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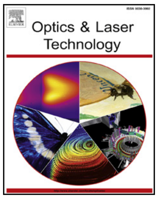

Full length article

Tunable luminescence and transmittance nature of CdS:PMMA nanocomposites for optoelectronic applications

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HIGHLIGHTS

- CdS reinforced PMMA nanocomposite transparent solid films with minimum thickness using in situ method.
- The emission spectra of the nanocomposite solid films are found to be in the visible region.
- Uniform and narrow distribution of CdS particles in PMMA matrix.
- Confinement and good encapsulation of particles in matrix without any additional capping agent other than polymer.
- CdS:PMMA nanocomposites with good transparency suited for optoelectronic applications.

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ABSTRACT

Optical and energy storage materials based on semiconductors are of great interest today. The present report explains the semiconductor nanocomposite centered on highly transparent Poly(methyl methacrylate) (PMMA) matrix and Cadmium Sulphide (CdS) nano particles. The solid films of CdS:PMMA composite was prepared using simple and cost effective solution casting technique. The surface morphology and the presence of CdS particles in PMMA matrix was analysed using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray spectra (EDX). The size of the particles was analysed using Atomic Force Microscopy (AFM) and Transmission Electron Microscope (TEM) and they revealed the presence of nano sized particles. The narrow size distribution of particles was identified from TEM and AFM analysis. The transmittance of the CdS:PMMA nanocomposite solid films was found to be above 90%. The blue and green emission of CdS:PMMA nanocomposite solid films were observed from Photoluminescence (PL) spectra.

1. Introduction

The optical properties of semiconductor nanoparticles incorporated into organic polymers called nanocomposites were of great interest owing to their new class of devices such as optical limiters, hybrid solar cells, laser light emitting diodes and in memory devices [1–3]. In the case of semiconducting nanoparticles, the electron-hole pair (exciton) confined in finite size where the size can be compared with the effective Bohr radius of the exciton. As the result of size confinement, the absorption edge was blue shifted and the band structures can be changed to discrete states [4]. Hence, the emission wavelength of the nanoparticles can be taken throughout the visible spectrum. Cadmium Sulphide (CdS), II-VI group of semiconductor exhibiting excellent optical properties because of its wide band gap in room temperature (2.4 eV) and its luminescence properties. Various methods had been adopted by many researchers to prepare CdS based nanocomposites. Polymers play a vital role in incorporating the semiconducting materials. Polymers, not only act as a matrix to incorporate the particles, but also it will encapsulate the particles from further growth and agglomeration [5,6]. Smaller particles having the size less than 15 nm and the possibility of transparent nanocomposites with improved optical and electrical properties can be obtained by using polymer as the matrix material. The objective of the present report is to synthesize transparent CdS:PMMA nanocomposite solid films of minimum thickness (less than ~1 mm) without using any capping agent other than the polymer. The novelty of the work lies in cost effective in situ preparation method of nanocomposite solid films of minimum thickness without compromising the transparency of the films and without any additional capping ligands.

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2. Materials and methods

Poly (methyl methacrylate) (PMMA) ($M_W = 3.5 \times 10^5$ g/mol) and Cadmium nitrate (Cd $(NO_3)_2 \cdot 4H_2O$) were supplied by Aldrich and have been used for the preparation of nanocomposites. The concentrations of Cd $(NO_3)_2 \cdot 4H_2O$: PMMA was taken as 1:20, 1:100, 1:200 and 1:400 M concentrations. Initially, PMMA was dissolved in 50 ml of Tetra hydro furan (THF) and stirred for more than 2 h. After that Cd $(NO_3)_2 \cdot 4H_2O$ was dissolved in the same solution containing PMMA and stirred further for the complete dissolution of salt. The solution was poured on to the petri dishes and dried in the ambient temperature. The formed films were then exposed to H_2S gas from Kipp's apparatus for half an hour under controlled environment (50 bubbles per minute). The formed films turned to yellow which was the indication of the formation of CdS particles in the matrix. The films were then characterized to study its different properties. The method of preparation did not utilize any special equipment to prepare the transparent films. The size of the CdS particles in the PMMA matrix was confirmed from AFM (NT-MDT model– tapping mode) and TEM (JEOL 2100 model operated at 80 KV) statistical analysis.

