

Rapid synthesis of CdSe nanocrystals in aqueous solution at room temperature

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Abstract. Water-soluble thioglycolic acid-capped CdSe nanocrystals (NCs) were prepared in aqueous solution at room temperature. We investigated the effects of pH values on the fluorescence intensity of the as-prepared CdSe NCs, and discussed the influence of the initial pH values on the fluorescence property. Their mean diameter was estimated to be 1.9 nm depending on the initial pH values in the preparation, the photoluminescence quantum yield could reach as high as 1.9%, almost comparable to the CdSe NCs prepared by an organometallic route. Finally, the products were characterized by Fourier transform infrared spectrometry (FTIR), atomic force microscope (AFM) and X-ray powder diffraction (XRD). AFM image showed that the NCs were ball-shaped with good dispersibility. XRD analysis disclosed that the CdSe NCs were of cubic zinc-blended structure.

Keywords. CdSe; nanomaterials; semiconductors; luminescence; synthesis.

1. Introduction

CdSe nanocrystals (NCs) have gained significant attention in the past decade because of their unique optical properties. Extensive researches have focused on the synthesis (Rogach *et al* 2000; Jasieniak *et al* 2005; Manoj *et al* 2008) of CdSe NCs. Based on their researches, the synthesis of CdSe NCs can be summarized in two chemical routes, one is nonaqueous trioctyl phosphine/trioctyl phosphine oxide (TOP/TOPO) technique, and another is using different thiols as stabilizing agents in aqueous solution. The most popular route for the synthesis of high quality CdSe NCs is nonaqueous technique, which originated from the work of Murray *et al* (1993) and developed by Peng and Peng (2001). However, a further process is needed for the NCs used in biological system due to as-prepared NCs often dispersing in nonpolar organic solvents. Under refluxing condition, the water-soluble CdSe NCs were prepared in aqueous solution using thiols as stabilizing agents, which was first reported by Weller's group (Rogach *et al* 1999). Up to now, many methods (Zhu *et al* 2000; Chen *et al* 2008; Xia and Zhu 2008) for preparing CdSe NCs in aqueous solution under refluxing condition have been developed. Recently, some research groups have synthesized water-soluble CdSe NCs at lower temperature. For example, Han's group (Han *et al* 2006) synthesized water-soluble CdSe NCs under high-intensity ultrasonic irradiation, however, their photoluminescence properties were not characterized. Yu

et al (Deng *et al* 2006) prepared citrate-stabilized CdSe at 75°C, after the product was illuminated with natural ambient light for 30 days, the final quantum yield was only little more than 4%. To the best of our knowledge, CdSe NCs with moderate photoluminescence quantum yield have not been prepared directly in aqueous solution at room temperature.

In this paper, a rapid and simple method was reported for synthesizing water-soluble thioglycolic acid-capped CdSe NCs at room temperature. We investigated the effects of pH values on the fluorescence intensity of the as-prepared CdSe NCs, then, discussed the influence of the initial pH values on the fluorescence property. Finally, the products were characterized by Fourier transform infrared spectrometry (FTIR), atomic force microscope (AFM) and X-ray powder diffraction (XRD).

2. Experimental

2.1 Materials

Cadmium chloride hemidihydrate ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$), Se power, sodium borohydride (NaBH_4), thioglycolic acid (TGA), (all were of analytical reagent grades acquired from the Shanghai Chemical Factory, Shanghai, China) were used for the preparation of CdSe.

2.2 Method of preparation

The preparation of CdSe NCs was conducted by modifying the procedures described elsewhere (Gaponik *et al*

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2002) for making thiol-capped CdTe NCs. Briefly, 0.4567 g $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ was dissolved in 100 ml deionized water in a 250-ml three-neck flask, and 0.5 ml TGA was added while stirring, followed by adjusting the pH to desired values with $1.0 \text{ mol} \cdot \text{L}^{-1}$ NaOH. The solution was deaerated by N_2 bubbling for 30 min. Under vigorous stirring, 1.0 ml oxygen-free NaHSe of $1.0 \text{ mol} \cdot \text{L}^{-1}$ was injected with a syringe to the above solution. When the colour of the solution was changed to orange, CdSe NCs was produced.

