

Synthesis, characterization and optical properties of nanosized CdS hollow spheres

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ABSTRACT

In the present paper, we synthesized the CdS hollow spheres by using PMMA sphere templates of 298-301 nm diameters and 20-51 nm of shell thickness. A CdS hollow sphere was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), optical absorption and photoluminescence technique. CdS products are all cubic face-centered structure with the cell constant $a = 5.815 \text{ \AA}$. We also explore the morphology, structure and possible synthesis mechanism. A possible template mechanism has been proposed for the production of the hollow CdS nano-particles. The band gap of bulk CdS is about 2.45 eV, showing an absorption onset of bulk at about 513 nm. This shows a blue shift in the absorption spectra due to the quantum size effect, which is quite possible due to the small size of the CdS nano crystals as is evident in XRD pattern. The diameter of the beads is about 265-310 nm. The change in beads size due to the CdS over-layer is not so apparent in structures, due to its small thickness. The average diameter of the sphere is similar to that of the beads. Therefore, the spherical shells were obtained after the removal of PMMA core. Copyright © 2010 VBRI press.

Keywords: CdS hollow spheres; nanoparticles; photoluminescence.



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Introduction

CdS is a typical II-IV semiconductor compound, and is widely used in flat-panel displays, electroluminescent devices, infrared windows, sensors and laser apparatus. Various efforts have been made to synthesize hollow spheres of chalcogenide semiconductors for example hollow ZnS spheres synthesized by using silica and polystyrene spheres [1], CdS spheres have been prepared by in situ source template interface reaction route [2-4]. For the synthesis of these hollow spheres, first the template should be modified to confer a certain ability to coax an inorganic precursor (salt or alkoxide) onto the surface layer of the template core. After that the inorganic shell is deposited outside the scaffold, the templates are eliminated, leaving behind a hollow shell [5]. The templates can be divided into hard and soft types. When hard templates (e.g., SiO₂ [6-8], C spheres [9-11], polymers [12-18], metal particles [19], bacteria [20]) are chosen, the morphology of the hollow product is similar to the template. But the removal of these templates by either thermal (sintering) or chemical (etching) methods is complicated. Soft templates (droplets [21], vesicles [22-24], etc.) are relatively easy to remove; however, the morphology and monodispersity of

the as-prepared hollow products are poor due to the deformability of the templates.

Caruso et al introduced a simple technique for the preparation of hollow spheres by depositing a uniform self-assembly film on colloidal beads and subsequent removal of cores with solvent or calcinations [25, 26]. Luminescent spherical core shell particles of CdTe-NPs were prepared by Yang et. al. by using layer by layer deposition of mercaptopropionic acid capped CdTe-NPs. This resulted in the formation of the composite polymeric core shell structures and hollow shells of CdTe [27]. Some special techniques such as sono-chemical, microwave, hydrothermal or gamma irradiation have also been applied to synthesize the hollow chalcogenide semiconductors [28]. Zhu and coworkers synthesized hollow CdSe spheres using Cd(OH)₂ as an in situ template via a sono-chemical route [29] while ZnS hollow spheres was synthesized in aqueous solution of an amphiphilic triblock copolymer at room temperature [30]. Sub micrometer sized hollow CdS spheres with a wall thickness of about 20 nm have been synthesized in aqueous solution of cadmium acetate and triblock copolymer at room temperature through the slow release of S²⁻ ions from thioacetamide [31,32]. The shape and size of inorganic nano materials have important influence on their electrical and optical properties. Small inorganic crystals are generally unstable due to their high surface tension, and have a tendency to transform to larger particles by Ostwald ripening. An important strategy was to create nano particles shielded by an organic legend, so called "core-shell" particles. The shell can not only avoid the aggregation and oxidation of the particles, but also can alter the dispersion characteristics of the particles by surface modification, so that the possibility is given to blend the core/shell particles into the polymer matrices, which is called hybrid materials [33]. Recently, the fabrication of uniform hollow spheres ranging from nanometer to micrometer dimensions has attracted considerable interest because of their specific structures and potential applications in a wide range of areas, such as fillers, catalysts, photonic crystals, and drug delivery systems etc. [34-37]. Various hollow spheres including carbon, polymers, metals and inorganic materials have been synthesized [38, 39]. Hollow spheres are generally prepared by the template technique [40, 41]. In this process, core-shell nano particles are prepared and then, hollow spheres are prepared by the removal of cores with solvent or by calcinations. Various templates have been used in the past. The use of silica, polystyrene or PMMA spheres is a widely accepted procedure, wherein hard templates of different sizes were used to generate core shell spheres or hollow spheres. In the present paper, room temp synthesis of Cds hollow spheres (300nm, 20nm diameter and shell thickness respectively) by using PMMA sphere template have been carried out successfully which was also characterized by XRD, SEM and optical absorption and photoluminescence techniques.

