Optical characterization of semiconductor CdS nanoparticles formed in polymer matrix

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The optical properties of CdS nanoparticles (NPs) are explored as a function of nanoparticle size and concentration. Nanocomposite (NC) thin films with semiconductor CdS nanoparticles formed in a polymer matrix using successive ionic layer adsorption and reaction (SILAR) technique showed very attractive optical properties due to quantum confinement effects. For bulk CdS materials, the absorption peaks can only be tuned in a narrow range. The nanostructure size and shape were characterized by scanning electron microscope (SEM), the optical properties were studied by UV-Vis spectroscopy, FT-IR and photoluminescence spectroscopy (PL).

1. Introduction

Semiconductor nanoparticles interact strongly with ultraviolet and visible photons due to the excitation of localized excitons [1-3]. CdS is one of the most studied materials because it has a well-established relationship between the optical absorption and the size of the particle. CdS is a group II–VI semiconductor, and as such, CdS nanoparticles have generated great interest due to their unique size-dependent physico-chemical properties [4-5]. CdS has band gap energy of 2.42 eV at room temperature [6], and it shows great potential for uses in photocatalyst [7], non-linear optical materials [8], display devices [9], X-ray detectors [10], photovoltaic cells [11] and application in the biological field [12]. In the case of photovoltaics, semiconductor nanoparticles especially CdS nanoparticles, offer the prospect of increasing device efficiency by reducing nanoparticle size and/or increasing light-trapping within active layer in photovoltaic devices. However, semiconductor nanoparticles can also decrease the efficiency of solar cells, for example due to absorption of light within the nanoparticle or by increasing reflectance of the front surface due to back-scattering and interface effects. Therefore, it is imperative that semiconductor nanoparticles are suitably designed to provide the correct optical properties for a given application and in this case the preparation technology plays a great role. There are different way to synthesize CdS nanostructures such as spray pyrolysis [13], chemical deposition [14], chemical bath deposition [15], sol-gel [16], colloidal particulate [17], thermal evaporation [18], ultrasonic [19] and SILAR [20]. However, among them, SILAR method is very simple and has evident advantages due to good composition control, low equipment cost, simplicity and nanoparticles size tunablity. In the present work, we report the SILAR method for preparation of CdS nanostructures. SILAR is a procedure that utilizes mutual attractions between deposited species (e.g. electrostatic, covalent, hydrogen-bonding, etc.) to build thin films onto a substrate [21, 22]. This technique has garnered much attention in the past three decades for the ability to create functional multilayer thin films for a wide variety of applications. The ability to assemble complex structures and tune macroscopic properties on the nanoscale using this simple process is very powerful. Semiconductor nanocomposites in the form of thin films have a wide range of applications including graded semiconductors for optoelectronics [23], solid electrolytes for batteries [24], degradable encapsulation [25], antireflection coatings [26], and controlling cell growth [27]. In the present study, CdS-Polymer nanocomposites in the form of film have been created to produce solar cell active layer with tunable behavior.

2. Experimental details

2.1. Instrument

Surface morphologies were studied using the LEO1430 VP scanning electron microscope (SEM) with 18 kV accelerating voltages. UV–Vis absorption spectra of the samples were obtained using a Shimadzu spectrophotometer (Japan, model 1650). Fourier transform-infrared (FT-IR) spectra were obtained using Perkin Elmer Spectrum RXI apparatus and the photoluminescence and photoluminescence excitation

spectra were taken by a Jobin Yvon INC Flurolog-3-21spectrofluorometer at room temperature.

2.2. Preparation of samples

CdS-PVA nanocomposites in the film form have been prepared in gelatin matrix by alternate immersion of substrate in Cd^{2+} source and S^{2-} source, kept at room temperature. Aqueous cadmium acetate solution was used as source of Cd ions, which its pH was 4. The second precursor was sodium sulfide which was obtained by dissolving 0.96 g of Na_2S in 20 ml of double distilled water was made alkaline by addition of aqueous ammonia solution to make the pH of solution 12.

First, the polymer (PVA) substrate was immersed in cadmium acetate solution so as to get cadmium ions adsorbed in the polymer matrix. After immersion of polymer matrix in the aqueous solution of sodium sulfide, the reaction occurred at polymer matrix to form CdS. After adsorption and reaction of cationic and anionic precursors, the polymer matrix was rinsed 3 times in distilled water to remove of loosely bounded particles. This cycle was repeated several times to increase the nanoparticles size in polymer matrix and also the thickness of a film. Five samples with different cycles of SILAR (2, 4, 6, 8 and 10 cycles) have been prepared.

