

Characteristics of CdTe nanocrystals synthesized by a Na₂TeO₃ source

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Abstract: Water-soluble cadmium telluride (CdTe) nanocrystals were synthesized in aqueous solution with thioglycolic acid (TGA) molecules as a stabilizer. A series of TGA-stabilized CdTe nanocrystals were prepared using sodium tellurite as a tellurium source, which avoids the cumbersome processes associated with H₂Te or NaHTe sources. The synthesized TGA-stabilized CdTe were characterized with X-ray diffraction, TEM and fluorescence spectrophotometer. The particles crystallized predominantly in cubic phase with narrow photoluminescence emission. The effects of reaction time, pH value, and precursor concentration on the photoluminescence properties were investigated in detail.

Key words: CdTe nanocrystals; sodium tellurite; thioglycolic acid; fluorescence

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1. Introduction

Semiconductor nanocrystals (NCs) have attracted extensive interest because of their variety of size-dependent optical and electrical properties^[1–4]. CdTe NCs have been substantially studied in industrial and biomedical applications, such as light-emitting devices (LEDs)^[5], photovoltaic devices^[6], solar cells, biological labels^[7, 8] and detection^[9, 10]. Compared with the organic dyes, CdTe NCs have a wide range of selected wavelengths, continued absorption spectra, great luminescence lifetime, good stability under relatively harsh environments, and small full width at half maximum (FWHM)^[11, 12]. In most of the aqueous approaches, NaHTe or H₂Te was used as the tellurium source, which needs a pretreatment to synthesize the unstable tellurium precursor and the process of preparing CdTe nanocrystals requires N₂ as the protective gas at the initial stage^[13–19]. Herein, we use Na₂TeO₃ as the tellurium source, and TGA as the stabilizer to synthesize fluorescent TGA-stabilized CdTe NCs in air conditions without the protection of N₂.

2. Experimental section

2.1. Materials

CdCl₂·2.5H₂O and thioglycolic acid (TGA) were purchased from Chengdu Kelong Chemicals Co., China. Sodium tellurite (Na₂TeO₃) was purchased from Shanghai Chemicals Co., China. De-ionized water was used in all experiments and all of the other chemicals were of analytical grade.

2.2. Synthesis of CdTe nanocrystals

In our experiments, CdCl₂·2.5H₂O was dissolved in 50 mL of de-ionized water in a breaker and an appropriate amount of TGA was added under stirring. The pH of the solution was adjusted by addition of a 1 M/L solution of NaOH. Na₂TeO₃ dissolved in 50 mL of de-ionized water in another breaker,

and then the solution of Na₂TeO₃ was mixed with the solution of CdCl₂·2.5H₂O under stirring. The molar ratio of Cd²⁺/TGA/Te²⁻ was set as 1 : 2.4 : 0.5. After stirring for 10 min, the mixed solution was transferred into a water bath kettle which was maintained at 95 °C for a certain time. In order to investigate the effects of reaction time, pH value, and precursor concentration on the photoluminescence properties, a series of samples were prepared.

2.3. Characterization

The XRD spectrum was measured by a RIGAKU D/MAX-IIIC X-ray diffractometer with CuK α radiation ($\lambda = 0.15418$ nm). A transmission electron microscopy (TEM) image was obtained with a JEM-100CX transmission electron microscope. The PL spectra were recorded by a HITACHI F-4600 FL spectrophotometer (photomultiplier tube, 400 voltages). All of the measurements were performed at room temperature under ambient atmosphere.

3. Results and discussion

3.1. Characterization of CdTe NCs by XRD and TEM

The particles were extracted by precipitation with the addition of 2-propanol to the solution. Then the resulting powders were dried at room temperature. Figure 1 shows the XRD spectrum of CdTe NCs powders. The XRD spectrum fits to the cubic zinc blend structure like bulk CdTe crystal. However, the diffraction peak positions of the CdTe NCs are between the values of the cubic CdTe and the cubic CdS phases^[14, 16], so there is a considerable shift in the diffraction peak positions according to the given standard XPD spectrum. The partial hydrolysis of thiols in the course of preparation led to the incorporation of sulfur into CdTe NCs^[14]. The broadening of the diffraction peaks indicates that the CdTe NCs are of small size.

