SYNTHESIS AND CHARACTERIZATION OF CdTe QUANTUM DOTS BY ONE-STEP METHOD

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ABSTRACT. L-Cysteine (Cys)-capped CdTe quantum dots (QDs) were prepared when sodium tellurite worked as a tellurium source and sodium borohydride acted as a reductant**.** The influences of various experimental variables, including pH values, Cd/Te and Cd/Cys molar ratios, on the photoluminescence (PL) quantum yield (QY) of the obtained CdTe QDs have been systematically investigated. Experimental results indicated that green to red emitting CdTe QDs with maximum quantum yield of 19.4% can be prepared at pH 11.5 and $n_{(Cd^{2+})}:n_{(Te^{2-})}:n_{(Cys)}$ = 1:0.07:2.0. X-Ray powder diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the crystal structure and shape of CdTe QDs. The results showed that the prepared CdTe QDs were of cubic zinc blend crystal structure in a sphere-like shape.

KEY WORDS: Semicondutor nanocrystal, Chemical synthesis, Optical properties, Luminescence

INTRODUCTION

In recent years, with the development of the preparing technology, semiconductor quantum dots (QDs) have been widely used in the research of biomedicine [1, 2] and optoelectronic devices [3, 4] because of their unique optical properties. So far, two successful routes, including organic synthesis [5, 6] and aqueous synthesis [7, 8], have been developed for the preparation of CdTe QDs. Compared with organic synthesis, aqueous synthesis is more reproducible, cheaper, less toxic, and the as-prepared QDs are more water-soluble and bio-compatible. Several improvements of the conventional aqueous synthetic method for thiol-capped CdTe QDs have been reported recently by different groups, including the hydrothermal synthesis, ultrasonic or microwave irradiation [9]. However, in most of these aqueous synthesis, Te powder [10, 11] or Al_2Te_3 lump [12, 13] is often used as tellurium sources, which needs a pretreatment to synthesize the instable tellurium precursor (NaHTe or H_2Te) and the process of preparing CdTe QDs requires nitrogen as the protective gas at the initial stage. In our previous report [14, 15], we have provided an alternative approach to prepare CdTe QDs using TeO_2 as the Te source. In this work, we synthesized Cys-CdTe QDs in air conditions, using Na_2TeO_3 as Te source and $NaBH_4$ as reductant. The influences of the precursor Cd/Te molar ratios, Cd/Cys molar ratios and the pH of original solution on quantum yield of the obtained CdTe QDs have been systematically investigated. The crystal structure and shape of CdTe QDs were characterized by XRD and TEM.

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EXPERIMENTAL

Reagents and materials

L-Cysteine hydrochloride monohydrate (99%), Na_2TeO_3 (97%), $CdCl_2·2.5H_2O$ (99%) and $NaBH_4$ (96%), (all from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were used for the preparation of CdTe. Rhodamine 6G with a photoluminescence quantum yield (PLQY) of 95% in water was obtained from Aladdin Chemistry Co., Ltd (China) to determine quantum yields of QDs. All chemicals were used as received without further purification. Double deionized water was used throughout the experiments.

Preparation of CdTe QDs

The water soluble Cys-CdTe QDs were one-step synthesized by using Na_2TeO_3, $NaBH_4$ and $CdCl_2·2.5H_2O$ as precursors. Typically, 0.7025 g L-cysteine hydrochloride monohydrate was added to 100 mL of 0.02 M $CdCl_2$ solution under stirring. Then, the solution was adjusted to pH 11.5 by dropwise addition of 1 M NaOH solution. The $NaBH_4$ (0.1 g) and Na_2TeO_3 (0.0323 g) were added to the solution under stirring. Afterward, the resulting mixture solution was heated to 100 ^{o}C and refluxed at 10, 30, 60, 180, 300 and 420 min for controlling the size of CdTe QDs.

Characterization

After the samples were diluted, the absorption and photoluminescence (PL) spectra were measured using a UV-2102PC spectrophotometer and a RF-5301 fluorescence spectrophotometer, respectively. The as-prepared QDs were precipitated for 10 min by adding three-fold volume isopropyl alcohol, and the sediment was collected after centrifugation at 4000 rpm for 5 min. After drying, the obtained powder was used for XRD analysis. The sample powder was placed onto sample holder plates, and the XRD spectra was carried out by using a Rigaku/Dmax-2500 X-ray diffractometer with Cu$K\alpha$ radiation (λ = 1.5406 $\overset{\circ}{A}$). The QDs solution was spread on ultra-thin carbon-coated film on 200 mesh copper grids and left to dry in air. Sample was then visualized using a FEI-TF30 transmission electron microscopy.

