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Facile Synthesis and Characterization of MPA Capped CdSe and CdSe/ZnS Nanocrystals

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Abstract: Nanosized metal chalcogenides have aroused great interest in the scientific community owing to their important non linear optical properties, luminescent properties, quantum size effects and other important physical and chemical properties. CdSe is one such material which shows strong fluorescence, that can be tuned by simply varying the size of the particle for use in various applications such as biological fluorescence labeling, solar cells, light emitting devices etc. In this work, we report the successful synthesis of 3-mercaptopropionic acid (MPA) capped CdSe and CdSe/ZnS nanocrystals through a simple, safe, non toxic, cost effective and easily reproducible chemical synthesis followed by hydrothermal treatment. X-ray diffraction (XRD), UV-Visible spectroscopy (UV-Vis), Photoluminescence spectroscopy (PL), Fourier transform infrared spectroscopy (FT-IR) and High resolution transmission electron microscopy (HR-TEM) were used to study the structural, morphological and optical properties of the as-synthesized CdSe and CdSe/ZnS nanocrystals. From the obtained results, it was found that the synthesized CdSe and CdSe/ZnS nanocrystals exhibited zinc blende phase with good nanocrystallinity and the size of the particles were found to be around 8 nm for CdSe and around 6 nm for CdSe/CdS nanoparticles.

Key words: Facile Synthesis, Characterization, MPA Capped CdSe, CdSe/ZnS Nanocrystals.

Introduction

In recent years, semiconductor quantum dots have attracted much attention for many potential applications such as biological labels¹, biosensors², lasers³, light emitting diodes⁴, solar cells⁴ etc. due to their unique size dependent optical and electronic properties attributed to quantum size effect⁵. Chalcogenides especially of cadmium, lead and zinc have proved their potential as efficient absorbers of electromagnetic radiation. Among these, cadmium selenide nanostructures with interesting physical and chemical properties form a technically important class of materials owing to their widespread utility in a variety of applications⁶. For these semiconductor nanocrystals, when the particle sizes are smaller than the exciton Bohr radius, they exhibit novel electronic, optical, chemical and magnetic properties, which can be tuned by simply varying the size of the nanoparticles⁷. Moreover, core/shell nanostructures constitute a very special class of nanomaterials, where a noticeable enhancement in the luminescence and conductive properties is achieved by modifying the core surfaces typically by the process of encapsulation with the shell of desired material⁸. The optical properties of the core-only structure are greatly improved when a semiconductor shell is grown on the core⁹.

CdSe is a direct band gap semiconductor with the band gap of 1.74 eV and ZnS is also a direct band gap semiconductor with the band gap of 3.54 eV. Combining CdSe and ZnS in a single nanostructure creates a material with heterogenous carrier confinement or mixed dimensionality, where holes are confined to CdSe while electrons can move freely between CdSe and ZnS phases spreading over the entire nanostructure¹⁰. There are several methods for the synthesis of core- shell nanostructures, among which, the aqueous synthesis methods are more reproducible, cheaper and less toxic.

The main goal of our work is to synthesize and characterize CdSe and CdSe/ZnS core-shell nanoparticles with enhanced fluorescent properties through a simple and facile water-based chemical synthesis. The chemicals used in this synthesis of CdSe and CdSe/ZnS nanoparticles are environmental friendly and can be easily extended to large scale, aqueous phase production.

Experimental

Synthesis of CdSe core nanocrystals

Mercaptopropionic acid capped CdSe core nanoparticles were prepared by the following method: Briefly, certain mmol of CdO and MPA were dissolved in the given amount of distilled water and pH of the solution was adjusted by the dropwise addition of NaOH (1.0 molL^{-1}) solution with continuous stirring. This was used as the cadmium source. Next, 10 ml fresh NaHSe solution was obtained by the reduction reaction of Se powder and NaBH_4 in a three necked flask with continuous stirring until the selenium completely reduces in NaBH_4 and gives a clear colorless transparent solution. This was used as the Se precursor and the entire reactions were carried out in the presence of inert gas atmosphere. The molar ratio of Cd: MPA: Se was set to be 1:4:1. After the complete reduction of selenium, the CdO-MPA solution was added into the NaHSe in three necked flask, for the formation of CdSe nanoparticles. After rapid stirring, the solution was loaded into the autoclave and kept in the furnace at 160°C for 1 hr. The obtained samples were precipitated by the addition of ethanol followed by centrifugation. The precipitated samples were dried in vacuum to get the CdSe nanopowder.