Figure 2 shows the TEM image of the CdTe NCs. The typical image of the sample reveals that the shape of CdTe NCs is

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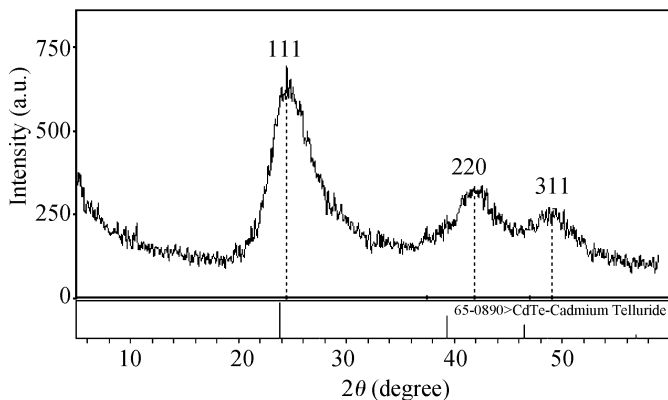


Fig. 1. XRD spectrum of TGA-stabilized CdTe NCs.

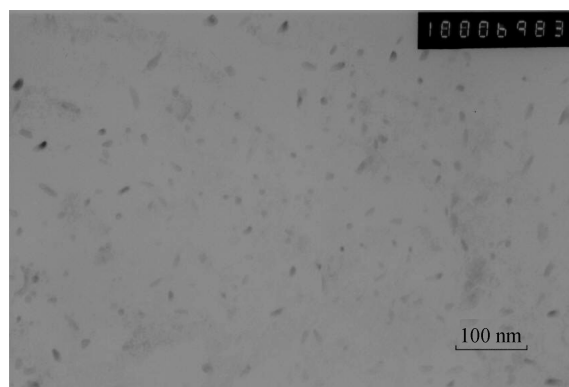


Fig. 2. TEM image of CdTe NCs.

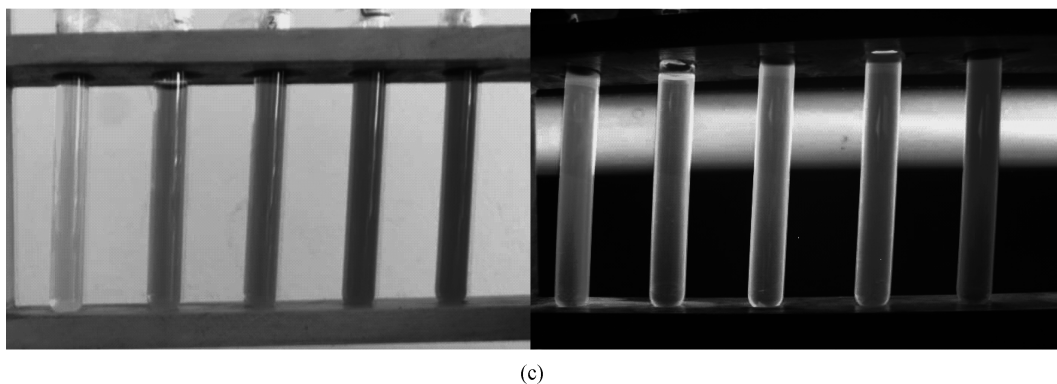
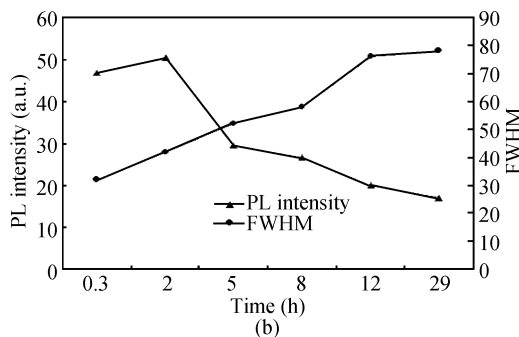
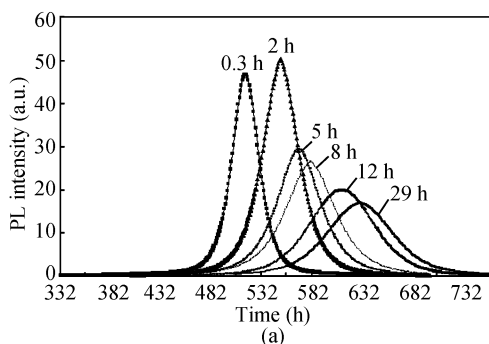