3. Results and discussion

Fig. 1(a) and (b) shows the UV-Vis absorption and transmission spectrums of CdS-polymer nanocomposite with different cycles of SILAR. The absorption band edge decreases with an increase in particle size. This phenomenon is attributed to a quantum confinement effect. The fact that the absorption onset is so strongly blue shifted in 2 cycles of SILAR indicates that formation of small nanoparticles. The quantum mechanical explanation of this is that the small-sized particles obtained in this synthesis have a wider band gap than particles using other synthetic methods. A greater energy is therefore required before excitation will take place. Apparently from Fig. 1, at lower numbers of cycles and small particle sizes, the band edge is smaller than the values in the case of CdS bulk crystals (2.42 eV). This is connected to quantum-dimensional effects in nanoparticles. With increased number of cycles, the band edge increases and becomes equals to the values for bulk crystals.
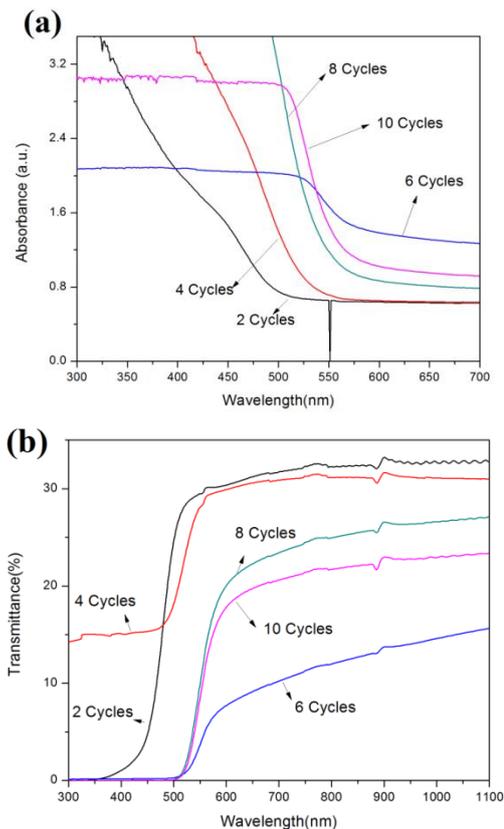

Fig. 1. (a) and (b): Optical absorption and transmission spectrum of CdS-polymer nanocomposites prepared at different cycles of SILAR

The FT-IR spectra of CdS-polymer nanocomposite with different cycle of SILAR were taken between the ranges of 400 to 5500 cm^{-1}. Fig. 2 show the FTIR spectrum of samples. The broad and strong band centered at 3437 cm^{-1} assigned to the stretching vibration of hydroxyl (O–H) group with strong hydrogen bonding. Two strong peaks at 2920 cm^{-1} and 2852 cm^{-1} are the characteristic bands of asymmetric and symmetric C–H stretching respectively. The stretching vibrational bands of C=O at 1650 cm^{-1}. The C=O bands were attributed to the carbonyl functional groups due to the residual acetate groups remaining after the preparation of PVA from hydrolysis of polyvinyl acetate or oxidation during preparation and processing. The absorption band at 1430 cm^{-1} is assigned as CH_2 bending vibration. While the C-H and OH bending is related with the absorption at 1325 cm^{-1}. A signal at 1240 cm^{-1} is due to CH_2 wagging and that at 1140 cm^{-1} is assigned as C–C and C–O–C stretching vibrations. The strong band at 679 cm^{-1} has been assigned to Cd-S stretching [28].
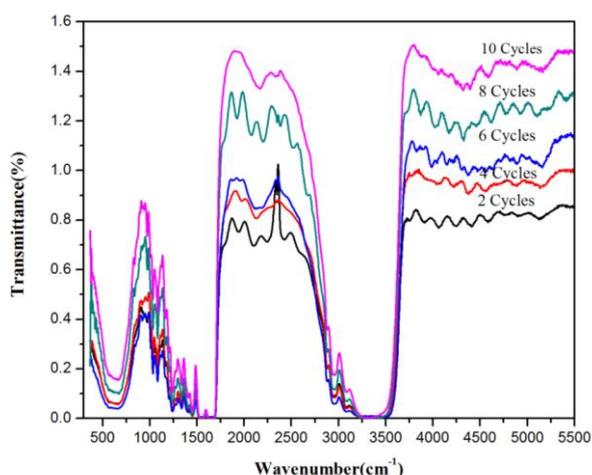
Fig. 2. FT-IR transmission spectrum of CdS-polymer nanocomposites prepared at different cycles of SILAR

