



Synthesis and luminescence enhancement of Cerium doped CdS nanoparticles

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ABSTRACT

Cerium doped cadmium sulfide nanoparticles (Ce:CdS) were synthesized by coprecipitation method with three different concentrations of cerium (1, 2 and 3 mol%). Powder X-ray diffraction pattern reveals the formation of cadmium sulfide nanoparticles with hexagonal (wurtzite) structure. It was observed that the presence of ceria does not alter the structure of CdS. Average particle size was measured to be ~3 nm. Reflectance spectra illustrate band-to-band absorption at 453, 500 and 507 nm respectively for 1, 2 and 3% Ce doped CdS nanoparticles. The presence of cerium was confirmed by EDX and ICP-OES analyses. The effect of dopant concentration on the photoluminescence (PL) intensity has also been studied. XRD and PL analyses demonstrate the Ce³⁺ ions uniformly substitute Cd²⁺ sites or interstitial sites in CdS lattice which influences the optical properties. Increase in the concentration of cerium slightly shifts the absorption and emission toward higher wavelength. Particle size and the crystallinity of Ce:CdS NPs were confirmed through HRTEM and SAED patterns.

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1. Introduction

Rare earth doped luminescent II–VI materials have drawn increasing attention as potential phosphor materials for use in optical display devices [1–3]. The rare earth ions offer the possibility of obtaining blue, green and red colors, which are necessary for full color devices. Thus, doping of II–VI compounds with trivalent ions like cerium, terbium and europium etc., has been extensively studied [4,5]. In general, the luminescence of rare earth-doped systems mainly reflects the properties of the dopant. The electronic structure of rare earth ions differ from the other elements because of incompletely filled 4fⁿ shells. The 4fⁿ electrons are shielded by 5s² and 5p⁶ electron orbitals. Excitation of materials doped with such ions results in sharp line emission due to intra 4fⁿ shell transition of rare earth ion core [6] which lies in a wide range covering UV, Vis, IR regions of the spectrum.

Relatively large radius and charge mismatching between the RE³⁺ and divalent Cd²⁺ ions were responsible for the unsuccessful incorporation of RE³⁺ into CdS, hence the inefficient energy transfer is often observed. A lot of nanoparticles doped with lanthanide ions have been reported, but most of these particles are prepared by high temperature processes [7,8] leading to particles without organic groups on the surface. Doping of rare earth element like cerium reduces the particle size of nanomaterials and also increases surface area [9,10].

Recently, Vij et al. [11] and Sharma et al. [12] reported the luminescence studies on Ce doped SrS nanostructures and Ce doped CaS nanoparticles synthesized by solid state diffusion method. Vinay Kumar et al. [13] reported luminescence investigations on Ce³⁺ doped CaS synthesized using the chemical co-precipitation method. To our knowledge there was no report on the investigations of cerium doped CdS nanoparticles. In this present work, we report the effect of cerium doping on the structural and optical properties of CdS nanoparticles synthesized by chemical coprecipitation method.

2. Experimental details

The raw materials used for the synthesis of cerium doped cadmium sulfide [Cd_{1-x}Ce_xS with x = 0.01, 0.02 and 0.03] were cadmium acetate dihydrate (99.99%), cerium nitrate (99.99%) and sodium sulfide (99.9%) purchased from Alfa Aesar. Mixed solvents of Ethylene diamine (en) and DI water (resistivity 10⁻¹⁸ mΩ) with 1:1 ratio, were used as a solvent.

20 ml solution of cadmium acetate (99 mole %) and 20 ml solution of cerium nitrate (1 mole %) with 0.07 M were prepared separately with en + DI water as a mixed solvent. Solution of cerium nitrate was added slowly into the cadmium acetate solution and the mixture was subjected to stirring at the room temperature for 30 min to achieve the dispersion of Cd²⁺ and Ce³⁺ into the solvent. With this, 20 ml solution of 0.07 M sodium sulfide was added dropwise and it was observed that the mixed solution turned to pale yellowish white and then to orange. The obtained precipitate was then ultrasonicated for 1 h to make nanoparticles evenly dispersed in the solution. The solution was subjected to centrifugation (4000 rpm) to