Fig. 3. (a) PL spectra of CdTe recorded after particle growth for 20 min ($\lambda_{ex} = 502$ nm), 2 h ($\lambda_{ex} = 533$ nm), 5 h ($\lambda_{ex} = 550$ nm), 8 h ($\lambda_{ex} = 554$ nm), 12 h ($\lambda_{ex} = 543$ nm) and 29 h ($\lambda_{ex} = 540$ nm). (b) Variation of PL intensity and FWHM with increasing time. (c) Photoluminescence photos of samples in day light (left) and in an ultraviolet lamp (right).

close to spherical. From the TEM image, we find that the CdTe NCs (reaction time was 29 h) are about 5.7 nm.

3.2. Fluorescence properties

3.2.1. Effects of reaction time

The effects of reaction time on the PL intensity, the fluorescent emission position of the PL maxima and the full width at half maximum (FWHM) are shown in Fig. 3. The samples were synthesized in this condition: the Cd precursor concentration was 40 mM, the pH value was 9.5 and the temperature was 95 °C. In Fig. 3(a), it is clearly seen that with increasing reaction time, the fluorescent emission position of the CdTe NCs shifts to the longer wavelength, from 551 to 631 nm, indicating that the CdTe NCs have different colors (green, yellow, orange

and red). In Fig. 3(b), it is observed that with increasing reaction time, the PL intensity of the CdTe NCs gradually decreases and the FWHM of the fluorescence spectra broadens from 32 to 78 nm, which indicates that the size of the CdTe NCs distributes in a larger extension. With a long heating time, about 38 h, there are lots of black depositions in the solution, which may be caused by the oxidization and aggregation of CdTe NCs due to the destruction of TGA. And the fluorescence intensity of the CdTe NCs decreases dramatically.

We have obtained the photoluminescence photos of CdTe NCs in day light and in an ultraviolet lamp, as shown in Fig. 3(c). The reaction times of 5 samples from left to right are 2, 5, 8, 12 and 29 h. It is clearly seen that with increasing reaction time, the color of the CdTe NCs turned from yellow to red in day light, and the fluorescence of the CdTe NCs in an

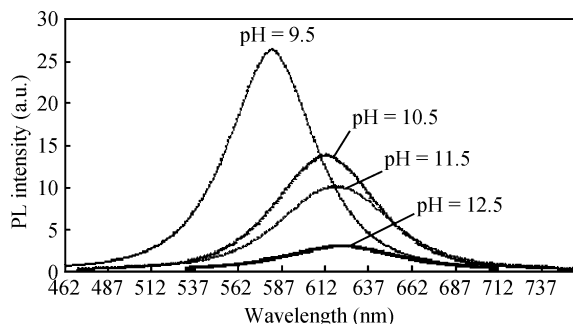


Fig. 4. Effects of pH value on PL intensity, emission position and FWHM.

ultraviolet lamp turned from green to red. The quantum yield (QY) of CdTe is estimated to be 27% using Rhodamine 6G as the PL reference.