3. Results and discussions

3.1. Structural and morphological properties

Fig. 1 shows the SEM (inset a) image of CdS:PMMA composite and their corresponding EDX images.

In CdS:PMMA composite of 1:20 (Fig. 1a), the concentration of CdS was high and the particles were seemed to be agglomerated. The formed agglomeration in the particles illustrates a chain like pattern in the polymer background because of ripening process. In order to lower the surface energy, the nano crystallites agglomerated themselves during the formation. By decreasing the concentration of CdS in the polymer matrix to 1:100 (Fig. 1b), the particles were well separated and dispersed in the PMMA matrix with little agglomeration. The well separated and dispersed particles with little agglomeration can be obtained by decreasing the CdS concentration in PMMA matrix. The EDX was used to confirm the presence of CdS in the PMMA matrix. The EDX spectra illustrate the presence of C, O, Cd and S peaks in all the concentrations. C and O might have originated from the PMMA matrix [7,8]. The appearance of Cd and S in the particular area of the SEM image was represented in the EDX spectra which confirm the presence of CdS particles in the polymer matrix. The atomic ratio of Cd:S was nearly equal to 0.75:1.25 for 1:20 CdS:PMMA concentration. For 1:100 CdS:PMMA concentration, the Cd:S ratio was 1:1. The stoichiometry can be achieved by decreasing the concentration of CdS in the matrix.

3.2. Particle size distribution

To confirm the size of the CdS particles in the polymer matrix, the AFM and TEM techniques were used.

Fig. 2 displays the AFM (a) and TEM (c) images of CdS:PMMA nanocomposites of 1:100 concentration along with their statistical distributions (b) of particle size. The SEM image revealed the uniformly distributed CdS particles in the polymer background. Around 50 to 60 particles were taken into account to measure the particle size using TEM and AFM independently. The average particles size estimated from the AFM statistical distribution was around 35 ± 5 nm and TEM distribution shows the average size as 24 ± 5 nm (inset image). From TEM image, the individual particle shows a minimum size of 5 nm. The variation in the particle size distribution was due to the radius of curvature of the AFM tip, which was approximately 10 nm and when it approaches the grain, the intrinsic enlarging effect of pin point leads to the overestimation of particle size in the matrix [9]. The AFM and TEM analysis confirms the narrow particle size distribution in nano scale [10].

3.3. Optical properties

In Fig. 3a, the optical transmittance was observed to shift towards shorter wavelength with decrease in particle size for all the concentrations of the nanocomposites. The composites show good transmittance in the region above 500 nm which is one of the pre requisites for optoelectronic device applications, especially for solar cell window layers [11]. The minimum transmittance for 1:20 concentration was 85% and the maximum transmittance for 1:400 was 92%. In the case of PL spectra (Fig. 3b), the spectrum of 1:20 CdS:PMMA concentration exhibits a broad peak having the maxima around 520 nm. A small shoulder was observed around 432 nm for the same. The broad peak was attributed to the surface trapped state luminescence of CdS nanocomposite. During photo excitation, the valence electron may combine with the hole in the conduction band minimum or with the surface trapped states. An appropriate excitation energy can excite several nano crystals simultaneously, producing a spectrum with more than one peak. Also, surface of nanocomposites usually contains high impurity level and defect states that leads to mid band gap states. The mid gap states will facilitate the non radiative recombination in the lower wavelength region, lower than the absorption edge. The peak at 432 nm which was lower than the absorption wavelength (489 nm) was attributed to mid band gap luminescence of CdS which was slightly broad.

The inset figure in Fig. 3b, shows the deconvoluted spectra for 1:200 concentration. The spectrum was deconvoluted into two peaks having

