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Synthesis and optimization of CdTe quantum dots with the auxiliary of erythorbic acid and ethanol

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ABSTRACT:

The effect of erythorbic acid (EA) and ethanol on the aqueous formation of CdTe quantum dots (QDs) was explored in this work. Without N_2 protection, CdTe QDs was synthesized with $CdCl_2$ and NaHTe as Cd source and Te source respectively, together with EA and 3-mercapto-propionic acid (MPA) as the co-passivating ligand. The experimental results indicate that the use of the oxygen scavenger, i.e., EA, was critical for the formation of the CdTe QDs with reasonably good optical properties. Ethanol was added in the synthesis system, and the photoluminescence intensity was improved with the addition of ethanol. To attain a good optical property, it is also important to tune experimental parameters such as pH, temperature, reaction time, molar ratio of MPA/Cd, and $NaBH_4$ dosage. The very reason for the EA promoted formation of CdTe QDs is due to its reducibility and passivation on the QD surface. The present study suggests that the use of EA and ethanol could be a practical means to promote the photoluminescence of CdTe.

INTRODUCTION

Nanostructured semiconductors, in particular quantum dots (QDs), are one of the most promising types of nanoparticles that hold potential for a variety of new applications such as light-emitting [1] , solar cell [2] , bio-labeling [3] due to their unique optical properties [4-8]. The CdTe QDs have the prominent features of sizable absorptions throughout the visible and near-infrared spectra, narrow and widely tunable photoluminescence along with high stability against photo-bleaching in comparison with traditional organic dyes, leading to intense studies and wide applications[9-18].

To date, several different synthesis methods including organic path and aqueous path have been developed to prepare CdTe QDs [19-23]. Although high-quality CdTe QDs can be prepared in organic phases, they are unable to be directly used in biosystems owing to the hydrophobility of the QDs. Compared with organic synthesis, aqueous synthesis has the advantages of simplicity, high reproducibility, less toxicity, and low cost [24, 25]. In addition, the aqueous process associated with relatively low temperature (typically 90-100 °C) is green and much cheaper, which is more attractive for the large-scale production of QDs.

In aqueous synthesis of QDs, weak reductive agents such as N_2H_4 can scavenge oxygen and usually promote aqueous QDs growth. It is a simple approach to improve luminescence of CdTe QDs by taking advantage of the reducibility of N_2H_4 to protect QDs and thiol ligands from oxidation [26-28]. In our previous study, erythorbic acid (EA), an efficient oxygen scavenger and weak reductive agents, was employed to promote luminescence of CdS in aqueous medium at room temperature[29]. In this work, EA was exploited as an efficient electron donor for scavenging photogenerated holes on CdTe QDs and promoting the fluorescence intensity of CdTe QDs. Also, ethanol was added in the synthesis system to improve the optical properties.

2. EXPERIMENTAL SECTION

2.1 Materials

$CdCl_2 \cdot 2.5H_2O$ (≥99%) and tellurium powder (≥99.99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. 3-mercapto-propionic acid (MPA, 98%) and erythorbic acid (EA, 99%) were purchased from Aladdin Chemistry Co., Ltd. NaOH (≥96%) was purchased from Beijing Chemical Works. $Na_2S \cdot 9H_2O$ (≥98%) was purchased from Xilong Chemical Co., Ltd. $NaBH_4$ (96%) was purchased from Shanghai Chunsheng Fine Chemical Technology Co., Ltd. All chemicals were of analytical grade and used as received.

2.2 Synthesis of aqueous CdTe QDs in the presence of erythorbic acid

A modified literature method for preparation of NaHTe was used [30]. Briefly, place 0.4 mmol of tellurium powder and 2 mmol of sodium borohydride in gas-tight syringe and draw up 10 mL of ultrapure water. Then put the syringe into a water bath at 80℃. The pinhead can discharge the resulting hydrogen. The syringe pinhead jointed with a pipe which was liquid sealed. After 30 minutes, the black tellurium powder disappeared, and the pink NaHTe solution was prepared.