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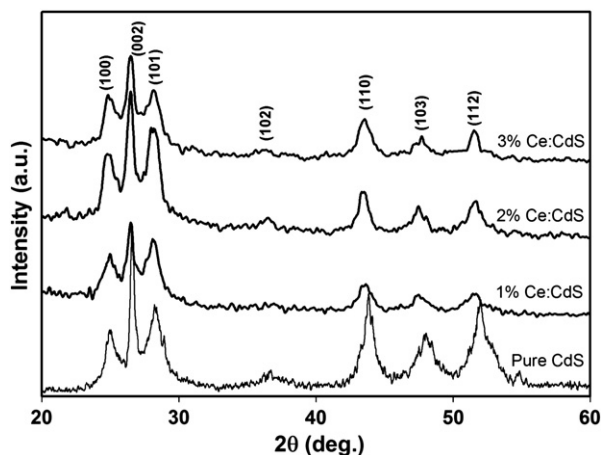


Fig. 1. XRD pattern for pure and cerium doped CdS nanoparticles.

settle down the nanoparticles and washed with ethanol and DI water for three times and dried in a hot air oven. Similar procedure was followed for other two concentrations of cerium (2 and 3 mol%).

The samples were characterized by X-ray diffraction analysis and the patterns were obtained using a PANalytical X-ray diffractometer (XRD) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Composition of the synthesized samples were analyzed with Hitachi S-3400 SEM-EDAX and confirmed with Nippon Jarrell-Ash, IRIS Advantage ICP-OES spectrophotometer. High resolution transmission electron microscope (HRTEM) images and SAED pattern were obtained at 200 keV using

JEOL JEM-3010 with LaB6 filament. Reflectance UV studies were carried out using CARY 5E UV-Vis Reflectance mode-UV spectrophotometer. Photoluminescence spectra were recorded using Shimadzu-5301 spectrofluorometer with 450 W Xenon lamp source.

3. Results and discussion

3.1. XRD, HRTEM, EDAX and ICP analyses

The XRD patterns of pure and cerium doped CdS (Fig. 1) show that the synthesized nanoparticles possess hexagonal (wurtzite) structure and the planes (100), (002), (101), (102), (110), (103) and (112) are clearly indexed. The absence of additional peaks in the XRD patterns shows the purity of the sample without noticeable traces of impurity, even with increasing doping concentration. The prominent peaks in the diffraction pattern are $(100)_h$, $(002)_h$, $(101)_h$ of CdS (JCPDS No. 75-1545). As there are no such peaks of Ce, CeS , Ce_2S_3 detected, thus confirmed the successful incorporation of Ce^{3+} ions into the crystal lattice of CdS nanoparticles. Compared to pure CdS, the diffraction peaks shift slightly toward smaller diffraction angle. The average crystallite size of 3.3 nm, 2.9 nm, 3.1 nm was calculated using Scherrer equation respectively for 1%, 2% and 3% Ce:CdS nanoparticles.

TEM micrograph in Fig. 2(a) shows well-formed nanocrystallites of cerium doped cadmium sulfide with nearly spherical in shape. It clearly shows the particles within a diameter of 4 nm, which is consistent with the value calculated from XRD analysis. The smallest well dispersed particles observed in Fig. 2(b) (indicated by circles) of these ordered entities are in the nanoscale regime. EDAX spectrum of Ce:CdS nanoparticles in Fig. 2(c) shows the presence of major