Experimental

Soft chemical approach was used to synthesize CdS hollow spheres. PMMA spheres were dipped in 0.01 M solution of CdCl₂ in ethanol for 10 minutes, filtered and dried in air.

Then these spheres were dipped in a 0.1 M aqueous solution of Na₂S for sulfurization. After 10 minutes, the spheres were filtered out, washed many times with deionized water to remove any loose particles sticking over the spheres. The yellow orange colour of PMMA spheres shows CdS (CdS-A) formation. To increase the thickness of CdS layer, sample CdS-B was prepared using a higher CdCl₂ concentration of 0.1 M. Hollow spheres of CdS-A1 and CdS-B1 were obtained by dispersing the CdS/PMMA core shell structures of CdS-A and CdS-B in acetone that dissolves PMMA.

Structural characteristics of CdS were performed by means of X-ray diffraction in 2θ range from 20 to 70° using Bruker Analytical X-ray diffractometer equipped with graphite mono chromatized CuKα radiation (λ=1.5418Å) which was obtained in thin film attachment after the powders were fixed on a glass piece with quick fix. Scanning electron microscopy (SEM) micrographs were recorded with the help of a JEM-2000FX (JEOL Ltd.) scanning electron microscope (operated at 20 keV). Thick film sensors were fabricated by screen printing technique on an alumina substrate. The paste was prepared by adding terpeneol, ethyl cellulose and butyl Carbitol. Thick film was annealed at 800 °C for 10 min. Optical absorption measurements were carried out by UV-Shimadzu UV-2400 PC spectrophotometer. Photoluminescence study of the samples was carried out by Horiba Jobin Yoon FL3-11 spectrophotometer in the solution itself. All the samples were excited with a wavelength of 370 nm.

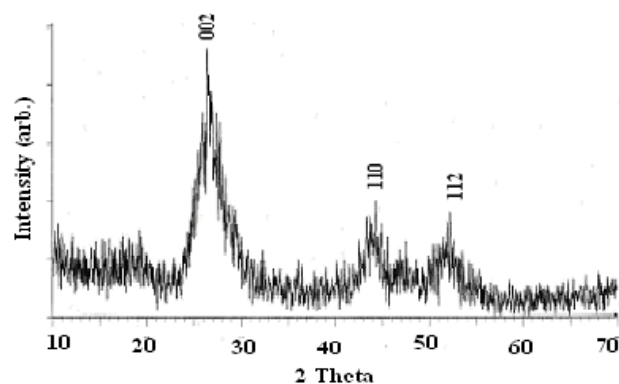


Fig. 1. Room temperature XRD pattern of CdS nanoparticles.

Results and discussion

XRD of CdS raw powder

Powder XRD pattern (Fig. 1) was obtained for CdS-B (thick over-layer). CdS normally exists in two different forms either hexagonal or cubic structure. All the diffraction peaks correspond to the characteristic diffractions of cubic CdS phase. All the peaks were broadened, which indicates that the CdS layer was composed of small sized crystallites. The main peaks correspond to the (002), (110) and (112) planes of cubic CdS phase. Lu et.al [5] reported the method for preparing nanocrystalline CdS hollow spheres using miniemulsion droplets as templates. He reported the average crystallite

size from Scherrer's formula is about 5-10 nm. The XRD reported by Lu et.al is very similar to our XRD.

From Scherrer equation (equation $P_{hkl} = 0.89 \lambda / \beta_{1/2} \cos \theta_{hkl}$, where λ is the wavelength of X-ray radiation, $\beta_{1/2}$ the width at half maximum of the diffracted peak and θ_{hkl} the angle of diffraction) the crystallite size of these nanoparticles from the XRD peak at $2\theta = 44.1^\circ$ was found to be ~ 5 nm. This shows that the CdS nano-particles were coated over the PMMA sphere templates.