Typically, the Cd source was prepared as follows: 5 ml of 40 mM $CdCl_2$ and 0.4 mmol of MPA were added into a beaker in sequence, followed by adjusting the pH to 8 with 5M NaOH, then 10 mL of 20 mM EA was added. The pH was tuned to 8 again, and the volume was adjusted to 30ml with water. One mililiter of NaHTe was injected into the Cd source from the syringe. The reaction was carried out at 95 °C for 3 hours to synthesize CdTe QDs. Samples of the obtained QDs solution were taken and diluted with water for UV/Vis and PL characterization. The samples were not purified before the characterization.

Then the as-prepared CdTe QDs were precipitated with excessive ethanol, and the precipitate was separated by centrifugation and re-dissolved in water. This process was repeated for several times to purify the CdTe QDs for XRD and HRTEM characterization.

2.3 Characterizations

UV visible absorption spectra were obtained using a Lambda 950 UV-VIS-NIR spectrophotometer. Fluorescence spectroscopy was performed with a Varian Cary Eclipse spectrophotometer. X-ray diffraction (XRD) pattern was recorded with a

Shimadzu XRD-6000 diffractometer. High-resolution transmission electron microscopy (HRTEM) analysis was conducted on a JEOL JEM-3010 microscope.

3. RESULTS AND DISCUSSION

3.1 XRD and HRTEM analyses of as-prepared CdTe QDs

Fig.1 shows the XRD pattern of the as-prepared CdTe QDs. The peaks at *ca*. 2θ = 24.51°, 40.83° and 46.82° agree with those of zinc blende in the JCPDS (Joint Committee on Powder Diffraction Standards) database, indicating that the as-prepared CdTe QDs has a zinc blende structure. The HRTEM image of the as-prepared CdTe QDs (Fig. 2) shows that the CdTe QDs are spherical particles with narrow size distribution and good dispersion and the particle size is about 3 nm. The quantum yield of the as-prepared CdTe QDs is 35%, which was measured according to the method described in literature[31].