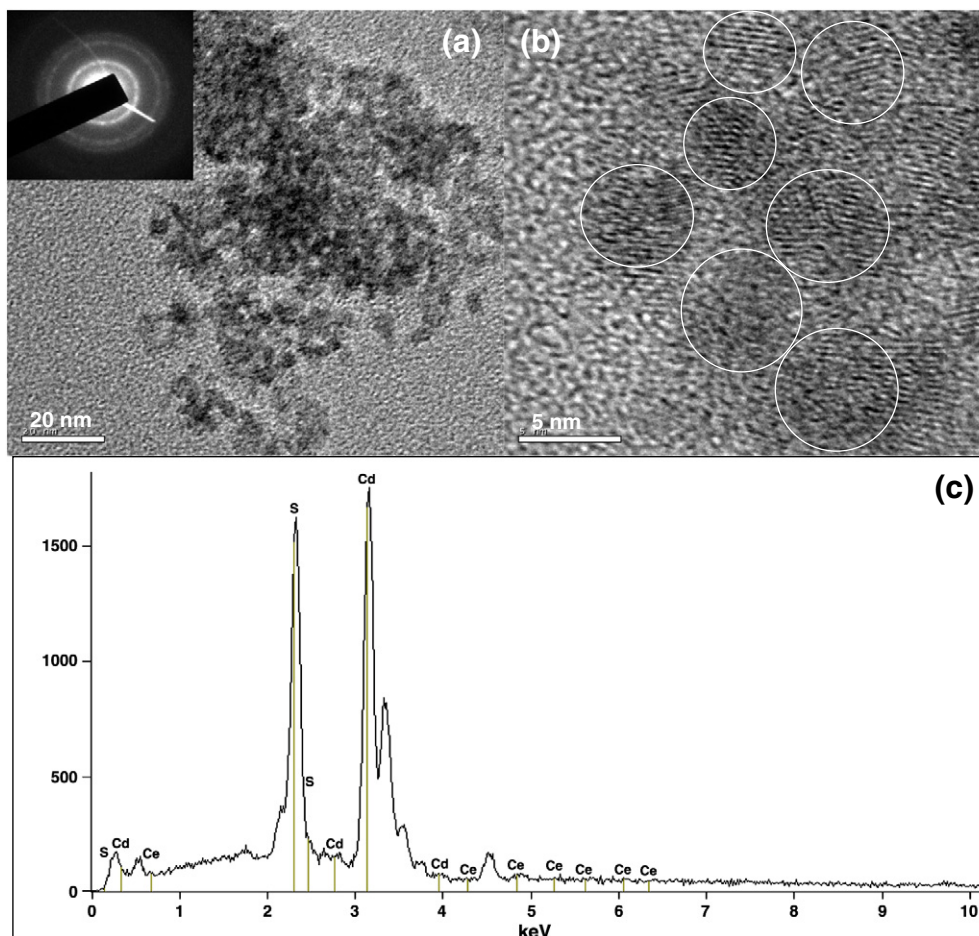


Fig. 2. (a) TEM (b) HRTEM images and (c) EDAX analysis of cerium doped CdS NPs.

chemical elements namely cadmium, sulfur and cerium. The elemental composition calculated using ICP-OES analysis for 3% Ce doped CdS was 76.30, 21.15 and 2.54 mol% of cadmium, sulfur and cerium respectively, which also confirms that majority of cerium ions doped with cadmium sulfide.

3.2. UV-reflectance analysis

UV-reflectance spectra of the Ce:CdS nanoparticles are shown in Fig. 3(a). Based on these reflectance spectra the absorption edge for each compound was determined. Using these absorption edge values, the bandgap energy was estimated by extrapolating the linear region of the plot. Band-to-band absorption at 453 (2.73 eV), 500 (2.48 eV) and 507 nm (2.44 eV) respectively for 1%, 2% and 3% Ce:CdS nanoparticles shows a blue shift in comparison with the bulk CdS, which may be ascribed to the quantum confinement effect.

It can also be seen that the increase in dopant percentage determines the red shift in the absorption shoulder, compared to pure CdS (2.75 eV) shown inset in Fig. 3(a). This was clearly due to the substitution of Ce^{3+} (1.034 Å) ions into the Cd^{2+} (0.97 Å) which increase the size of the crystal lattice. This is in compliance with Brus equation [14].