Measurement of quantum yields

The PLQY was obtained by comparison with rhodamine 6G (QY = 95%) and using data derived from the luminescence and the absorption spectra [16]. Briefly, rhodamine 6G was chosen as a reference standard (QY = 95 %), the absorbance for the standard and the CdTe QDs samples at the excitation wavelength and the fluorescence spectra of the same solutions were measured, respectively. The expression to calculate quantum yield is provided as following:

$$Y_u = Y_s \times \frac{F_u \times A_s}{F_s \times A_u} \tag{1}$$

In Eq.(1), Y is quantum yield, F is the integrated emission peak area, and A is the absorbance at excitation wavelength. The subscripts s and u denote standard (such as rhodamine 6G) and test samples, respectively. The absorbance at the excitation wavelength (365 nm) of rhodamine 6G and the QDs sample was set to a similar value (below 0.1).

RESULTS AND DISCUSSION

UV–Vis absorption and PL spectra

Figure 1 shows the absorption (solid line) and PL (dashed line) spectra of the typical Cys-CdTe QDs. The excitation absorption peaks of the QDs are quite obvious, with reflux from 10 to 420 min, the maximum absorption peaks appeared at 490, 508, 521, 584, 561 and 579 nm, respectively. Compared with CdTe bulk material (827 nm) [17], the excitation absorption peaks of CdTe QDs have significant blue shift, which showing obvious quantum confinement effect. The maximum absorption peak of QDs took place an obvious red-shift from 490 nm to 579 nm with increasing size of the QDs as a consequence of the quantum confinement. According to the empirical formula [18]:

$$D = (9.8127 \times 10^{-7}) \, \lambda^3 - (1.7147 \times 10^{-3}) \, \lambda^2 + (1.0064) \, \lambda - 194.84 \qquad (2)$$

where λ is the first absorption maximum, the diameter of samples was estimated to 2.0, 2.5, 2.9, 3.2, 3.3 and 3.5 nm, respectively. Similar to absorption spectra, PL emission spectra also take place a red shift with the increasing refluxing time. In addition, the PL emission spectra are located close to the absorption thresholds, indicating that the PL of CdTe QDs is from the excitation luminescence of elections between valence band and conduction band transitions [13]. The full width of half maximum of PL spectra is between 30 nm and 55 nm, meaning that the particle sizes are evenly distributed.
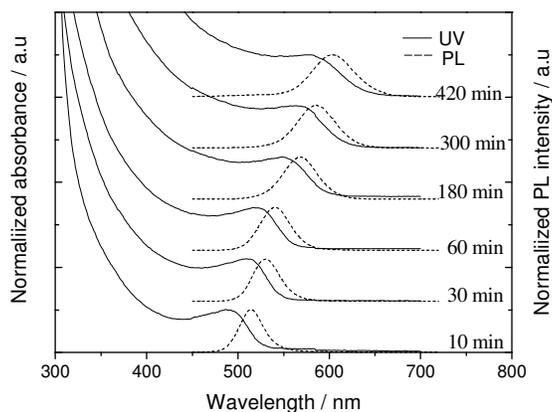
Figure 1. Temporal evolution of UV-Vis absorption (solid line) and PL spectra (dashed line) of CdTe QDs.

XRD and TEM

The XRD pattern of the as-prepared CdTe QDs that was refluxed for 180 min at 100 °C is shown in Figure 2. The diffraction peaks at $2\theta = 24.535°$, $40.589°$, and $48.037°$ can be readily assigned to the (1 1 1), (2 2 0), and (3 1 1) planes, respectively. The position of the XRD peaks matches well those of the bulk CdTe cubic structure (JCPDS No.65-1046). These peaks are comparatively wider than that of the bulk materials due to the finite crystalline size.

The TEM image of corresponding sample was shown in Figure 3. The CdTe QDs appear as spherical particles with the average size of about 3.0 nm, which was in an agreement with that