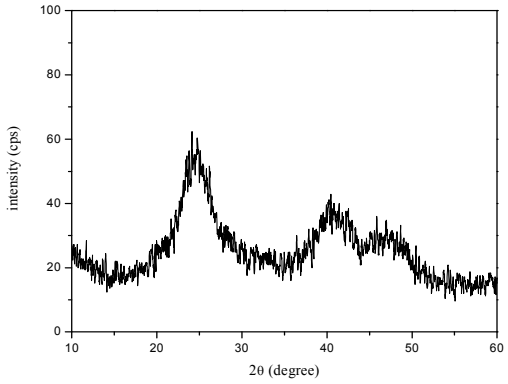

Fig. 1. XRD pattern of EA promoted MPA-capped CdTe QDs

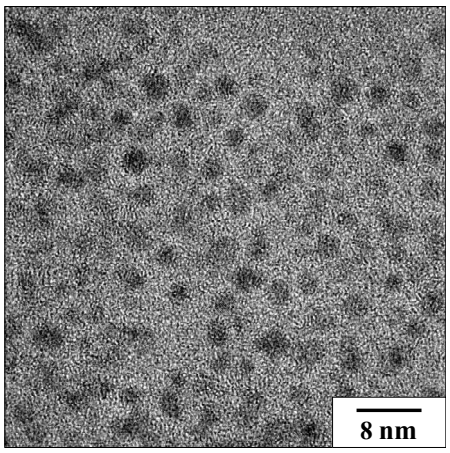

Fig. 2. HRTEM image of EA promoted MPA-capped CdTe QDs

3.2. Effect of pH value of Cd precursor

pH value is an essential factor that strongly influences the optical performance of QDs via aqueous synthesis[32]. With a molar ratio of Cd/MPA as 1:2, reaction temperature at 95℃ and reaction time of 3 h, the effect of pH values of Cd precursor at 6.0–13.0 on the QDs' UV−vis absorption spectra was studied. It can be seen from Fig.3 that with the decrease of pH, the absorbance of the solution slightly increases owing to the large aggregates of CdTe. As the aggregates grow in size and the QDs continue to form colloidal suspension, scattering increases. The absorbance measurements, which are sensitive to scattering from colloidal aggregates, are reflective of the dispersion of QDs in solution. Lower pH promotes the formation of free thiols and uncoated QDs. As a consequence, lowering the pH value enhances the formation of aggregates of as-prepared CdTe QDs [33]. With higher pH, the absorption spectra of the QDs become broader and show marked red shift. This phenomenon was due to the effect of pH values on the surface S-H bond strength. With the increase of pH value, the binding force and capped Cd^{2+} increased, resulting in the formation of larger QDs. However, when the pH value was too high, the formation of $Cd(OH)_2$ interfered with QDs' surface nature, leading to the decline of optical properties. Therefore, pH=8 was determined as a suitable parameter.

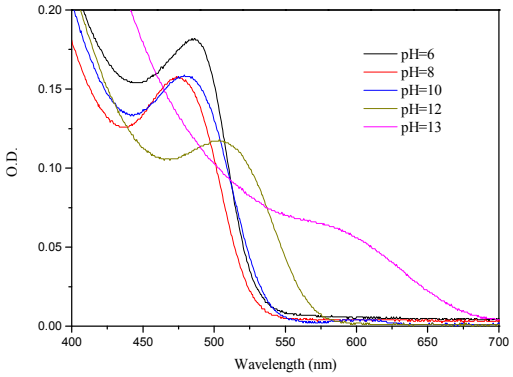

Fig.3. UV−vis absorption spectra of EA promoted MPA-capped CdTe QDs prepared with different pH

3.3. Effect of reaction temperature

The increase of reaction temperature from 25℃ to 200℃ had a significant effect on the UV−vis absorption spectra of the as-prepared CdTe QDs as shown in Figure 4. Reaction temperature, which controls the nucleation rate, is an important factor for QDs quality [34]. With moderate increase in temperature from 25℃ to 100℃, the QDs started to grow quickly, indicating the growth of crystals requires a relatively higher temperature [12]. The rising temperature affected the complex constants, leading to the increase of the free monomer concentration in the subsequent growth. In the Ostwald ripening stage, it was expected that the equilibrium process existed between the stabilizer and the water molecules on the CdTe surface sites. However, when the temperature was too high, the detaching rate of ligands form QDs surface was accelerated [35], leading to fast growth of CdTe QDs, and the crystals grow too fast to allow sufficient reaction with stabilizers [13]. At temperature more than 100℃, it was possible that fewer ligands occupied the surface sites, and more surface defects easily appeared due to the lower coverage provided by the ligands, suggesting that there existed a certain amount of dangling bonds at the surface of QDs [36]. Thus, the optical properties of the CdTe QDs lowered. The experiments proved that the CdTe QDs prepared at 100 °C had the best optical properties.

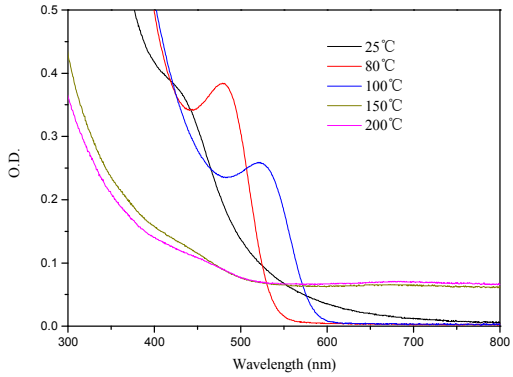

Fig.4. UV−vis absorption spectra of EA promoted MPA-capped CdTe QDs prepared with different temperature

3.4. Effect of reaction time

Reaction time is another important factor for the synthesis of high quality QDs. Fig. 5 shows the fluorescence spectra of the QDs prepared at 95 ℃ and different reaction time. The PL spectra of the EA promoted MPA-capped CdTe QDs shifted to longer wavelengths with the growth of CdTe QDs. With the increase of reaction time from 10 min to 30 min, the fluorescence intensity decreased slightly, most likely due to the oxidation of the stabilizer molecules which resulted in reduced stabilization effect of the ligands and increased surface defects of QDs [12]. The fluorescence intensity increased with the prolonging of reaction time from 30 min to 6 h accompanied with obvious red shift of the maximum emission wavelength from 520 nm to 610 nm, reaching the maximum intensity with a reaction time of 6 h. The red shift of emission maximum position and spectral broadening with increasing reaction time were probably due to the increase in size and/or aggregation of the QDs [37].