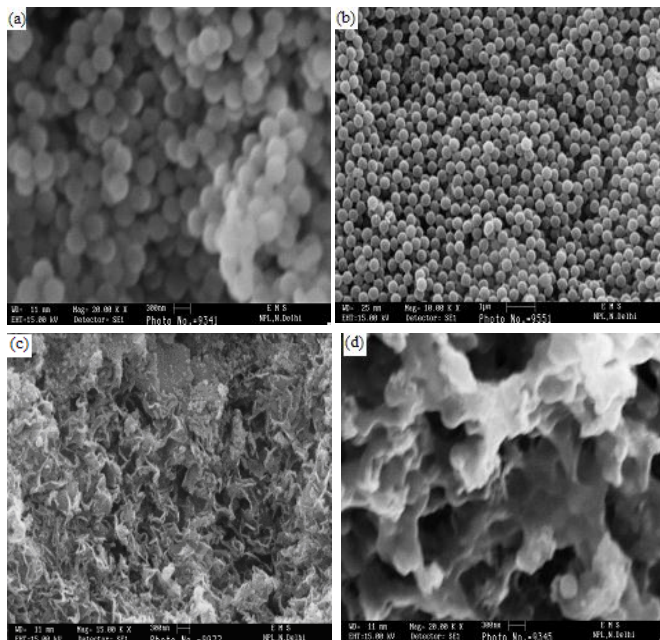


Fig. 2. SEM Micrograph of (a) CdSA, (b) CDS-B, (c) CDS-A1 and (d) CDS-B1 samples.

Microstructure

Fig. 2 (a) and (b) shows the microstructure of CDS-A and CDS-B. The diameter of the beads is about 265-310 nm. The change in beads size due to the CdS overlayer is not so apparent in (SEM or TEM) structures, due to its small thickness. The average diameter of the sphere is similar to that of the beads. Therefore, the spherical shells were obtained after the removal of PMMA core. Fig. 2 (c) and (d) shows the microstructure of CdS-A1 and CdS-B1. Some of the broken beads could clearly be observed, revealing the inner porous structure. This shows that the CdS shell comprising primary particles was not completely solid and most of the PMMA core was washed out through the small holes in the outer shell, leading to the formation of hollow CdS sphere. It is generally found that the hollow sphere prepared by soft chemical route using solutions consisted of a porous rather than a solid shell that allowed for the transfer of the core material out of the shell. Similarly, this technique can be used to fill the pores with other materials. In the EDAX spectrum (not shown here) of CdS coating, peaks were found which correspond to S, O and Cd. The other small peaks may be due to glass piece over which the spheres were mounted to be observed in SEM. The quantitative analysis shows the stoichiometry of the compounds have a little S deficiency. In general, CdS is usually S deficient showing n-type behavior due to S vacancies.

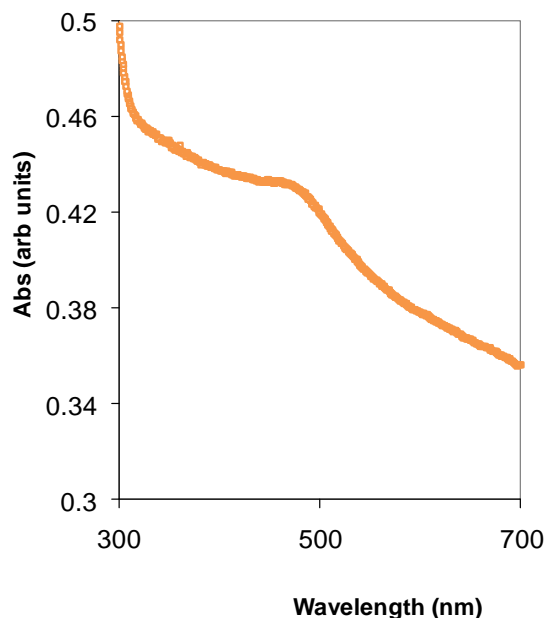


Fig. 3. UV-vis. absorption spectra of CdS-B sample.

Optical properties

The optical properties of the composites were investigated by UV-vis spectroscopy. Fig. 3 shows the U-visible absorption spectra of obtained core shell CdS/PMMA (CdS-B) sphere, which were obtained after the dried powder was re-dispersed in water. At 463 nm we got the peak in absorption spectrum. The band gap of bulk CdS is about 2.45 eV, showing an absorption onset of bulk at about 513 nm. This shows a blue shift in the absorption spectra due to the quantum size effect, which is quite possible due to the small size of the CdS nano crystals as is evident in XRD pattern. According to the experimental correlation between the absorption onset and the particle diameter for CdS, the particle size was estimated to be ~ 3 nm. It suggests that the size of the CdS nano crystallites constituting the hollow sphere is about 3 nm, which is in good agreement with XRD. The use of these composites and hollow spheres depend on the optical properties; because of it reflect the band to band shift and volume ratio of nano crystal.