3.2.2. Effects of pH

We have investigated the role of the pH value in determining the PL properties of CdTe NCs. The samples were synthesized in this condition: the Cd precursor concentration was 40 mM, the reaction time was 8 h and the temperature was 95 °C. The PL spectra of CdTe NCs obtained under different pH values are shown in Fig. 4. It is clearly seen that the PL maximum gradually decreases with the pH changing from 9.5 to 12.5. This should most likely be attributed to the thickness of surface cadmium-thiol complexes on quantum dots (QDs). A lower pH likely resulted in the formation of the thicker cadmium-thiol complex shell^[14]. The effective surface passivation by the formation of cadmium-thiol complexes was the origin of high photoluminescence quantum yields^[20]. Furthermore, the fluorescent emission position shows a red-shift and the FWHM of fluorescence spectra broadens from 58 to 84 nm with increasing pH of Cd precursor solution. And we found in our experiments that the CdTe NCs solution obtained by the Cd precursor solution with higher pH had a low stability. When the pH of the Cd precursor solution was adjusted to 13.5, some depositions emerged in the CdTe NCs solution after being kept for 9 days at room temperature. This may be the result of instability of CdTe NCs in a solution with a high pH. However, when the pH of the Cd precursor solution was adjusted to 8.5, some black deposition (CdTeO_3) immediately emerged in the mixed solution and the PL intensity of the samples disappeared.

3.2.3. Effects of precursor concentration

The effects of precursor concentration on the PL intensity are shown in Fig. 5. It is clearly seen that a lower precursor concentration has a positive for obtaining higher PL intensity in the initial stage of NC growth, but it becomes a disadvantage in the following Ostwald ripening. At the initial stage of QD growth, the number of CdTe nuclei was dependent on the Cd and Te precursor concentration. At a higher precursor concentration, more nuclei were formed, and these nuclei quickly expended the remaining monomers with the growth of nuclei. Thus, the few remaining Cd monomers probably caused the ineffective passivation of nanocrystal surface defects, which induced the weak luminescence. However, at a lower precursor concentration, fewer nuclei were formed and relatively more

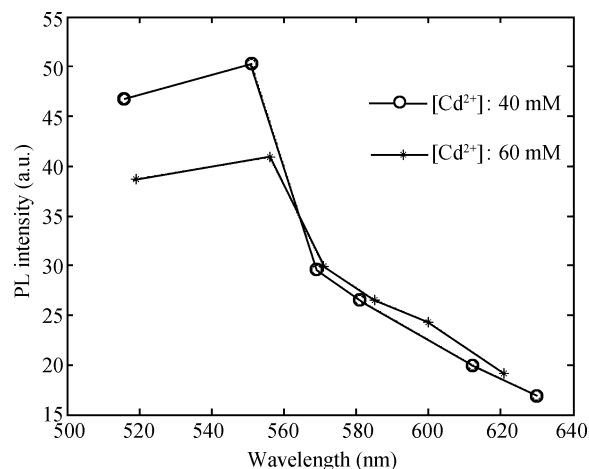


Fig. 5. Effects of precursor concentration on the PL intensity.

cadmium monomers remained in the solution, which were favorable for surface ordering and reconstructions of CdTe QDs during the growth of NCs, thus favorable for achieving a higher PL intensity before the stage of Ostwald ripening^[14]. Once the excess cadmium monomers were expended, Ostwald ripening took place, during which a larger NC ensemble grew while the smaller ones dissolved. And during the Ostwald ripening stage, the lower precursor concentration became disadvantageous in contrast to the initial stage. This was attributable to the lesser degree of Ostwald ripening occurring at a higher precursor concentration; Ostwald ripening mostly happened at a low precursor concentration, and the low concentration increased the average surface disorder of the NCs, which induced the weak PL intensity^[13].

4. Conclusions

In this paper, we have represented an important progress for the aqueous synthesis of CdTe NCs. The methods in Refs. [13–19] need strict anaerobic conditions, using NaHTe (synthesized by NaBH_4 and Te powder) as the tellurium source. This increases the complexity of the operation, due to the extreme instability of NaHTe in air. Compared to the aforementioned method, we used sodium tellurite as the tellurium source, which avoids the cumbersome processes associated with NaHTe sources because of the strong stability of sodium tellurite in air. So the preparation process of CdTe NCs eliminates the need for strict anaerobic conditions, and significantly improves the operability and reproducibility of the experiments. We synthesized CdTe NCs at low temperature, low pH and high precursor concentration, which indicates that our method is much cheaper and more productive. The results indicate that the size of CdTe NCs can be controlled in a wide range, and the CdTe NCs have high PL intensity, which enables its application in biological labels.

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