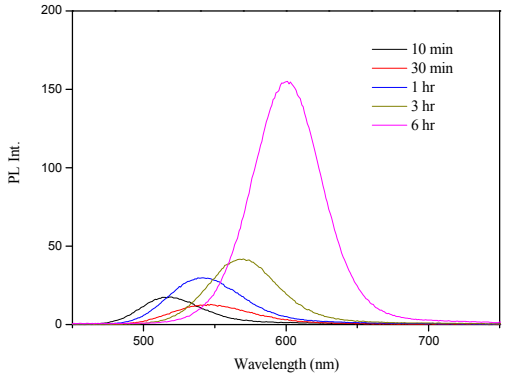

Fig.5 PL spectra of EA promoted MPA-capped CdTe QDs prepared with different reaction time

3.4. Effect of molar ratio of MPA/Cd

The proper passivation of the QDs surface with ligands can produce high-quality semiconductor nanocrystals [38]. The MPA molecules on the surface sites instead of Te atoms favor the removal of the dangling bonds of Te atoms from the surface, and also prevent the oxidation of Te atoms[39]. Excessive MPA coverage may eliminate the surface defects of the QDs that are generally adverse to luminescent emission. Molar ratio of MPA/Cd was varied from 1.5 to 16 to investigate the effect of stabilizer concentration on the optical properties of CdTe QDs. As shown in Fig. 6, with increasing MPA/Cd molar ratio, the UV absorption peak of QDs became wider, which indicates a worse size focusing and monodispersity. One possible explanation is that a large amount of ligand molecules may crosslink with each other on the surface of QDs, resulting in more surface defects. When the MPA/Cd was 16, the UV absorption peak was red shifted. This can be explained by the fact that the excessive amount of MPA in solution led to an increasing hydrolysis of MPA, and as a result, a higher sulfide S^{2-} content in the reaction medium that accelerated the QDs growth [36]. The excess monomers in the precursor solution can be consumed to cause a fast growth of CdTe QDs, leading to the coarse surface and low optical property.

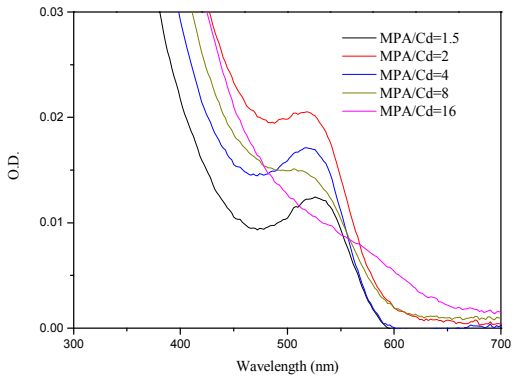

Fig.6. UV−vis absorption spectra of EA promoted MPA-capped CdTe QDs prepared with different ratio of MPA/Cd

3.5. Effect of EA dosage

The effects of EA dosage on the optical properties of CdTe QDs were investigated. It can be seen from Fig. 7a that with the increase of EA dosage, the absorption peak became blue shifted due to competing light-induced surface oxidation processes. As can be seen from Fig.7b, there was an enhancement in the luminescence intensity when EA was added to the QDs synthesis system. The intensity of CdTe QDs increased with the incremental dosage of EA. This was due to the reduction of the oxidized states on the surface and the passivation of CdTe QDs by EA. It was reported that certain antioxidants consume the oxidized surface atoms resulting in the fluorescence restoration. It can be thus deduced that the formation of Cd-erythorbate protective layer is responsible for the increase in the emission intensity.