Fig 4 (a) is for the CdS over coated layer CdS-A and (b) hollow spheres CdS-A1. The peak at 423 may be due to band to band transition and the higher wavelength peak may be due to S vacancies or surface defects. The second component near 600 is more intense which is as expected, since the nano crystals in this case (hollow shells) are not protected. The high surface /volume ratio of the nano crystals would show the defect band more intense. The luminescence intensity for CdS-A is better, as the nano crystallites are protected at least in one side with PMMA. The observed shift in the peak towards blue is related to the quantum effect. The defect band for this sample is at 679 nm, with a weak intensity. Therefore the PL emission of the hollow spheres indicated they actually consisted of primary CdS nano crystals showing quantum confinement effect.

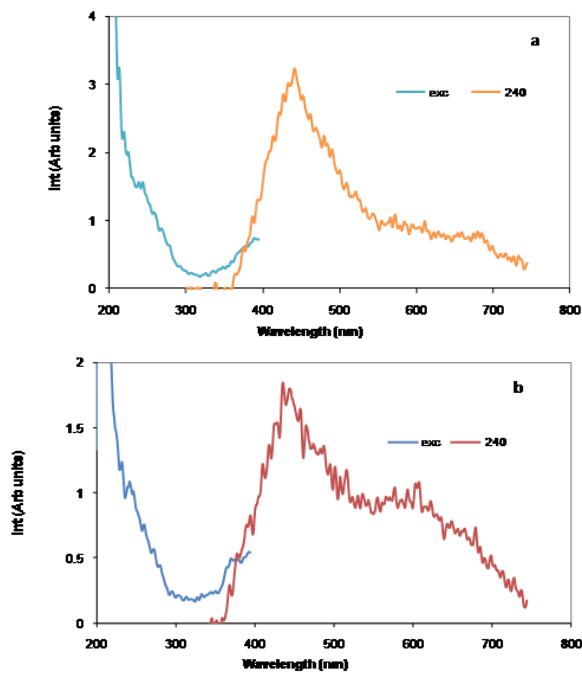


Fig. 4. PL excitation and emission pattern for (a) CdS-A and (b) CdS-A1 samples.

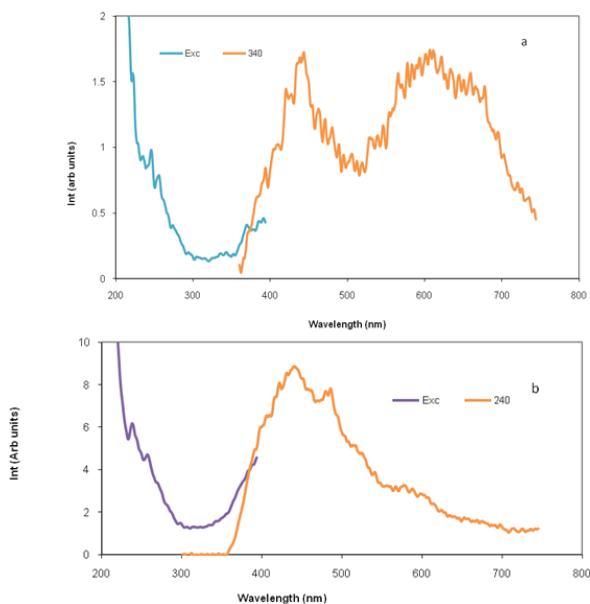


Fig. 5. PL excitation and emission pattern for (a) CdS-B and (b) CdS-B1 samples.

Fig. 5 (a, b) shows the PL excitation and emission pattern for the thicker over layer CdS-B, and after PMMA removal CdS-B1. The defect band is present at ~600 nm. No shift in the position of this peak with excitation wavelength suggests that this peak must also be related to intrinsic defects. The band to band transition peak (Excitonic peak) is observed at 444 nm, which clearly shows a large increase in the optical band gap due to the

nano sized coating. The hollow spheres showed a wider spectrum similar to sample CdS-B.

Conclusion

In summary a CdSe hollow structure of submicrometer size was prepared with this simple and novel method. Compared with the conventional routes, this method is simpler and more convenient. These hollow spheres have a wall thickness of about 5nm which consisted of CdS nano crystals with a cubic zinc blend structure. The CdS spheres show PL at 430 nm. This convenient synthetic route to prepare hollow CdS spheres can be readily extended to other technologically important metal chalcogenide semiconductors.

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