

Synthesis and characterization of aqueous MPA-capped CdS–ZnS core–shell quantum dots

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Abstract. The novel CdS–ZnS core–shell nanoparticles are synthesized using simple one-step aqueous chemical approach. 3-mercaptopropionic acid (MPA) was used as the capping molecule. The structural and optical properties of the prepared samples are characterized by X-ray diffraction (XRD), UV–vis absorption spectroscopy, photoluminescence (PL) spectroscopy, energy-dispersive X-ray (EDX) and transition electron microscopy (TEM). The studies show that pH contributed noticeably to the growth and optical properties of nanoparticles. The TEM results indicate that the prepared particles have core–shell structure.

Keywords. CdS–ZnS core–shell; pH effect; optical response.

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1. Introduction

Nanostructures have drawn a lot of attention because of their promising potential applications in biological tagging [1–5], photovoltaic [6–10] and display devices [11]. Semiconductor nanocrystals can attain some novel properties by coating them with a different inorganic shell. Groups II–VI semiconductor core–shell structured nanocrystals, which are expected to exhibit unique optical and electronic properties, have been successfully synthesized by epitaxial growth. For example, the small lattice mismatch of 7.3% between CdS and ZnS is responsible for the epitaxial growth of the CdS–ZnS core–shell nanocrystals. These type I core–shell nanocrystals with a high PL quantum yield (QY) are widely used in light-emitting diode (LED) biological labelling [12–15]. Enhancement of QY was attributed to the effective passivation of surface traps by the formation of the shell. Mekis *et al* [16] have showed that QY can be enhanced up to a maximum of 85%

by forming a shell of CdS around CdSe core. Over the past two decades, numerous colloidal chemistry or solution chemistry methods were developed for preparing CdS QDs [17]. The chemical synthesis of CdS QDs utilized organic stabilizers to cap the surface atoms of nanoparticles to control the growth process. In particular, these nanocrystals can be easily modified with various functional groups during or after preparation, which make them multifunctional. Numerous studies are known to focus on surface chemistry, capping strategies and enhancement of photoluminescence (PL) efficiencies. The type of stabilizer is of great importance as it affects the chemical as well as the physical properties of the semiconductor QDs, from stability to solubility to light emission. Also, by introducing high-temperature organometallic approach and its alternative using tri-octylphosphine oxide, long-chain amine, or long-chain carboxylic acid as capping agents [18,19], the synthesis of CdS QDs became more effective. Even though the conventional organometallic hot injection route is highly successful even with high cost, unfriendly and rigorous experimental conditions, there are some inherent limitations in this route. For example, these as-prepared QDs cannot be directly used in biological applications due to their hydrophobic character. Along with the success of organic synthetic routes, aqueous synthetic routes have been developed to prepare CdS QDs. Compared with the non-aqueous synthesis, aqueous synthesis is more productive, less costly, more environment friendly and the 'as-prepared' samples are more water soluble and biocompatible. In the aqueous phase synthesis of CdS NCs, the conventionally homogeneous phase arrested the precipitation using phosphates, various thiols or hydrophilic polymers as capping reagents are usually adopted [20]. In recent years, there is an increased interest in coating nanoparticles with shell materials for various applications [21,22]. There are many parameters for controlling the size, shape and properties of core-shell nanoparticles. At present, work is in progress to control the physical properties of core-shell nanoparticles more systematically. In this paper, we describe a simple one-step aqueous synthesis method to produce CdS and CdS-ZnS nanocrystals using 3-mercaptopropionic acid (MPA) as the capping molecule. The structural and optical properties of the nanoparticles samples are investigated precisely.

