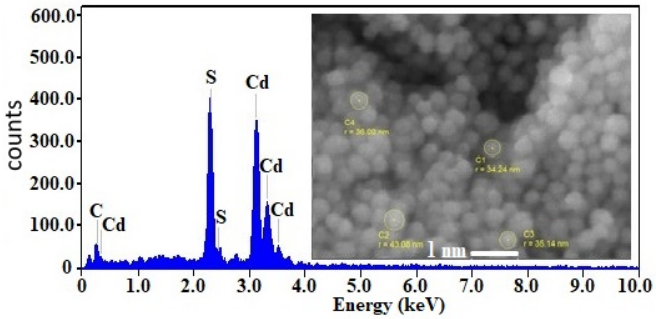


Fig. 2. FTIR spectrum of the synthetized CdS nanospheres.

Figure 3 show the scanning electron microscopy (SEM) image and energy dispersive spectroscopy (EDS) results of CdS synthesized nanospheres under non-vacuum and vacuum conditions, respectively. The analysis was performed to identify the morphology and elemental chemical composition of the sample. For the nanospheres synthetize under non-vacuum condition, SEM image of Fig. 3a shows the formation of nanospheres with sizes ranging from ~ 100 to 283 nm, according to the scale bar. The large size distribution could be attributed to the non-homogeneous temperature distribution inside the chamber due to the non-vacuum conditions. In addition, the EDS analysis reveals the presence of S and Cd in the spheres. Also, a carbon (C) peak appears, which is due to traces of organic compounds such as EG or absorbed CO_2 from the environment [27, 28]. In contrast, For the nanospheres synthetize under vacuum condition, SEM image of Fig. 3b reveals homogeneous size particles with average diameter of ~ 40 nm. In addition, the EDS analysis shows the S and Cd peaks and the no presence of C. This result is attributed to the purity of the synthesized particles given by the uniform temperatures inside the chamber due to the vacuum condition.



(a)



(b)

Fig. 3. EDS spectrum and SEM image (inset) of synthetized CdS nanospheres; (a) under non vacuum conditions; (b) under vacuum conditions.

Figure 4 shows the absorbance spectra of the synthesized CdS nanospheres. It is observed in Fig. 4 absorbance peaks at 260, 480 and 747 nm which are typical characteristic of CdS nanospheres [29]. This absorbance property makes the synthetized nanospheres a great candidate for thin film deposition in transparent window layer of solar cells and photodiodes. Figure 5 shows the SEM images of one, two and three deposited layers of CdS nanospheres after a thermal treatment of 140°C. All layers where deposited by spin-coating technique. Figure 5a shows the one layer deposited substrate, it is seen a non-continuous film with large areas without nanoparticles. Figure 5b shows the two layer deposited substrate, it is observed higher density of the deposited nanoparticles than the one layer. Figure 5c shows the three layer deposited substrate, it is observed higher density of nanoparticles with complete covered substrate area.

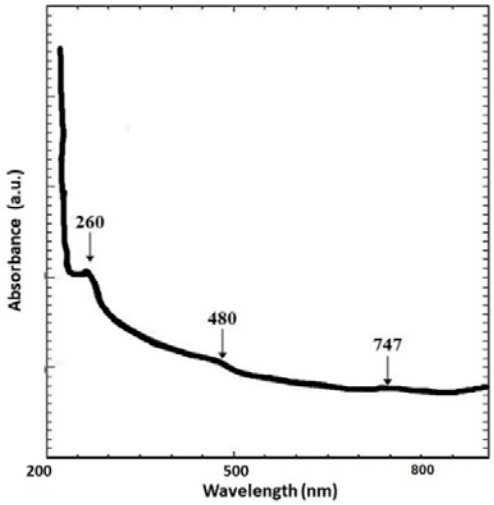


Fig. 4. Absorbance spectra of the CdS nanospheres.

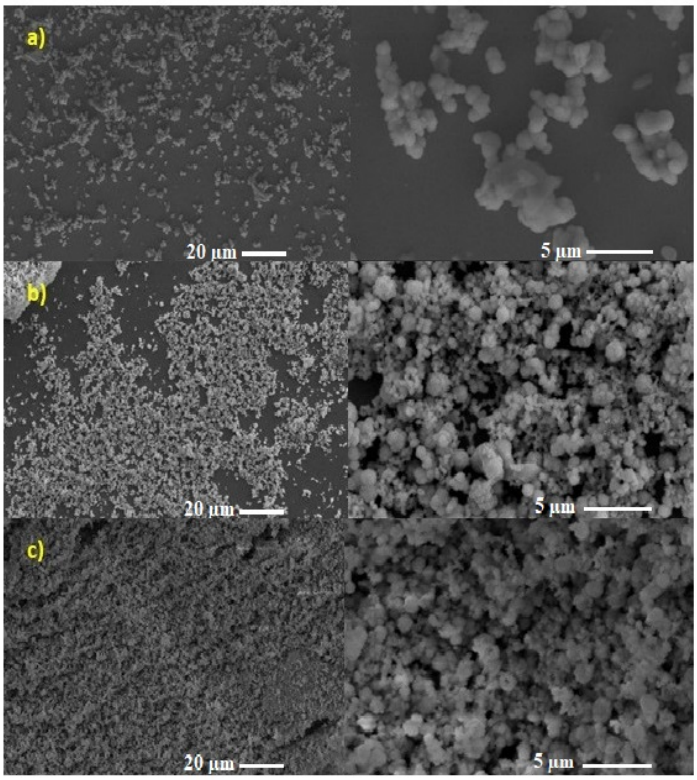


Fig. 5. SEM images of one, two and three deposited layers of CdS nanospheres after a thermal treatment of 140°C; (a) one deposited layer ; (b) two deposited layers and (c) three deposited layers.