calculated from the UV-Vis absorption spectra, and the sample were mono-disperse and homogeneous.
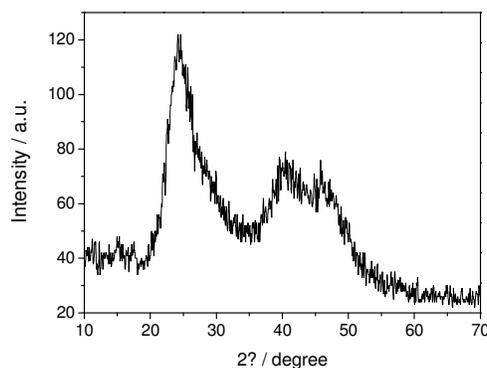
Figure 2. The XRD pattern of CdTe QDs.   Figure 3. TEM image of CdTe QDs.
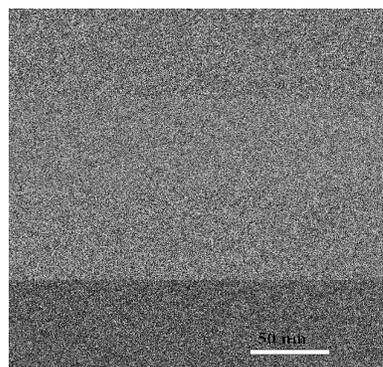
Influence of pH value, Cd/Te and Cd/Cys molar ratios on optical properties

It has been demonstrated that cadmium and thiol can form different polynuclear compounds in water and that the formation of cadmium thiol compounds strongly depends on pH of the solution [19]. When the pH is less than 4.0, there is little cadmium thiol compound existed. Consequently, the pH of solution should be controlled in a certain range when CdTe QDs are synthesized in aqueous solution whose stabilizer is thiol, to ensure enough cadmium thiol compound existing. In the experiment, the initial pH values was adjusted to 10.5, 11.0 and 11.5 under the molar ratio of $Cd^{2+}/Te^{2-}/Cys$ was 1:0.05:2, respectively, we investigated the influence of various initial pH values on the PL QYs of CdTe QDs. It can be seen in Figure 4, being refluxed for 60 min, the highest quantum yields of QDs was obtained in three different pH values up to 13.2%, 14.3% and 16.2%, respectively. In addition, the quantum yields of the corresponding reflux time were improved with the pH of original solution increase. It could be easier to form Cd^{2+}-Cys coordination bond higher while reducing surface defects or a thin layer of CdS shell was formed to passivate the quantum dots surface, and improve the luminous efficiency with higher pH. Experimental results show that the appropriate pH of synthesizing Cys-CdTe QDs is 11.5.

The Cd/Te molar ratios also played an important role in improvement of quantum yield of CdTe QDs. In previous reports [20-22], different Cd/Te molar ratios (changing from 1:0.2 to 1:0.5) were adopted in the aqueous synthesis of CdTe QDs using Te powder or Al_2Te_3 lump as tellurium source. In the present study, the Cd/Te molar ratio was varied from 1:0.05 to 1:0.2 with fixed Cd/Cys molar ratio at 1:2 and pH value at 11.5, we investigated the influence of various Cd/Te molar ratios on the PLQY of CdTe QDs, and the obtained experimental results are shown in Figure 5. It can be seen that the CdTe QDs prepared at Cd/Te molar ratio 1:0.07 possess a high PLQY value, and the maximum quantum yield up to 19.4%. While the PLQY value of the resulting CdTe QDs were relatively low at the Cd/Te molar ratio 1:0.2. The literature report [23] revealed that highly luminescent CdTe QDs possess much fewer Te atoms on the surface than that of CdTe with low luminescence. Here, we suppose that, with the fixed amount of Cd and Cys, increasing the amount of Te, the relative coverage rate of the particle surface with Te atoms will increase, which results in the low luminescence. Herein, a proper Cd/Te molar ratio is important for preparation of high quality CdTe QDs, in our experiment, the optimal ratio is 1:0.07.
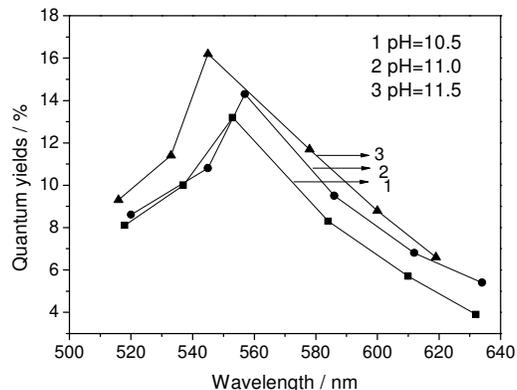
Figure 4. QY of CdTe QDs at different emission peaks as a function of pH. From left to right, the QDs are obtained for refluxing 10, 30, 60, 180, 300 and 420 min.
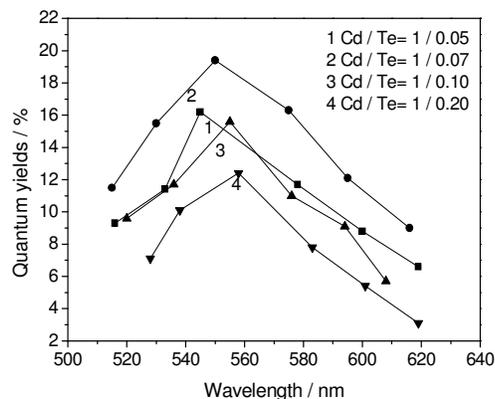
Figure 5. QY of CdTe QDs prepared at different Cd/Te molar ratios. From left to right, the QDs are obtained for refluxing 10, 30, 60, 180, 300 and 420 min.