Synthesis of CdSe/ZnS core/shell nanocrystals

Core CdSe nanocrystals were synthesized by the procedure described above. For the synthesis of CdSe/ZnS nanocrystals, additional amount of ZnCl_2 and MPA were dissolved in certain amount of distilled water in a separate beaker and pH of the solution was adjusted to 9 by 1.0 M NaOH solution. In another beaker, 0.8 mmol of thiourea is taken and dissolved in distilled water. The prepared ZnCl_2 - MPA and thiourea solutions were added into the core CdSe nanocrystals in sequence. After several hours of stirring, the resulting mixture was loaded into autoclave and maintained at 160°C for 1 hr. The obtained sample was collected by centrifugation and washed with distilled water and ethanol several times and dried in vacuum to get the CdSe/ZnS nanopowder.

Results and discussion

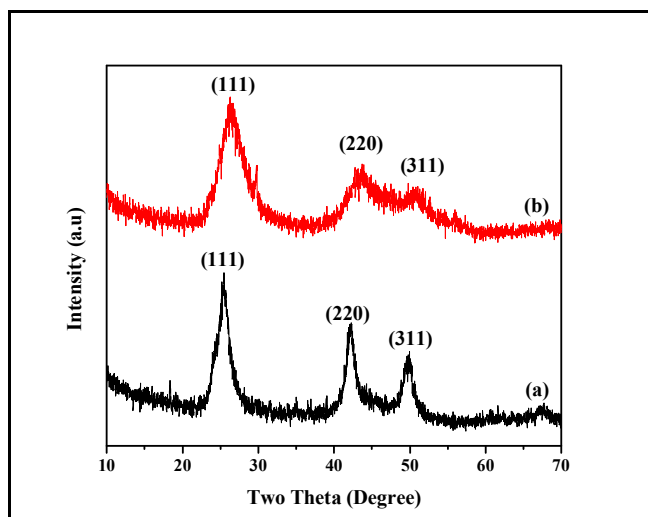


Figure 1 X-ray Diffraction patterns of MPA capped (a) CdSe nanoparticles (b) CdSe/ZnS nanoparticles

The X-ray diffraction pattern of the synthesized CdSe and CdSe/ZnS nanoparticles are shown in the Fig.1. The broad diffraction peaks for CdSe and CdSe/ZnS nanoparticles clearly indicates the nanocrystalline nature and the finite size of the nanoparticles. From the XRD pattern, it is observed that the CdSe nanoparticles exhibited three peaks at angles (2θ) of 25.37° , 42.08° , 49.75° whereas in the case of CdSe/ZnS nanoparticles the three peaks have been shifted towards larger angles (2θ) of 26.45° , 43.76° , 50.83° which confirms the formation of ZnS shell over the CdSe core nanoparticles. The observed diffraction peaks due to reflections from (111), (220) and (311) for both CdSe and CdSe/ZnS nanoparticles corresponds to the cubic zinc blende phase. This is in agreement with the standard JCPDS data 19-0191.

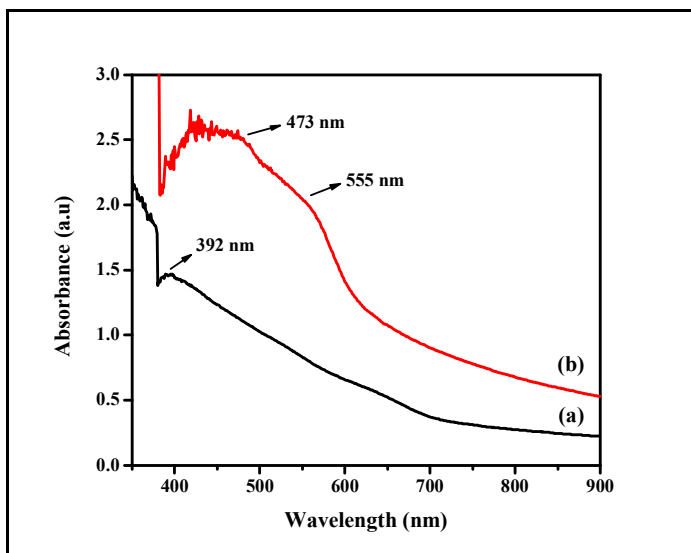


Figure 2 UV-Vis absorption spectra of MPA capped (a) CdSe nanoparticles (b) CdSe/ZnS nanoparticles

