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Synthesis and photoluminescence spectra of CdS and CdS/ZnO doped PVK nanocomposite films

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Organic/inorganic hybrid materials consisting of quantum dots and conjugate polymers are important for the application in light emitting devices. In the present work, we have studied the effect of CdS and CdS/ZnO nanoparticle addition on the structure and fluorescence properties of spin coated PVK (poly(N-vinyl carbozole)) nanocomposite films. CdS nanoparticles were synthesized by simple co-precipitation technique and ZnO shell was grown on the CdS nanoparticles by simple wet chemical approach. The nanoparticles and the hybrid nanocomposites have been characterized by using XRD, SEM, FT-IR, optical absorption and fluorescence spectroscopic techniques. The absorption peak for pure PVK remains at 345.5 nm accompanied with minor hump ~480 nm resulting from the incorporation of nanoparticles. It has been observed that the addition of nanoparticles to the hybrid material results in the enhancement of fluorescence intensity at 410 nm to 450 nm spectral regions. These results are important for the development of new light emitting devices at low fabrication costs.

Keywords: *nanoparticles; hybrid materials; XRD; optical and fluorescence properties*

1. Introduction

Quantum dots have been rigorously investigated recently for improving the characteristics of light emitting devices requiring low power and low fabrication costs. The new organic/inorganic hybrid materials utilize the unique optical and electronic properties of each component [1]. The shape, size and spatial distribution of nanoparticles in the organic matrix are important factors which influence various properties of the hybrid nanocomposites for functional devices [2–4]. Musa et al. [3] showed the increase in efficiency of composites containing ZnO with small particle size and decrease in carrier lifetime with the increase in concentration of nanoparticles in MEH-PPV/ZnO nanocomposites. Mastour et al. [4] theoretically supported the enhancement of fluorescent intensity of P3HT/ZnSe nanocomposites. The phase immiscibility resulted in enormous increase in luminescence of spin coated polyvinylpyrrolidone (PVP) and polyphenylene oxide (PPO) polyblends [5]. Poly(N-vinyl carbozole) (PVK) is a blue light emitting and hole transporting semiconducting polymer with excellent carrier generation efficiency and the ease of processing for fabricating luminescent devices [6]. The solution casted films of poly(butylene succinate) (PBS)/poly(N-vinylcarbazole) (PVK) composites possess fine luminescent properties for potential use as blue fluorescent biodegradable materials [7]. Zhang et al. [8] fabricated a hybrid photodetector with high photoresponse and narrow bandwidth due to efficient carrier separation and convenient charge transport between ZnO and PVK. An increase of conductivity and a quenching of the photoluminescence have been observed when the nanocomposite layer was inserted in ITO/PVK:CdS (6 nm particle size)/Al structures [9]. An enhancement of emission intensity of the poly(N-vinylcarbazole) and quantum dots composite films deposited in the field of silver nanoparticles embedded in quartz substrate was observed [10]. Electrical bistability and negative differential resistance were reported in the current-voltage characteristics for CdS nanoparticles with different sizes in PVK, when studied in glass/indium tin oxide (ITO)/PVK:CdS/Al system [11]. The improvement in interface quality

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between CdS and PVK polymers favored fast interfacial carrier transfer giving enhancement of photoconductivity of PVK/CdS nanocomposites [12]. Also the enhanced photoconductivity has been reported for finely dispersed CdS/ZnO core/shell nanoparticles acting as sensitizers in PVK polymer matrix serving as a charge transport medium [13]. However, there are no reports on the effect of CdS/ZnO core/shell nanoparticles on the fluorescence properties of PVK polymer matrix.

In this work, we report the optical and fluorescence properties of PVK-CdS/ZnO nanocomposites studied by optical and photoluminescence spectroscopies.

2. Experimental

The CdS nanoparticles have been synthesized by simple co-precipitation method taking 0.1 M cadmium acetate $Zn(CH_3COO)_2 \cdot 2H_2O$ and 0.1 M sodium sulfide Na_2S, each in 100 mL of double distilled water. The ZnO shell on CdS nanoparticles has been grown using a method reported by Jiang et al. [14]. In a typical process, appropriate amount of CdS nanoparticles was dispersed ultrasonically in double distilled H_2O and rigorously stirred for 1 h and 2 h, respectively. Then, 0.1 M NaOH aqueous solution was slowly added until the pH value of the solution reached ~10. Thereafter, 20 mL of 0.1 M zinc nitrate and 20 mL of 0.1 M NaOH solutions were successively added in 1 mL portions to the solution for getting the desired thickness of the shell. Finally, the core/shell nanoparticles were separated by centrifugation and washed several times with double distilled water and ethanol. The precipitate was dried in a hot air oven at 50 °C overnight to get a powder sample.