2.3 Characterization

Absorption and emission spectra were measured using a UV-2102 spectrometer and a RF-5301 fluorescence spectrometer, respectively. Estimates of quantum yields (QY) were obtained by comparing the integrated emission from Rhodamine 6G (QY = 95%) in ethanol with that of CdSe NCs dispersed in buffer solution (pH = 4.0). FTIR spectra were recorded on a Nexus-470 spectrometer. The morphology measurement was performed using a SPA-400 atomic force microscope. X-ray powder diffraction (XRD) was taken on a Rigaku D/max 2500V diffractometer equipped with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$).

3. Results and discussion

In the presence of NaHSe, NCs were formed immediately. However, almost no fluorescence was detected. Based on the report that the fluorescence intensity of CdTe solution strongly depended on pH values (Gao *et al* 1998), a set of fluorescence intensities under different pH values from CdSe were recorded, and figure 1a displayed the relative fluorescence intensity at different pH values. It can be seen that the fluorescence intensity reached its maximum at pH = 4.0, and pH values both lower and higher than 4.0 resulted in a significant decrease. The research (Bowers *et al* 2005) on CdSe demonstrated that the photoluminescence of CdSe NCs was attributed to defect-related emission. Because of the extremely small diameter, there are many trap sites on the surface of CdSe NCs, the more the trap sites, the lower the fluorescence efficiency. The synthetic route in aqueous phase, cadmium and thiol were excessive, cadmium thiol complexes were formed in the solution. It was observed that the formation of the cadmium thiol complexes strongly depended on the pH of the solution, when pH was less than 4.0, no complexation occurred (Hayes *et al* 1989). When the CdSe solution becomes acidic, free thiols and cadmium ions will be released from the cadmium thiol complexes, the relative coverage rate of the particle surface with thiols was increased. Therefore, the trap sites on the CdSe surface will be removed, and the fluorescence efficiency was improved. When $\text{pH} < 4.0$, the thiols attached to the NCs were detached from the surface, more surface

defects formed, resulting in a decrease of the fluorescence intensity.

In preparation, the initial pH values were adjusted to 5.3, 7.4, 9.2 and 11.2 (called samples 1, 2, 3 and 4 below), respectively. We investigated the influence of initial pH values on the optical properties of CdSe NCs. The original solutions of various initial pH values were diluted with buffer solution (pH = 4.0), and the absorption and fluorescence spectra were shown in figure 1b. As can be seen, in all cases, the excitonic absorption peak was not very distinct, but it appeared at around 440 nm, indicating the formation of CdSe NCs with wide particle size distribution. The mean diameter was estimated to be 1.9 nm based on the work of Yu *et al* (2003). All of the maximum emission peaks were found almost at 524 nm with a full width at half maximum of about 100 nm, suggesting that the sizes of CdSe NCs were independent of the initial pH values. Chen *et al* (2009) disclosed that the initial ratio between Cd and Se played a major role in determining the nucleation and growth rate of CdSe NCs. In our experiments, the molar ratio of Cd/Se was set to