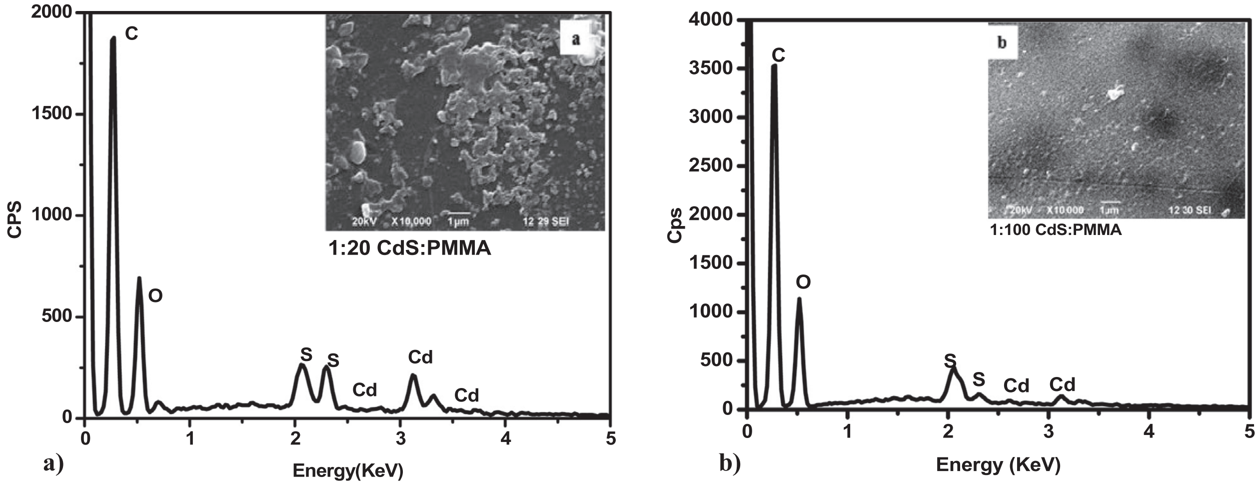

Fig. 1. SEM (inset) and EDX images of CdS:PMMA nanocomposite solid films (a) (1:20) (b) (1:100).

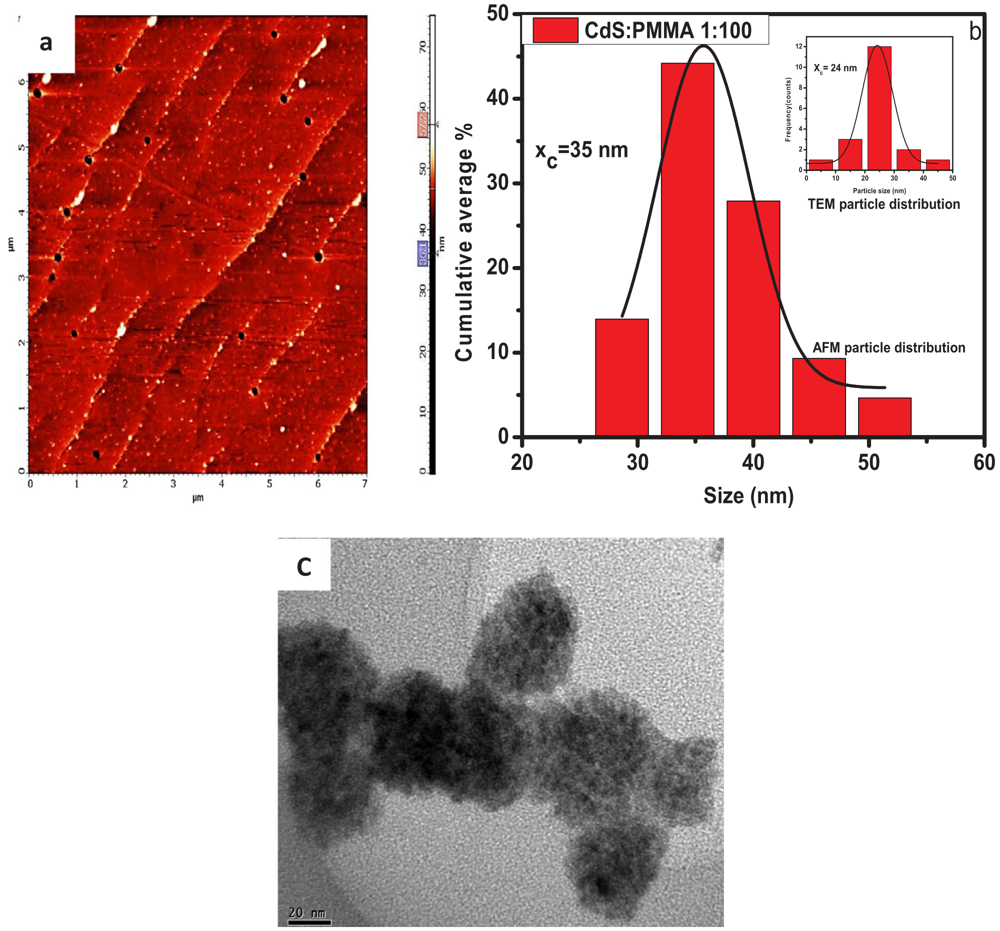

Fig. 2. (a) AFM (b) Particle size distribution using AFM and TEM (inset) (c) TEM particle size distribution of CdS:PMMA nanocomposites (1:100).