2. Experimental details

2.1 Materials and synthesis of MPA-capped CdS and CdS-ZnS nanoparticles

All the chemicals were used as received without further purification and were obtained from Merck. The typical synthesis procedure is as follows: solutions of CdCl₂ and MPA were mixed, titrated to pH = 9.2, 10.2, 11.2, 12.2 with NH₄OH, and saturated with N₂ for 1:30 h. An aqueous solution of Na₂S·9H₂O was then quickly injected into CdCl₂ solution. The molar ratio of Cd²⁺ : stabilizer : S²⁻ was fixed at 1 : 2 : 1. For the ZnS shell growth, first, solutions of Zn(NO₃)₂ and MPA were mixed, titrated to pH = 11.2 with NH₄OH, and saturated with N₂ for 1:30 h.

Then Zn(NO₃)₂ solution at pH = 11.2 was added to CdS solution at pH = 11.2. Finally, Na₂S solution was added slowly. The molar ratio of [CdS]/[ZnS] was 2. The powder samples were precipitated from the QDs suspension by adding ethanol followed by centrifugation and dried in room temperature.

2.2 Characterization methods

The structure of nanoparticles was identified by X-ray diffraction (XRD), using a Philips PW 1800 with Cu K_{α} radiation at $\lambda = 1.5418 \text{ \AA}$. UV–vis measurements were made with a Scan Carry 100 spectrometer. The photoluminescence spectra were taken with Perkin-Elmer LF 5 at room temperature using 360 nm wavelength as the excitation wavelength. The transmission electron microscopy (TEM) studies were done with Philips CM 10 operated at 200 kV and the chemical composition of the samples were investigated by the energy-dispersive X-ray (EDX) spectroscopy system, Philips CM 10.

3. Results and discussion

3.1 The UV–vis characterization of the MPA-capped CdS nanoparticles

Figure 1 shows the UV–vis absorption spectra of MPA-capped CdS nanoparticles at different pH. The four spectra have a blue shift compared to the bulk CdS (515 nm) due to smaller size of the particles and the increased band-gap energy (quantum confinement effect) [23]. The thiol group of the MPA attached to the Cd cations on the surface of the particles and the carboxyl groups on the other end of the MPA were fully charged at high pH. MPA was fully charged at high pH and it was an important factor for the colloidal [24] stability and particle size of nanoparticles. The absorption edge of the MPA-capped CdS at pH = 11.2 was smaller than other samples with different pH.

3.2 The PL characterization of MPA-capped CdS

Figure 2 shows that increase in pH of the solution from 9.2 to 11.2 during synthesis increases emission intensity of the CdS QD. This can be understood by the properties of MPA. The pH of the thiol group is about 8.3. At higher pH, more thiol

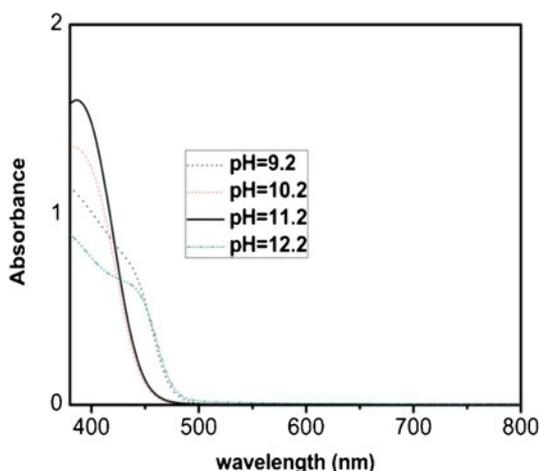


Figure 1. Absorption spectra of MPA-capped CdS nanoparticles at different pH.

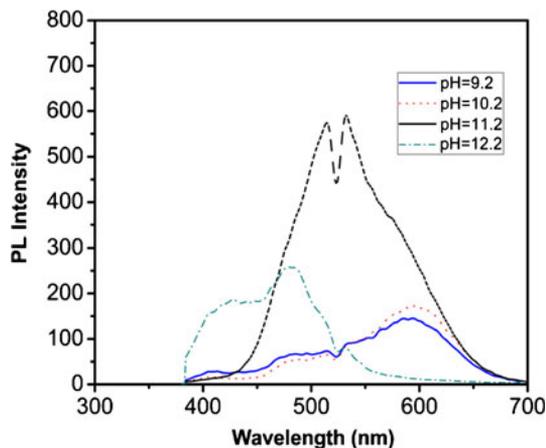


Figure 2. PL spectra of MPA-capped CdS nanoparticles at different pH (obtained after excitation at 360 nm and at room temperature).