The optical properties of the as-synthesized MPA capped CdSe and CdSe/ZnS nanoparticles were determined by UV-Vis spectroscopy and photoluminescence measurements. Figure 2 illustrates the UV-Vis absorption spectra of the MPA CdSe and CdSe/ZnS nanoparticles. The absorption spectrum of CdSe nanoparticles exhibits an absorption edge at around 392 nm with the band gap of 3.16 eV. For CdSe/ZnS, the maximum peak absorption is seen around 470 nm, also an absorption shoulder at 555 nm and an absorption edge at 611 nm with the band gap of 2.62 eV. In both the cases, the absorption peak has been blue shifted in comparison with the bulk CdSe value of 716 nm (1.74 eV) and this is achieved due to the quantum confinement of the nanoparticles. In addition, the absorption peak of CdSe/ZnS nanoparticles has been red shifted in comparison to the absorption peak of the synthesized CdSe nanoparticles, which clearly supports the core-shell formation.

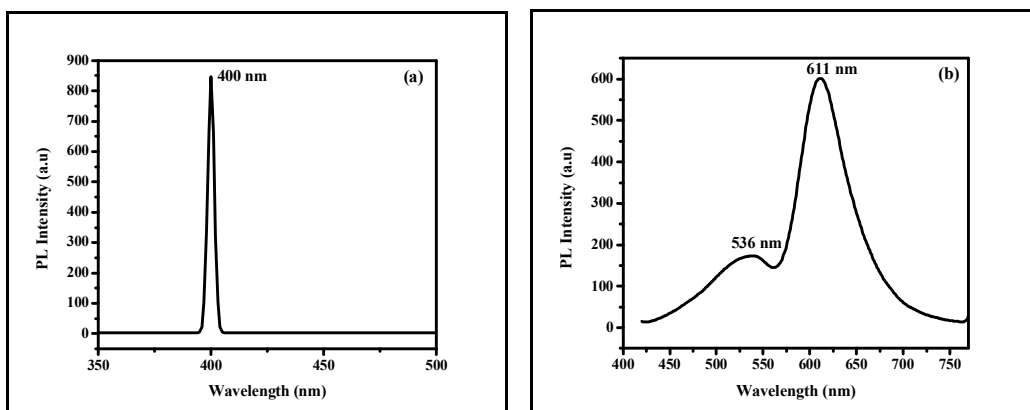


Figure 3 PL emission spectrum of MPA capped (a) CdSe nanoparticles (b) CdSe/ZnS nanoparticles

The photoluminescence spectra of MPA capped CdSe and CdSe/ZnS nanoparticles are illustrated in Figure 3. The CdSe nanoparticles show a narrow and strong emission peak at 400 nm. In contrast, the CdSe/ZnS nanoparticles show a broad and strong emission peak at 611 nm and a weak emission peak at 536 nm, in both the cases with an excitation wavelength of 400 nm. Blue shifting of the emission peaks has been

observed for CdSe and CdSe/ZnS in comparison with the bulk value of CdSe and for CdSe/ZnS the emission peak has been red shifted to nearly about 211 nm from the emission peak of the synthesized CdSe nanoparticles. This red shift of the emission peak for CdSe/ZnS nanoparticles is due to the capping of ZnS shell over the CdSe core and the quantum confinement effect caused by the decrease in particle size. Moreover, the photoluminescence spectrum also indicates that the ZnS capping enhances the luminescence to a greater extent.