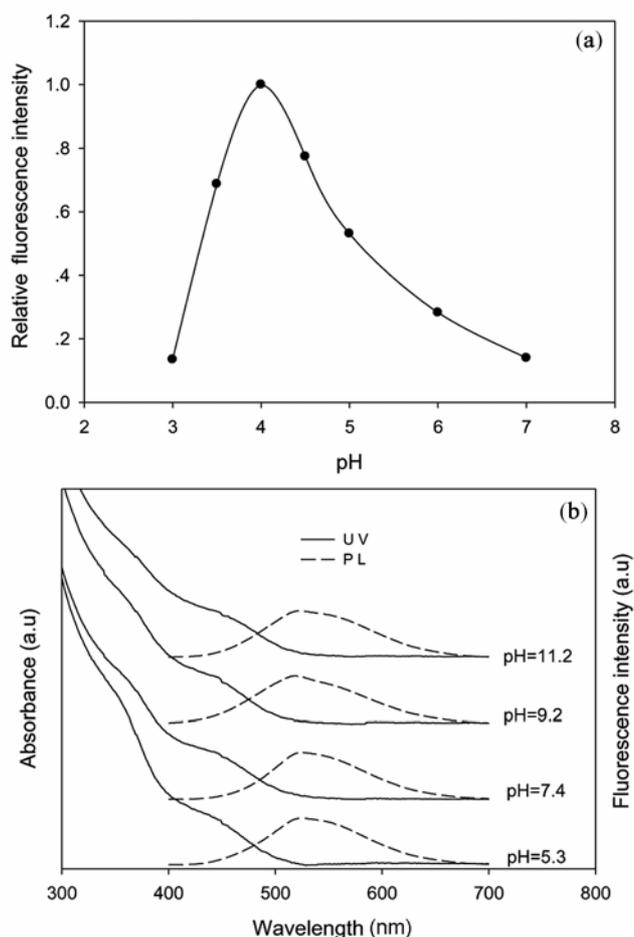


Figure 1. (a) Relative fluorescence intensity of CdSe NCs at different pH values and (b) absorption and fluorescence spectra of CdSe NCs prepared at different initial pH values.

2 : 1, and the reaction temperature was kept the same. Therefore, the emission peaks of all samples almost appeared at the same location. In contrast, under the same condition, the fluorescence intensity varied with the initial pH values, for samples 1, 2, 3 and 4, the QYs were 1.0%, 1.3%, 1.5% and 1.9%, respectively. According to the theory of acid-base equilibrium, the initial pH value of original solution determines the dissociation state of TGA and the coordination between stabilizer and Cd^{2+} ion. The dissociation constants of TGA are $\text{p}K_{\text{a}1} = 3.60$ and $\text{p}K_{\text{a}2} = 10.56$. When pH was less than 3.60, the precursor solution was milk-like, no cadmium thiol com-

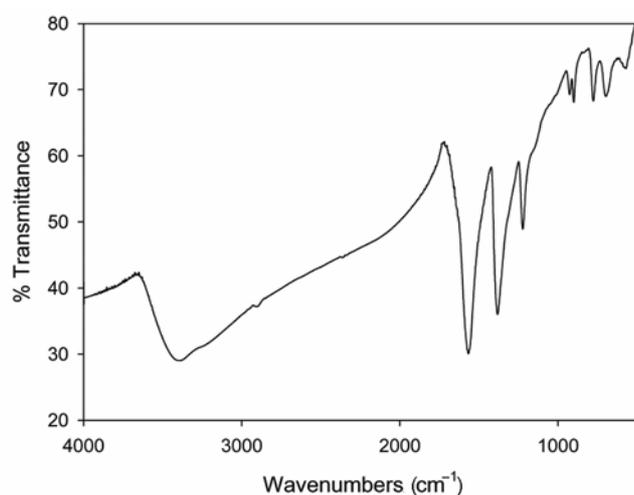


Figure 2. FTIR spectra of TGA-capped CdSe NCs.