The organic host consisting of 30 mg of PVK in 20 mL of chlorobenzene and composite films of CdS or CdS/ZnO with different weights (5 mg, 10 mg, 15 mg, 20 mg, 25 mg) were used for preparing the solutions by sonication and rigorous stirring for 1 h each, respectively. Ten layers of PVK polymer and its composites with CdS and CdS/ZnO nanoparticles have been sequentially deposited at the rates of 200 rpm for 10 s, 800 rpm for 15 s, 2500 rpm for 30 s, using a spin coating technique (Model No. SpinNXG-P1, Apex Instruments, Kolkata). The films were then dried at 60 °C in the hot air oven after each coating. The optical absorption and photoluminescence spectra were studied using UV-Vis spectrophotometer (UV1800, Shimadzu, Japan) and fluorescence spectrophotometer (Cary Eclipse, Agilent, USA). The prepared samples were analyzed in terms of their structure and phase identification by X-ray diffraction using X-ray diffractometer (X'Pert PRO, PANalytical, UK) equipped with a goniometer PW3050/60 working with CuKα radiation (λ = 1.5406 Å) in the 2θ range of 20° to 80°. The surface morphology of the nanocomposite films was studied by using SEM (JSM-6510, JEOL, Japan). Fourier transform infrared spectroscopy (FT-IR) was used to study molecular structure in the 700 cm^{-1} to 30 cm^{-1} spectral region using the KBr pellet method (Model: Spectrum RX-FT-IR, PerkinElmer, USA).

3. Results and discussion

Fig. 1a shows the XRD patterns of CdS and CdS/ZnO core/shell nanoparticles. The peaks identified at 26.82°, 44.3° and 51.4° correspond to (1 1 1), (2 2 0) and (3 1 1) planes of the hexagonal wurtzite structure of the nanoparticles (JCPDS Card No. 75-1546). The considerable broadening of the diffraction peaks indicates the nanophase formation. The crystallite size D was calculated using the Debye-Scherrer equation:

$$D = 0.9\lambda/\beta\cos\theta \tag{1}$$

where λ is the wavelength of the radiation, β is the full width half maximum (FWHM) of diffraction peak and θ is the Bragg angle. The average crystallite size of CdS nanoparticles was 2.3 nm.

Fig. 1b shows the FT-IR transmission spectra of the CdS and CdS/ZnO nanoparticles in the spectral region of 30 cm^{-1} to 700 cm^{-1}. The absorption peaks at 60.3 cm^{-1}, 136.3 cm^{-1}, 246.7 cm^{-1}, 432.7 cm^{-1}, 566.8 cm^{-1} and 665.1 cm^{-1} correspond to CdS nanoparticles. However, the formation of ZnO shell on CdS nanoparticles resulted

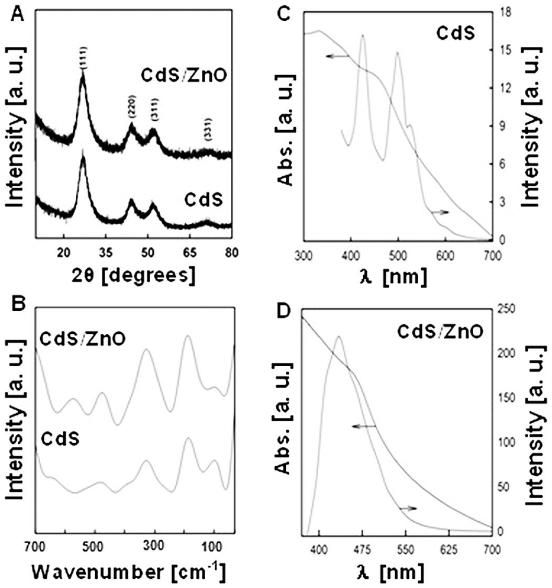

Fig. 1. (a) XRD patterns, (b) FT-IR spectrum, (c) optical absorption and (d) photoluminescence spectra of CdS and CdS/ZnO core-shell nanoparticles.