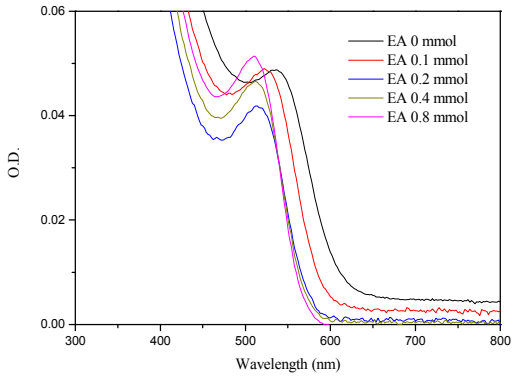

Fig.7a UV−vis absorption spectra of EA promoted MPA-capped CdTe QDs prepared with different dosage of EA.

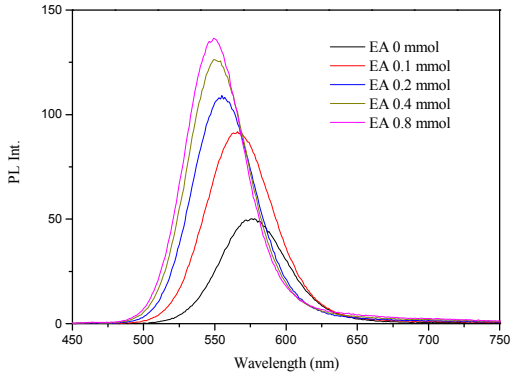

Fig.7b. PL emission spectra of EA promoted MPA-capped CdTe QDs prepared with different dosage of EA.

3.6. Effect of ethanol dosage

In comparison with other aqueous-phase approaches, the main difference of the route in this work is the use of ethanol and water mixture as a solvent for the preparation of NaHTe. The water/ethanol ratio in the mixture was 1:4, 1:1, 4:1 and 4:0 (pure water) respectively. It can be seen from Figure 8a that the fluorescence property was enhanced with the increase of the water/ethanol ratio from 1:4 to 4:1. When the water/ethanol ratio was 4:1, the photoluminecence intensity was higher than that by the approach with pure water solvent. The super PL performance can be attributed to

particle aggregation that was caused by weak hydrogen bonds of stabilizer with ethanol [40]. However, the PL intensity decreased with more ethonal added into the synthesis system because free MPA were scarce due to the weak hydrogen bond with ethanol and most of them were either directly bonded to the surface of the QDs or close to the QDs via hydrogen bond within MPA molecules. Also, the quenching mechanism was attributed to the non-radiative recombination due to the esterification reaction that occurred between ethanol and the carboxylic group of the stabilizer[41]. It can be seen from Fig. 8b that the first exciton peaks of the QDs are noticeably red shifted with the increase of the reaction time from 2 h to 11 h regardless of the water/ethanol ratio.

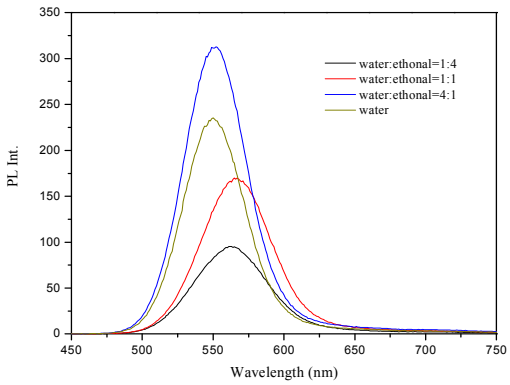

Fig.8a PL emission spectra of EA promoted MPA-capped CdTe QDs prepared with different water/ethanol ratio