As previously demonstrated, the occupation of surface sites by stabilizer molecules instead of Te atoms has a tremendous contribution in removing the dangling bonds and preventing the oxidation of Te atoms, which is greatly favorable for the formation of high-quality QDs [24]. Therefore, the thiol plays an important role in the synthesis of thiol-capped CdTe QDs, and in most of the "traditional" aqueous approaches, the stoichiometric ratio of Cd to thiol was often set as 1:2.45 [13, 25]. In our experiments, the Cd/Cys molar ratio was changed from 1:1.6 to 1:2.2 with fixed Cd/Te molar ratio (1:0.07) and pH value (11.5), we investigated the influence of various Cd/Cys molar ratios on the PLQY of CdTe QDs. As can be seen in Figure 6, when the Cd/Cys = 1/1.8, the PLQY of the resulting CdTe QDs were relatively low due to the absence of adequate Cys molecules. The population of Cys molecules on the surface of QDs was increased, accompanied by decrease of the Cd/Cys molar ratio, thus, the PLQY was gradually enhanced and up to the maximum while the Cd/Cys molar ratio reached the optimum value of 1:2. However, an excessive number of stabilizer molecules might distort the surface, consequently, the rough surface gave rise to new nonradiative defects. As a result, the PLQY

was distinctly diminished when the Cd/Cys = 1/2. Therefore, the Cd/Cys molar ratio 1:2.0 is optimal for the synthesis of Cys-CdTe QDs.
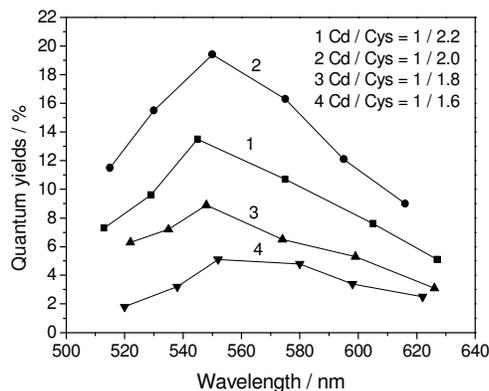
Figure 6. QY of CdTe QDs prepared at different Cd/Cys molar ratios. From left to right, the QDs are obtained for refluxing 10, 30, 60, 180, 300 and 420 min.

Mechanism for the preparation of CdTe QDs

The formation of QDs in solution often involves in two stages: nucleation and growth. In this synthesis process, the following mechanism is proposed to elaborate the formation of CdTe QDs [9]: firstly, cadmium thiol complexes (Cys-Cd^{2+}) were formed in the strong alkaline solution (Eq. 3), when the TeO_3^{2-} was introduced to the three-neck flask, it can be reduced by $NaBH_4$ to produce Te^{2-} (Eq. 4) that reacted with the Cys-Cd^{2+} complexes, resulting in the formation of CdTe nuclear (Eq. 5). Finally, with the CdTe nuclear growing gradually, the CdTe QDs was formed under the condition of reflux (Eq. 6).

$$Cd^{2+} + Cys \rightarrow Cys\text{-}Cd^{2+} \tag{3}$$

$$4TeO_3^{2-} + 3BH_4^- \rightarrow 4\,Te^{2-} + 3BO_2^- + 6H_2O \tag{4}$$

$$Cys\text{-}Cd^{2+} + Te^{2-} \rightarrow Cys\text{-}CdTe \tag{5}$$

$$n\,Cys\text{-}CdTe \rightarrow (Cys\text{-}CdTe)_n \tag{6}$$

CONCLUSIONS

We developed a technology to synthesize Cys-CdTe QDs by one-step method, using Na_2TeO_3 as Te source and $NaBH_4$ as reductant. The green to red emitting CdTe QDs with maximum quantum yield of 19.4% can be prepared at pH 11.5 and $n_{(Cd^{2+})}:n_{(Te^{2-})}:n_{(Cys)} = 1:0.07:2.0$. Compared with Te powder and Al_2Te_3 lump route, the Na_2TeO_3 route is an environment-friendly and low-cost synthesis route, which is suited for large-scale synthesis.

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