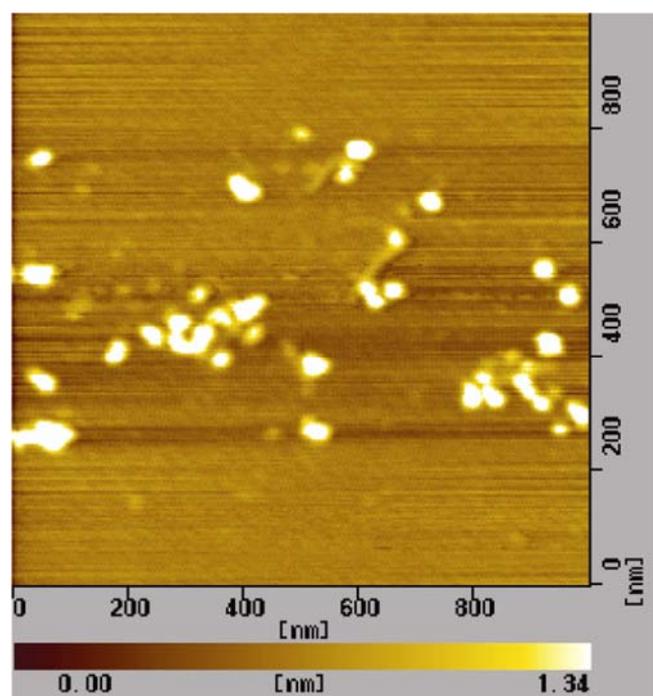


Figure 3. AFM image of CdSe NCs.

plexes occurred. As pH enhanced, complexation happened gradually. After addition of NaHSe solution, the more the complexation happened, the more CdSe with lower defect produced. On the other hand, increasing the amount of OH^- can favour the reaction between Cd^{2+} and HSe^- . As pH was higher than 10.56 in precursor solution, the concentration of $^-\text{SCH}_2\text{COO}^-$ was higher than that of $\text{HSCH}_2\text{COO}^-$, it was easy to get CdSe NCs with high quality, so the QY of sample 4 could reach as high as 1.9%.

To further confirm the formation of CdSe NCs and investigate the interaction between TGA and CdSe NCs, the FTIR spectrometry was measured. As shown in figure 2, a broad absorption band around 3400 cm^{-1} was assigned to O–H vibration of the absorbed H_2O . An absorption band due to S–H vibration observed at 2560 cm^{-1} disappeared. The characteristic absorption band of C=O vibration was shifted from 1700 cm^{-1} to 1556 cm^{-1} . Therefore, these results strongly suggest that the thiol groups of TGA coordinated with Cd^{2+} ions on the NCs surface, and the hydrophilic hydroxyl groups faced outward, making NCs water-soluble.

The AFM image of sample 3 in figure 3 showed that the NCs were ball-shaped with good dispersibility. The powder XRD pattern of sample 4 is presented in figure 4. From the XRD pattern, three typical distinct features of the zinc-blended structure can be distinguished: the one at $2\theta = 25.3^\circ$ is due to the (111) reflection, and the other two appearing at $2\theta = 42.0^\circ$ and 49.7° result from the (220) and (311) reflections (Joint Committee on Powder Diffraction Standards file No. 19-0191), respectively. Moreover, no typical diffraction of the wurtzite lattice structure can be found, which further confirms the cubic zinc-blended structure.

4. Conclusions

In conclusion, a rapid and simple method for synthesizing TGA-capped CdSe NCs at room temperature was reported

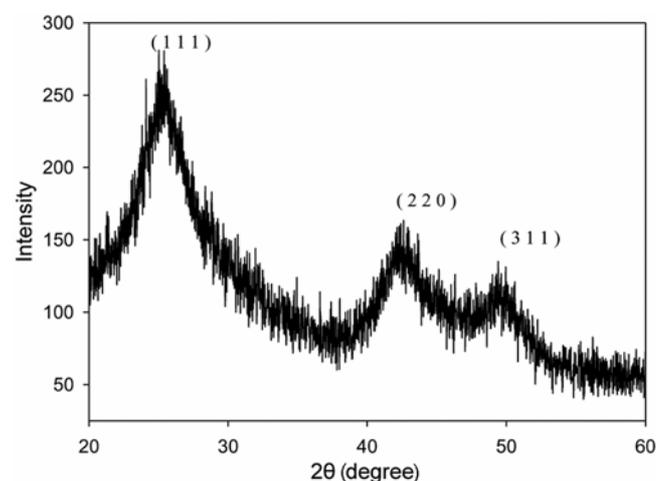


Figure 4. XRD pattern of CdSe NCs.

in this paper. The products were ball-shaped with zinc-blended structure. The technique makes the synthesis of water-soluble CdSe NCs convenient, economic and safe.

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