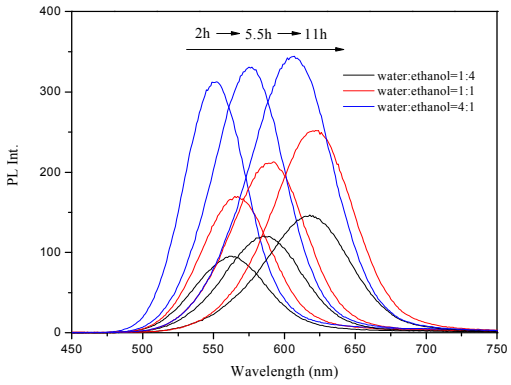

Fig.8b PL emission spectra of EA promoted MPA-capped CdTe QDs prepared with different water/ethanol ratio and reaction time

3.7 Effect of $NaBH_4$ dosage

$$4\ NaBH_4 + 2\ Te + 7\ H_2O \xrightarrow[2\ h]{80℃} 2NaHTe + NaB_4O_7 + 14H_2$$

$$NaHTe + CdCl_2 \xrightarrow[95℃,\ 3h]{MPA,\ EA} \text{MPA-EA co-capped CdTe} + NaCl + HCl$$

Scheme1. Equation for the formation of EA promoted MPA-capped CdTe QDs

$NaBH_4$ played two roles in the synthesis of CdTe QDs. The first was to lead to a fast reduction of Te to Te^{2-} as showed in Sheme1. The second was to supply a protective surrounding to avoid the oxidation of Te^{2-} even without N_2 protection. So an excess of $NaBH_4$ was adopted. $NaBH_4$ concentration had a significant effect on the conversion of Te to Te^2. In this work, $NaBH_4$ was used as a reducing agent to treat the surfaces of thiol-capped CdTe QDs since $NaBH_4$ was found to change the surface property as well as the PL efficiency of some II–VI compound QDs [42]. It can be seen from Fig.9 that when the $NaBH_4$ dosage was 1mmol which was slightly excessive by stoichiometry, the PL intensity was weak. The reason may be ascribed to $NaBH_4$ oxidation. The PL intensity of the QDs increased markedly with the increase of $NaBH_4$ dosage from 1mmol to 2mmol. However, the PL intensity decreased when $NaBH_4$ dosage further increased from 2mmol to 10mmol. Too much $NaBH_4$ caused the detachment of thioglycolic ligands from the QD core, resulting in the aggregation

and precipitation of QDs [42, 43], thus a worse optical property. The PL spectra of the CdTe QDs prepared with different $NaBH_4$ dosages exhibited emission peaks at the same wavelength with a narrow full width at half maximum (FWHM).

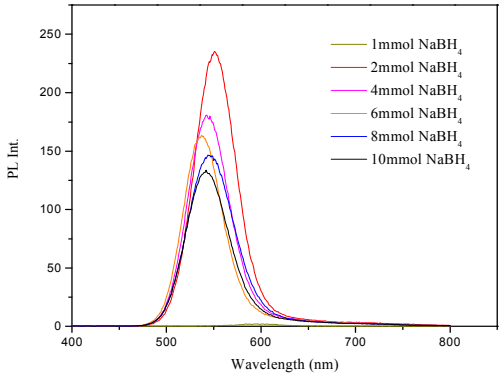

Fig.9 PL emission spectra of EA promoted MPA-capped CdTe QDs prepared with different $NaBH_4$ dosages

4. CONCLUSIONS

This paper demonstrates a simple route to enhance the optical properties of QDs via the addition of EA and ethanol. Various parameters such as pH, reaction temperature, reaction time, amount and ratio of the reagents were investigated to optimize the synthesis process, and luminescent CdTe QDs with different emission wavelength were synthesized. The key of this synthesis was the reducibility of EA, which provided a protective surrounding to avoid the oxidation of QDs and MPA. The Cd-erythorbate protective layer led to CdTe QDs passivation, which was responsible for the enhancement of the optical properties. Ethanol was also found to improve the optical properties of CdTe QDs because of its weak hydrogen bond. The combination of EA and ethanol offers an easy and environmentally benign pathway for producing high quality photoluminescent QDs.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China

(No. 21176013), the Program for New Century Excellent Talents in University of China (NCET-12-0760), and the Fundamental Research Funds for the Central Universities (Nos. ZY1307).

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