Fig. 3 shows the photoluminescence (PL) spectra of CdS-polymer nanocomposites at different cycles of SILAR. The intensity of the PL emission from this nanocomposite varies by the number of cycles. That the PL peak position also varies significantly. The variation in emission intensity and energy are related to size nanoparticles.
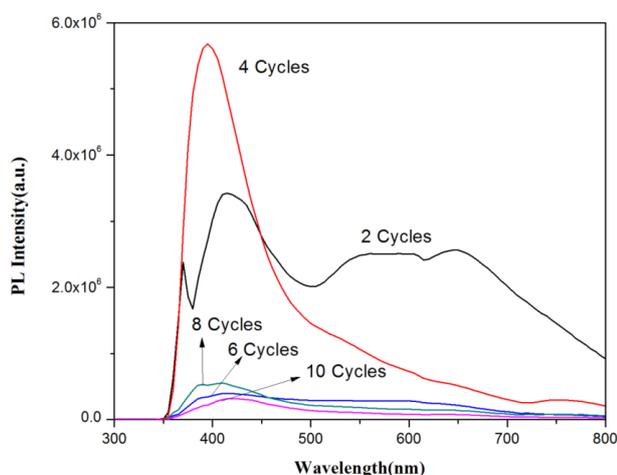

Fig. 3. PL spectrum of CdS-polymer nanocomposites prepared at different cycles of SILAR

Surface morphology of CdS-polymer nanocomposites were studied using SEM. Fig. 4 shows The SEM images of samples. The polycrystalline nature is revealed from the micrographs and these micrographs illustrate the formation of nanometer crystallites distributed not uniformly over the surface, therefore, we cannot distinguish the real size particles. The surface containing some pits and voids, such type of porous structure resulted due to the film formation is based on the nucleation and coalescence. Morphology of the prepared samples shows the agglomeration of small particles with increase the number of cycles.
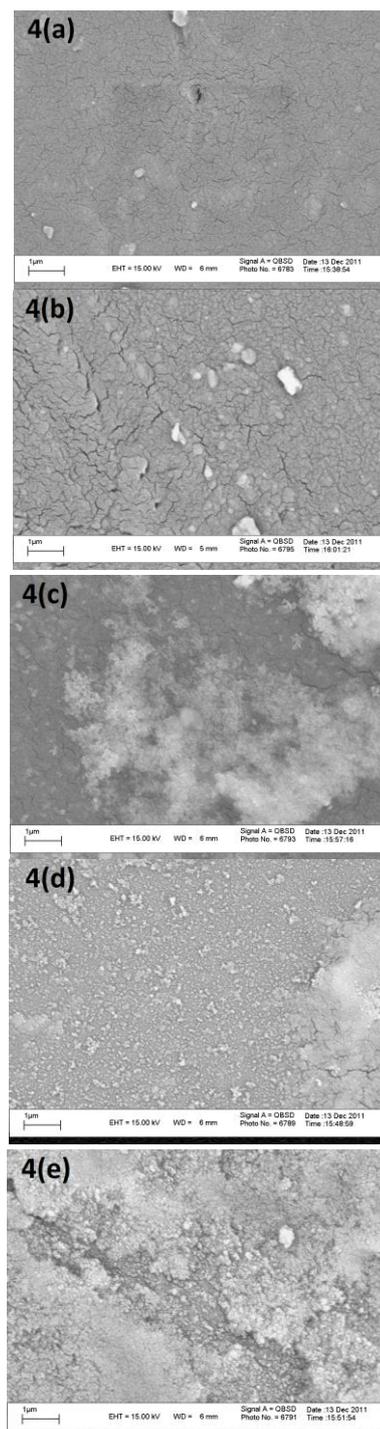

Fig. 4. SEM images of CdS-polymer nanocomposites prepared at different cycles of SILAR, 4(a): 2 cycles, 4(b): 4 cycles, 4(c): 6 cycles, 4(d): 8 cycles and 4(e): 10 cycles

4. Conclusion

In this paper CdS-polymer nanocomposites were successfully grown in polymer matrix by SILLAR method. These samples were investigated using UV-Visible spectroscopy, PL, FT-IR and SEM. UV-Visible absorption spectroscopy showed an increase in band gap with

decrease in crystallite size. The FT-IR analysis reveals the energy between functional groups in changed. The SEM images show the agglomeration of small particles with increase the number of cycles. The PL spectroscopy showed variation of peaks position and intensity.

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