emission maxima around 474 nm and 512 nm. Both peaks were in the green region and the higher energy peak was attributed to selectively excited photoluminescence [12]. In 1:400 (inset figure) CdS:PMMA concentration, the peak was deconvoluted and it consists of two peaks, one around 424 nm and another around 457 nm respectively. The peak corresponds to 424 nm was attributed to the near band edge emission of CdS:PMMA nanocomposites. The peak maxima shifted towards blue region when the CdS:PMMA concentration changed from 1:20 to 1:400 indicating the confinement of CdS particles. On decreasing the CdS concentration, the peaks were blue shifted which indicates the good encapsulation of CdS particles in the PMMA matrix. In all the concentrations, the broad peaks at higher wavelength involve donors, acceptors and trapped state defects. In CdS, the defect consists of cadmium vacancies, sulphur vacancies, interstitial sulphur and interstitial cadmium. The broad peaks observed in the higher wavelength side were attributed to one of the aforementioned defects. The difference in the shape of the emission peaks may be due to some variation in the CdS cluster surface property in addition to the defects. In all the concentrations (1:20,1:200 and 1:400), the emission was in the blue and green region and hence the CdS:PMMA nanocomposites can be used for optoelectronic applications.

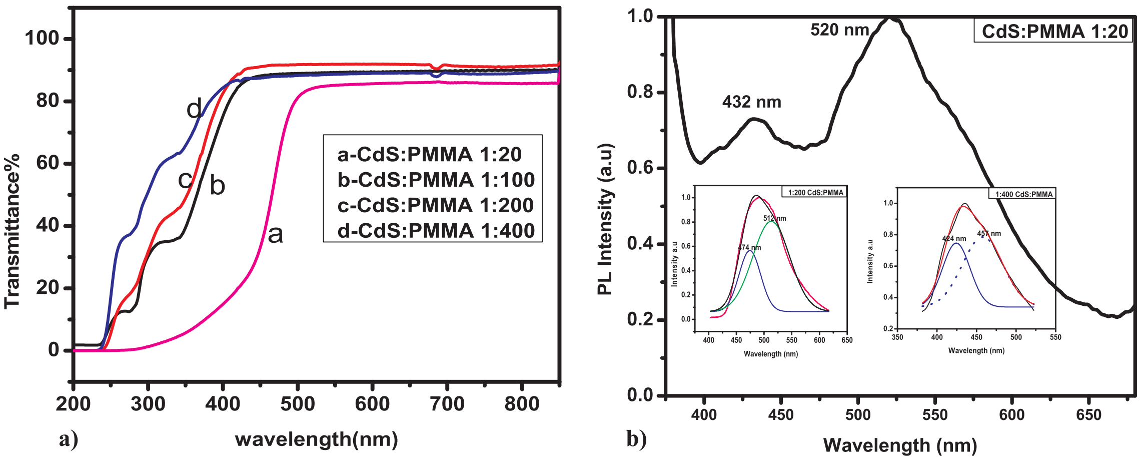

Fig. 3. (a) Transmittance (b) Photoluminescence images of CdS:PMMA nanocomposites of various concentrations.

4. Conclusions

CdS:PMMA nanocomposite solid films of different concentrations have been prepared. The surface morphology shows the distributed CdS particles in the polymer back bone and EDX reveals the presence of CdS particles in the PMMA matrix. The AFM and TEM analysis shows the presence of nanosized CdS particles in PMMA matrix. The maximum transmittance obtained for CdS:PMMA nanocomposites of 1:400 concentration was around 92% which will be suitable for device applications. Green and blue emission was obtained from PL spectra whose peak maxima was shifted towards blue region by decreasing the concentration of CdS in PMMA matrix. The photoluminescence nature of CdS:PMMA nanocomposites makes them interesting candidate for light emitting diodes and optical limiter applications.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.optlastec.2018.11.038.

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