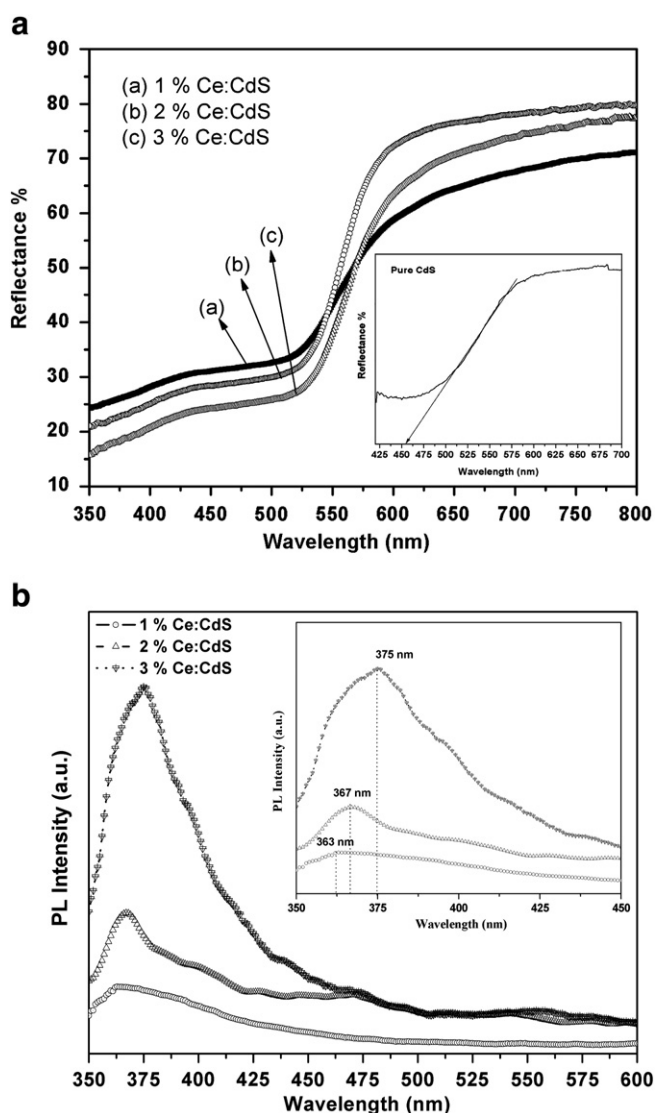


Fig. 3. (a) UV-Reflectance spectra of cerium doped CdS nanoparticles (inset shows pure CdS). (b) Photoluminescence emission spectra of Ce:CdS nanoparticles excited at 350 nm.

3.3. Photoluminescence studies

Upon excitation at 350 nm, the samples show luminescence in the blue region, with an emission peak positioned around 350–450 nm as shown in Fig. 3(b). There is no defect related emission peaks observed in the spectra. As shown in the inset of Fig. 3(b) the peak position of NBE emission slightly shifts toward longer wavelength region with higher intensity, from 363 nm to 375 nm when the concentration of dopant increases to 3 mol%. Thus it confirms that luminescence property of CdS nanoparticles enhanced when Ce^{3+} was introduced into the CdS. Maleki et al. [15], attributed the peak at 363 nm was attributed to higher level excitonic transition and its energy was calculated to be 3.38 eV. Similar explanation was given by Devi et al. [16] for the peak at 376 nm in nanocrystalline CdS. Usually the fluorescence emission of doping ions has higher photostability than the defect related luminescence of semiconductive nanomaterials, because the defects are greatly affected by synthesis conditions and environments.

4. Conclusion

Ce:CdS nanoparticles with different cerium concentrations have been synthesized by chemical coprecipitation method. XRD pattern reveals the formation of hexagonal structure of Ce:CdS with shift toward lower angle which confirms the incorporation of cerium. HRTEM images and SAED pattern adequately demonstrated the well dispersed and crystalline nature of the synthesized nanoparticles. Compared to pure CdS, the calculated bandgap energy value of Ce:CdS nanoparticles illustrates quantum confinement effect. For 3 mol% of Ce^{3+} doped CdS, the emission intensity was found to be a maximum with slight shift toward the higher wavelength compared to 1 and 2 mol%. Intense emission was observed for the incorporation of cerium ions into CdS NPs, which will be useful for high efficient EL devices and also possible for making full color device applications.

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