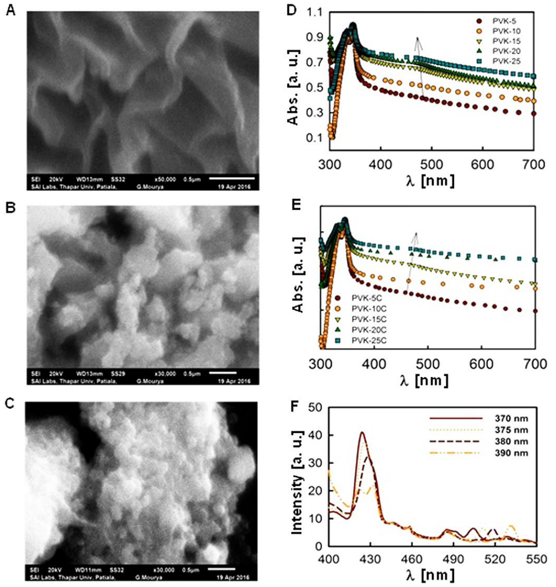

Fig. 2. SEM images of spin coated (a) PVK polymer, (b) PVK-CdS and (c) PVK-CdS/ZnO nanocomposite films on glass substrates. Optical absorption spectra of PVK nanocomposite films doped with different concentrations of (d) CdS, and (e) CdS/ZnO, (f) photoluminescence spectra of pure PVK films at different excitations.

in the formation of IR absorption bands centered at 62.8 cm^{-1}, 119.1 cm^{-1}, 245.0 cm^{-1}, 421.7 cm^{-1}, 523.1 cm^{-1} and 625.4 cm^{-1}. A feature at 150 cm^{-1} is due to disorder activated longitudinal acoustic phonons, the broad features between 200 cm^{-1} to 300 cm^{-1} are caused by transverse optic and surface optic modes reported by Milekhin et al. [15] and the modes at 658.0 cm^{-1} correspond to stretching vibrations of Cd–S bonds reported by Selim et al. [16] for small crystallites of CdS. The absorption band at 441.2 cm^{-1} was assigned to Zn–O stretching vibrations of the ZnO by Kaur et al. [17]. Therefore, the stretching vibration of Cd–S bonds was found to shift from 665.5 cm^{-1} for CdS nanoparticles to 625.4 cm^{-1} for CdS/ZnO nanoparticles and the increase in the absorption corresponds to the Zn–O stretching vibrations of ZnO shell on CdS nanoparticles. Also, the low-frequency mode ∼100 cm^{-1} is commonly related to the disorder-activated acoustic phonons appearing in smaller NCs. Therefore, the observed band at ∼60.3 cm^{-1} for CdS nanoparticles was found to shift to longer wavenumbers with a decreased intensity upon the shell formation in the studied nanocrystals.

Fig. 1c and Fig. 1d show the optical absorption and luminescence spectra (excited at 370 nm) for CdS and CdS/ZnO nanocrystals. The absorption peak at 451.3 nm (or band gap, $E_g = 2.75$ eV) and luminescence band centered at 425 nm with feeble intensity are due to prominent surface defects related to the band centered between 470 nm and 580 nm. However, the absorption peak at 462.1 nm and luminescence band centered at 436.0 nm with enhanced intensity are due to the passivation of surface defects in the CdS/ZnO core-shell nanoparticles. The grain size of nanoparticles can also be estimated by adopting the procedure as described in the literature [18] using the Brus equation:

$$E_{eff} = E_g + \frac{h^2}{8\mu R^2} + 1.8\frac{e^2}{4\pi\varepsilon\varepsilon_0 R} \qquad (2)$$

where E_g is the optical gap of bulk CdS (2.46 eV), μ is the reduced mass of the effective masses of electrons (0.19 m_0) and holes (0.8 m_0) with m_0 as a rest mass of electron, R is the radius of a particle,

ϵ is the dielectric constant (5.7) and ϵ_0 is the permittivity of free space. The particle size of CdS nanoparticles was found to be 3.15 nm (from optical absorption spectrum) and 2.5 eV (from luminescence peak at 425 nm) which is very near to that calculated from XRD analysis.

Fig. 2 shows the SEM images of the spin coated (a) PVK polymer, (b) PVK-CdS and (c) PVK-CdS/ZnO nanocomposite films on the glass substrates. The lamellar structured films for the pure PVK film and the incorporation of nanoparticles as clusters of polymer and nanoparticles has been observed in the fabricated films.

Fig. 2d and Fig. 2e show the optical absorption spectra of CdS (PVK-x) and CdS/ZnO (PVK-xC) nanocomposites in PVK matrix with x = 5 mg, 10 mg, 15 mg, 20 mg, 25 mg of nanoparticles, respectively. It has been observed that the absorption peak for pure PVK (not shown in the graphs) remains at 345.5 nm with the incorporation of nanoparticles accompanied with a minor hump at 480.0 nm. Similar values of absorption peak have been reported by Alias et al. [19]. Conventional energy absorption occurs due to $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions [20] and the 345.5 nm peak is associated with $n \rightarrow \pi^*$ transition. This peak shifts to smaller or longer wavelengths with the addition of CdS and CdS/ZnO nanoparticles, respectively. This change may be due to the interactions of bare and core/shell nanoparticles with the polymer.