groups became dehydrogenated, which was expected as the strength of the covalent bonding between MPA and Cd^{2+} on the surface of the QDs increased. In addition, the higher pH promoted the negative charge of the carboxyl groups of MPA and helped to disperse the nanoparticles better. Furthermore, the solubility of CdS decreased with increasing pH which benefited from the nucleation and growth of QDs and therefore generated more nanoparticles. All these effects would help improve the PL intensity of QDs at higher pH. When $\text{pH} = 12.2$ there was a decrease in the intensity of emission. So CdS nanoparticles, with $\text{pH} = 11.2$ which have the highest emission intensity and the best peak absorption, have been chosen as the core.

3.3 The UV-vis characterization of CdS-ZnS core-shell

Figure 3 shows the UV-vis absorption spectra of MPA-capped CdS and CdS-ZnS nanoparticles synthesized at molar ratio 2. Quantum confinement effect is evident in these graphs [23]. The absorption edge of CdS-ZnS shifts to lower wavelengths from that of CdS alone. So, shell formation was confirmed by the observation of a red shift in the UV-vis absorption spectra. Peng *et al* [25] and Dabbousiet *et al* [26] have also observed similar behaviour for CdSe-CdS and CdSe-ZnS core-shell structures.

3.4 The PL characterization of MPA-capped CdS-ZnS core-shell

The PL spectra of CdS and CdS-ZnS are shown in figure 4a at an excitation wavelength of 360 nm along with the optical absorption spectra. It can be seen in figure 4b that there

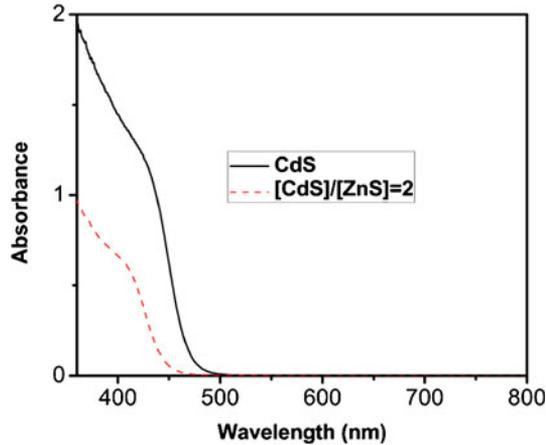


Figure 3. UV–vis absorption spectra for MPA-capped CdS and CdS–ZnS nanoparticles.

is a strong emission peak at 410 nm for CdS–ZnS nanoparticles. This peak is similar to the result of the UV–vis absorption wavelengths of the corresponding CdS–ZnS nanoparticles and the above emission peak is due to band-edge emission [27,28]. The emission peaks, at 514 nm and 532 nm, resulting from surface defect, belong to shallow and deep trap emission of CdS [29,30]. For CdS–ZnS nanoparticles, the intensity of these three emission peaks is stronger than that for CdS nanoparticles. This should come from the luminescence quench effect.

3.5 The XRD characterization

Figure 5 shows the XRD patterns of the as-prepared MPA-capped CdS QDs and the core–shell CdS–ZnS QDs at the room temperature. All the XRD peaks can be indexed to the