Figure 6 shows the Raman spectra of the sample with three deposited layers of the CdS nanospheres. The doted plot represents the Rama spectra of the sample before the annealing process, while the no-doted plot represents the Rama spectra of the sample after the annealing process. Both plots exhibit the first (1LO) and second order (2LO) longitudinal optical phonon peaks at 302 cm^{-1} and 596 cm^{-1}, respectively, which are typical for CdS [24].

It is important to note that according to Klyuchikhin et al., the ratio between the 1LO and 2LO intensities depends on the degree of perfection of the sample and should increases when defects are introduced [30 - 31]. It is important to note that he annealed sample presents a lower ratio than the non-annealed sample, which indicates a higher increases in crystalline level after the annealing process.

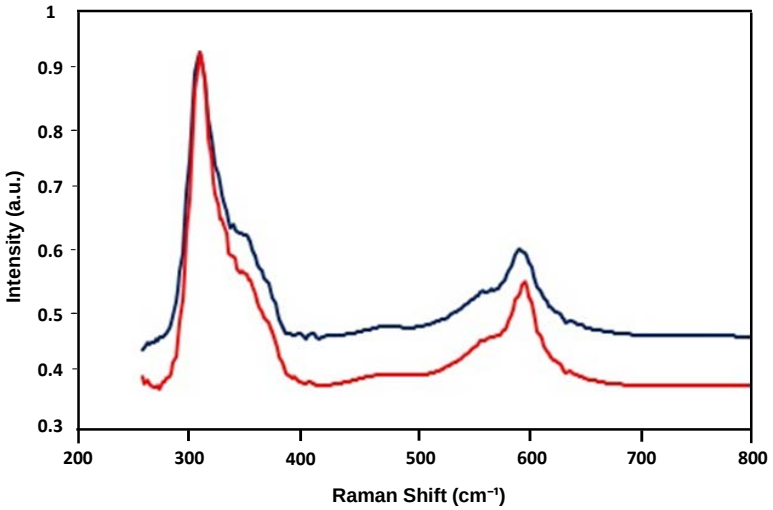


Fig. 6. Raman spectra of the sample with three CdS nanospheres deposited layers before and after the annealing process.

Figure 7 shows the X-ray diffraction (XRD) pattern of the three layers CdS nanosphores deposition by spin coating technique. The XRD patterns show the crystalline phases identification, a characteristic polycrystalline feature with mixed hexagonal and orthorhombic crystalline phases. An intense and sharp peak at 51.19° correspond to (1 1 2) crystallographic plane with a hexagonal crystalline structure and P63mc space group. Characteristic peaks at 26.58° and 43.91° correspond to (0 0 2) and (1 1 0) crystallographic plane. The orthorhombic phase peaks present at 2θ, the values of 31.72°, 41.61° and 61.8°, which correspond to (1 1 0), (1 1 1) and (2 1 1) planes respectively. These results are in agreement with the reported in Joint Committee on Powder Diffractions and Standards (JCPDS 00-002-0549). Since, no elemental sulphur has been observed in the XRD that could suggest being caused by the nature of sulphur precursor, mixed phases of orthorhombic and hexagonal CdS can be due the growth conditions such as temperature and pH [32].

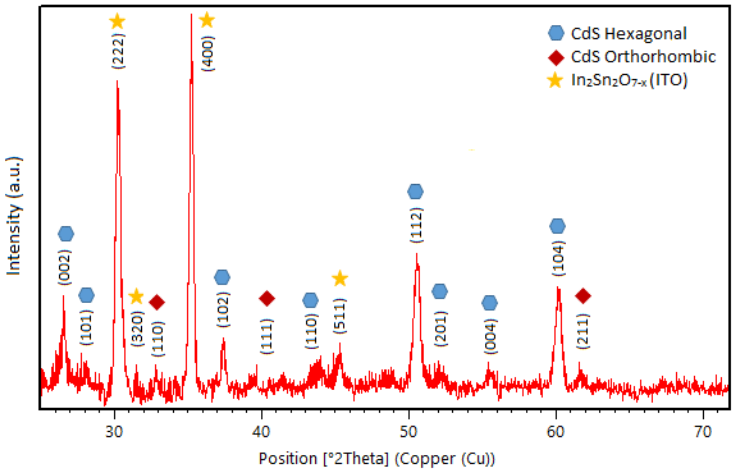


Fig. 7. CdS nanospheres thin film XRD Pattern.

5. Conclusions

CdS nanospheres with high purity and homogeneous morphology and average size were successfully synthesized by a modified colloidal solvothermal technique. The nanoparticles were obtained by reaction between a polymeric matrix, cadmium nitrate, and thiourea during 60 min at 140 ºC under a vacuum of 40 Torr. The synthesized CdS nanospheres were successfully deposited as a thin film on glass/ITO using spin-coating. SEM images revealed the formation of CdS nanoparticles with homogeneous morphology and average size of 40 nm. The results obtained by EDS and FTIR indicate the presence of high purity CdS. Raman spectroscopy shows characteristic 1LO and 2LO bands at 302 cm^{-1} and 596 cm^{-1}, respectively, indicating a good degree of perfection in the sample. Optical analysis was made by UV-Vis spectrum shows a characteristic CdS absorption peak at 480 nm, this property allows the synthesized material to be used as a window material when deposited as a thin film. XRD results confirmed hexagonal and orthorhombic structure.

The obtained results indicate that high quality nanospheres of CdS can be synthesized in vacuum. This material is suitable for many optoelectronic applications such as PV cells and photodiodes and further preparation for core/shell quantum dots. According to the obtained results, the use of vacuum during the heating is necessary to ensure similar size and morphology of the particle

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