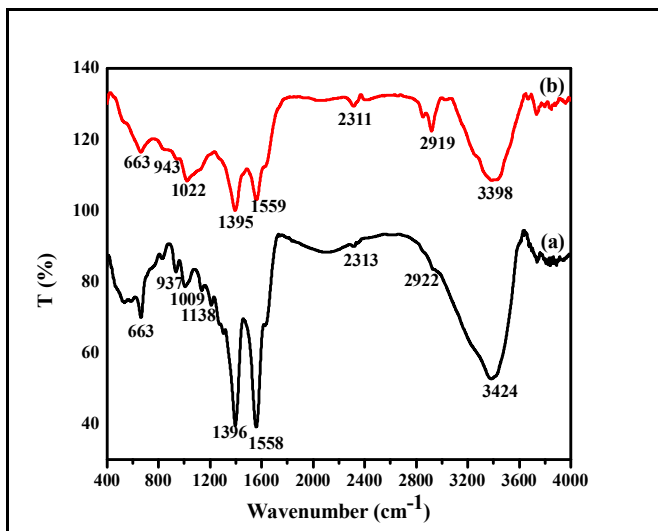


Figure 4 FTIR spectra of MPA capped (a) CdSe nanoparticles and (b) CdSe/ZnS nanoparticles

The FTIR spectra of the as-synthesized CdSe and CdSe/ZnS nanoparticles are shown in the Figure 4. The strong absorption peak at 3424 cm^{-1} for CdSe and 3398 cm^{-1} for CdSe/CdS arises due to the hydroxyl bond (O-H) stretching which confirms that the OH groups remain intact on the surface. The weak IR peak at 2922 cm^{-1} for CdSe and 2919 cm^{-1} for CdSe/CdS corresponds to the $\text{CH}_2\text{-S}$ stretching. These peaks support the onset of covalent bonds between S and Zn^{2+} ions at the nanoparticle surface, thus binding the ZnS shell onto the CdSe core. The narrow and strong peaks at 1558 cm^{-1} , 1396 cm^{-1} for CdSe and a short peak at 1559 cm^{-1} , 1395 cm^{-1} for CdSe/ZnS nanoparticles correspond to the COO^- vibrations. The bands positioned at 1009 cm^{-1} for CdSe and, at 1022 cm^{-1} for CdSe/ZnS are due to the C-O stretching. The peak 1138 cm^{-1} , which appears in CdSe spectrum does not exist in CdSe/ZnS which confirms the capping of ZnS.

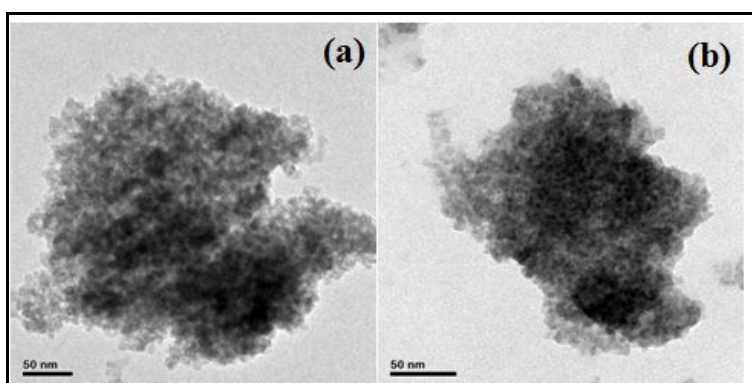


Figure 5 HRTEM images of MPA capped (a) CdSe nanoparticles and (b) CdSe/ZnS nanoparticles

The morphology and the size distribution of the synthesized CdSe and CdSe/ZnS nanoparticles were characterized using the HRTEM. The HRTEM images (Figure 5) of both CdSe and CdSe/ZnS nanoparticles depict that the particles are monodisperse, spherical in shape and dense with the tendency of agglomeration. In addition, the average diameters of the particles were found to be around 8 nm for CdSe nanoparticles and around 12 nm for CdSe/CdS nanoparticles. The lattice spacing of CdSe and CdSe/ZnS nanoparticles can be clearly observed from the HRTEM images.

Conclusion

In summary, mercaptopropionic acid capped CdSe and CdSe/ZnS have been successfully synthesized through a chemical synthesis involving the non toxic precursors for an environmentally benign approach. Several techniques such as; XRD, UV-Vis absorption spectroscopy, PL, FT-IR and HRTEM were used to characterize the synthesized CdSe and CdSe/ZnS nanoparticles. Experimental results confirmed the formation of CdSe and CdSe/ZnS nanoparticles with good absorption and luminescence property. The FTIR analysis confirmed the capping of MPA and ZnS shell formation over the CdSe core nanoparticles. These type of nanoparticles are the most promising candidates for applications relying on good photoluminescence properties such as biological labeling or displays and lighting.

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