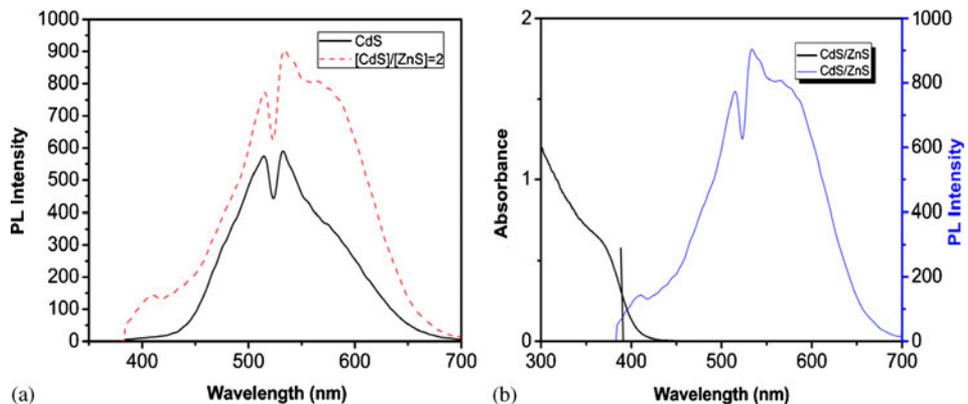


Figure 4. (a) PL spectra of MPA-capped CdS and CdS–ZnS nanoparticles and (b) intersection of PL and absorption spectra which shows absorption edge.

cubic zinc blend structure of CdS. The three main peaks corresponding to the (1 1 1), (2 2 0) and (3 1 1) planes are indicated in figure 5. It can be observed that these peaks are broad compared to the bulk CdS, confirming the nanocrystalline nature of all the samples and the size of particle is very small. In the case of composite samples, we observe very broad bands which arise due to the overlapping of XRD peaks of both CdS and ZnS [31,32] but apparently no peak is observed for free ZnS particles. Also, the position of diffraction peaks are closer to CdS bulk than to ZnS bulk which means that no alloy sample was formed as otherwise peaks position will be closer to ZnS bulk [33]. The crystallite size of the samples was calculated from the peak width (111) using the Debye–Scherrer formula [34] ($D = k\lambda/\beta \cos \theta$, k is the Scherrer constant, λ is the X-ray wavelength, β is the peak width of half maximum and θ is the Bragg diffraction angle). The average crystallite size D of CdS and CdS–ZnS nanoparticles obtained is about 2.7 nm and 1.7 nm at room temperature, respectively.

3.6 Energy-dispersive X-ray spectroscopy of MPA-capped CdS–ZnS nanoparticles

The chemical components of the core–shell samples were investigated by EDX and FTIR spectroscopy. From the EDX pattern (figure 6) of the sample, Zn element can be seen clearly in the results. The results of EDX measurement reveal that the core–shell nanocrystals have a high purity and the ratios found were 42.9% S, 20.7% Zn and 36.39% Cd. The Cd/S ratio of 0.8 and Cd/Zn ratio of 1.75, are in a very good agreement with the values used in the experiment Cd/Zn = 2, Cd/S = 1 (§2.1).

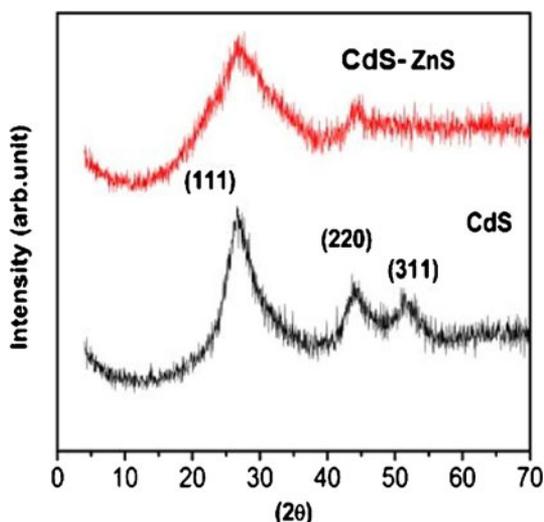


Figure 5. XRD peak patterns for MPA-capped CdS and core–shell CdS–ZnS QDs at room temperature.