Fig. 2f shows the PL spectra of spin coated PVK films at different excitation wavelengths. The first broad peak centered at 423 nm along with the shoulder peak at 432 nm and the other minor peaks at 484 nm, 492 nm and 504 nm have been observed for the excitation at 370 nm wavelength. However, the lower energy excitation at 390 nm wavelength resulted in the formation of doublets at 422 nm and 432 nm, respectively, accompanied by a decrease in their intensity. The other two peaks at 482 nm and 496 nm did not shift in their position with the excitation energy. The peaks centered at 504 nm for the first excitation wavelength shifted to 510 nm, 518 nm and 531 nm, respectively, at the other excitations. The main luminescence band can be attributed to the triplet-singlet transitions while the other three luminescence bands between 480 nm and 505 nm may be attributed to the large number of triplet excitons [21]. However, the photoaging caused dramatic change around 430 nm to 550 nm spectral range under ultraviolet light irradiation due to the change in π-stacking alignments of the carbazole units, i.e. intra-chain partial and full face-to-face overlaps of the carbazole groups of the PVK [22].

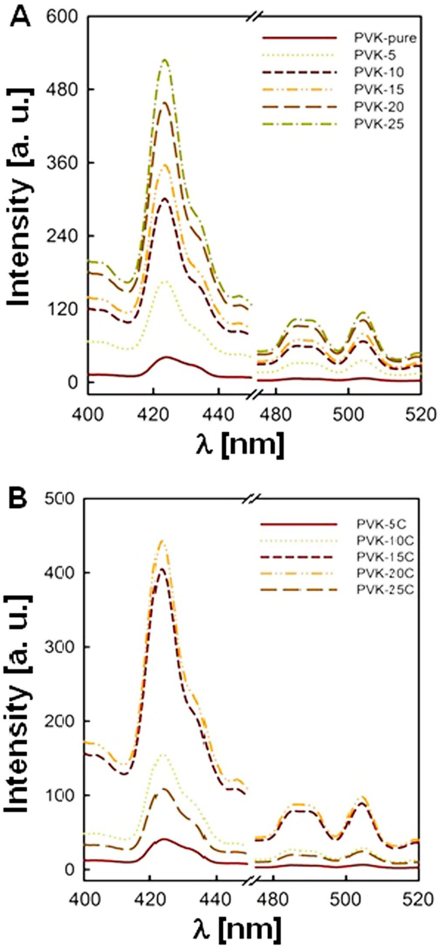

Fig. 3. Photolumenescence spectra of (a) pure PVK and PVK-CdS, (b) PVK-CdS/ZnO nanocomposite films at different concentrations of nanoparticles, excited at 370 nm.

Fig. 3a shows the photoluminescence spectra of pure PVK and PVK-CdS nanocomposite films excited at 370 nm. It is observed that the incorporation of CdS nanoparticles favored an increase in intensity of characteristic band along with an increase in intensity of the peaks in 480 nm to 520 nm region of the spectrum. The annealing of PVK films under iodine atmosphere favored the degradation of excimer states of PVK polymer [23]. However, the addition of CdS nanoparticles resulted in the enhancement of the characteristic band of PVK in these nanocomposites. Similar change in the emission spectra has been observed for the PVK-CdS/ZnO nanocomposites as shown in Fig. 3b, but the intensity of the main band was found to decrease above 20 mg CdS/ZnO nanoparticles in the nanocomposite films.

4. Conclusions

The effect of CdS and CdS/ZnO nanoparticles on the optical and fluorescence properties of PVK polymer films was systematically investigated. The growth of a shell around the nanoparticle was found to passivate the surface defects yielding the enhancement in fluorescence intensity. The absorption peak for pure PVK remained at 345.5 nm accompanied with a minor hump at ~480 nm caused by the incorporation of nanoparticles. The emission peaks at 423 nm along with a shoulder peak at 432 nm were dominant, while the other minute peaks at 484 nm, 492 nm and 504 nm were observed for the excitation at 370 nm. It was observed that the addition of nanoparticles resulted in the enhancement of fluorescence intensity of the hybrid materials in 410 nm to 450 nm spectral region. We also observed that the highest concentration of CdS/ZnO nanoparticles resulted in the decreasing trend of the characteristic emission band of the PVK polymer.

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