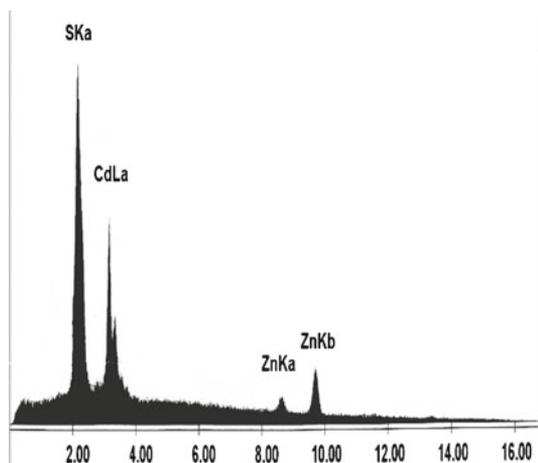


Figure 6. EDX analysis of the prepared CdS–ZnS nanoparticles.

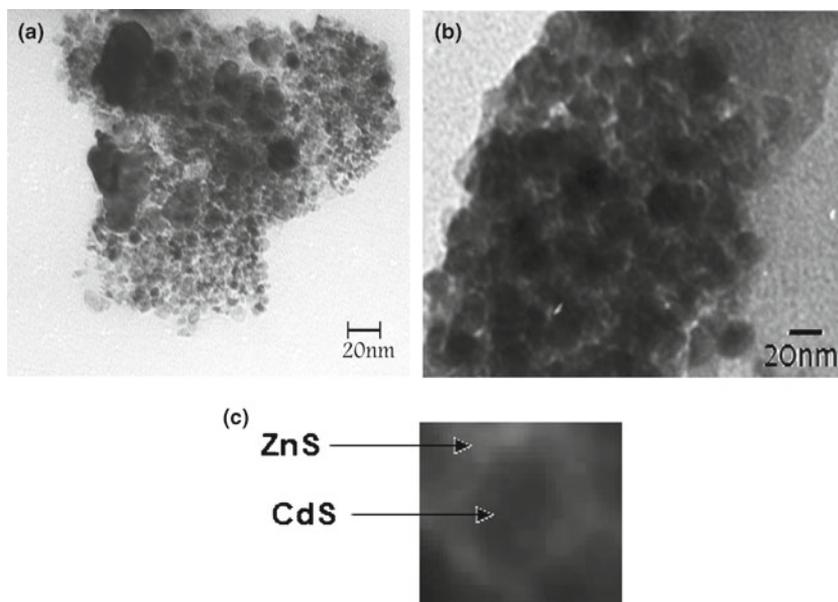


Figure 7. TEM images of the prepared MPA-capped (a) CdS nanoparticles, (b) CdS–ZnS nanoparticles, (c) single nanoparticle core–shell. TEM image scale is given in 20 nm.

3.7 TEM images of MPA-capped CdS and CdS–ZnS nanoparticles

The morphology and microstructure of the samples were investigated by the transmission electron microscopy (TEM). Figures 7a, b show TEM micrographs of MPA-capped CdS

and CdS–ZnS nanoparticles respectively and figure 7c shows the single core–shell particle. A drop of ethanol-dispersed QDs is placed on a carbon-coated grid, and allowed to dry. The mean size is calculated by measuring an average of 50 nanoparticles per micrograph. Dispersion and aggregation of particles is evident in the image and zoom the image, the round particles is determined. From the image, we can see the light gray shells of ZnS surrounded the darker CdS nanoparticles as cores. The average size of the particle was estimated to be about 2.7 nm for CdS and about 1.7 nm for CdS–ZnS core–shell which is consistent with the value calculated from XRD diffraction peak. The aggregation may have occurred during the spreading and drying of nanoparticles on the carbon-coated grid as sample holder in TEM instrument.

4. Conclusions

A simple one-step aqueous synthesis method was used to produce the novel core–shell CdS–ZnS nanoparticles using 3-mercaptopropionic acid (MPA) as the capping molecule. It is also shown that the pH value of the solution and capping layers played important roles in the formation of particles. The TEM results indicated that the prepared particles have a core–shell structure. The CdS core has a cubic phase and the average crystallite size of CdS and CdS–ZnS core–shell were 1.7 nm and 2.7 nm, respectively. The thickness of ZnS shell can be tuned by controlling the amount of shell precursor solution.

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