

Communications

Aqueous Synthesis of Luminescent CdSe Quantum Dots from Selenium Tetrachloride

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Received January 21, 2014, Accepted February 24, 2014

Key Words : Semiconductor nanocrystal, Chemical synthesis, Optical properties, Luminescence

CdSe quantum dots (QDs) are of special interest for its broad application in photovoltaic devices,¹ solar cells,² sensors³ and biological labels.⁴ Up to now, two chemical routes, organic and aqueous syntheses,^{5,6} have been suggested for the preparation of CdSe QDs. Compared with organic synthesis, aqueous synthesis is more reproducible and cheaper. The as-prepared samples are more water-soluble and bio-compatible. Several improvements of the conventional aqueous synthetic route for thiol-capped CdSe QDs have been reported recently by different research groups.⁷⁻⁹ In most aqueous routes, Se powder,¹⁰ Na₂Se,¹¹ Na₂SeO₃¹² or SeO₂¹³ is used as selenium precursor. Selenium tetrachloride (SeCl₄), which is easily hydrolyzed to form H₂SeO₃, can be thought of as an alternative selenium precursor in the synthesis of CdSe. Here, we employed SeCl₄ as selenium precursor to prepare mercaptosuccinic acid (MSA) - capped CdSe QDs. Two main advantages of this method are significant: (1) the synthesis is carried out in air atmosphere with one step, and (2) these QDs are highly luminescent, for instance, one of their photoluminescence quantum yields (PLQY) reaches up to 32.4%, which is higher than those of MSA-capped CdSe QDs synthesized using other selenium precursor.^{6,12}

In a typical synthesis of CdSe QDs, 1.0 mol/L NaOH solution was used to obtain a pH 11.8 in a mixed aqueous solution composed of 0.4567 g (2 mmol) CdCl₂·2.5H₂O and 0.4207 g (2.8 mmol) MSA. After several minutes, 0.1105 g SeCl₄ (0.5 mmol) and 0.1 g NaBH₄ was added successively into the above solution under magnetic stirring, and the pH of the resulting mixture solution was readjusted to 11.8. Then, the solution was refluxed at 100 °C for different time to control the size of the CdSe QDs.

The aqueous synthesis of QDs is based on the Ostwald ripening phenomenon, and the formation of QDs in solution involves two stages: nucleation and growth. In this synthesis the formation of CdSe QDs can be illustrated as follows: first, Cd²⁺-MSA complexes were formed under alkaline condition. Then the NaBH₄ would react with H₂SeO₃, a product from SeCl₄, to form Se²⁻ ions that combined with Cd²⁺-MSA complexes to generate CdSe nuclei. With the CdSe nuclei growing under refluxing, the CdSe QDs formed at last.

The temporal evolution of the size of CdSe QDs was

studied by taking samples from the reaction mixture at different intervals and monitored via the UV-vis absorption and PL spectra. The diameter of QDs was calculated from the absorption peak using the empirical equation¹⁴ as follows:

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57 \quad (1)$$

In Figure 1(a), the absorption peaks of the CdSe QDs are quite obvious, with reflux from 0.5 h to 7 h, the absorption

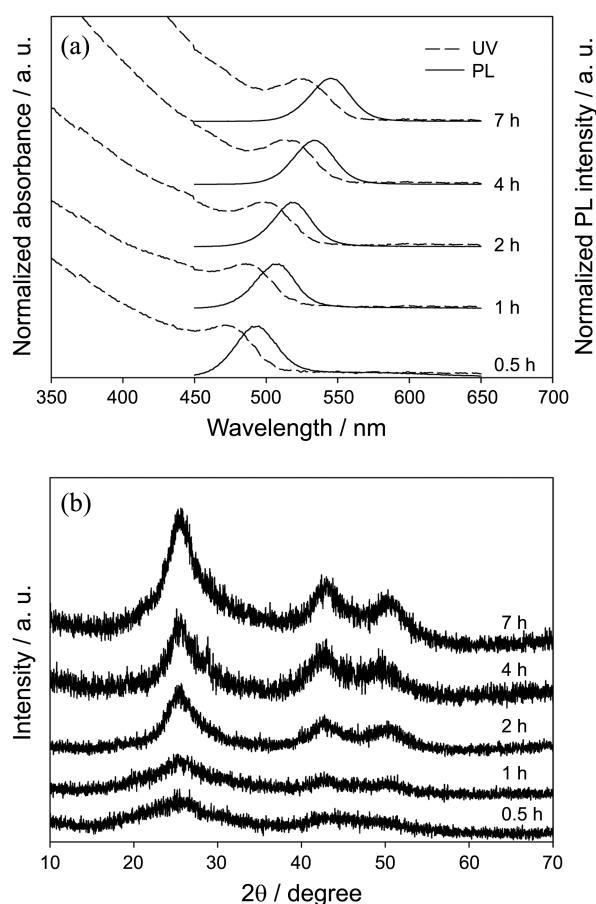


Figure 1. (a) Temporal evolution of UV-Vis absorption (dash line) and PL spectra (solid line) of CdSe QDs; (b) XRD patterns of CdSe QDs prepared at different refluxing time.

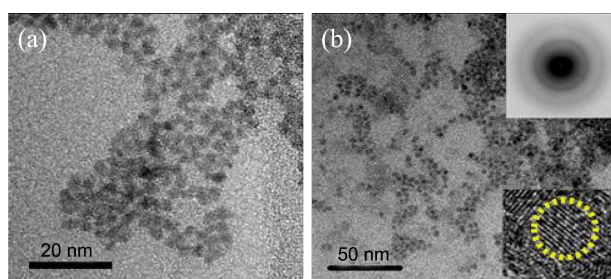


Figure 2. TEM images of CdSe QDs refluxed for (a) 4 h and (b) 7 h. The inset shows the HRTEM image of a single CdSe QD. The selected area electron diffraction (SAED) pattern is given in the same figure as an inset.

peaks are 475, 488, 500, 514 and 523 nm, respectively. Compared with CdSe bulk material (716 nm),¹⁵ the absorption peaks of CdSe QDs have significant blue shift, showing obvious quantum confinement effect. According to the empirical formula, the average sizes are estimated to 2.1, 2.2, 2.3, 2.5 and 2.6 nm, respectively. The particle size increases from 2.1 to 2.6 nm over a period of 7 h, which indicates the growth kinetics is slow. As described in Figure 1, the PL bands of the obtained CdSe QDs are located close to the absorption thresholds (so-called band-edge or “excitonic” photoluminescence) and are sufficiently narrow (full width at half-maximum, FWHM, is about 35 nm). This is probably a result of the strong capping of Cd²⁺ ions with MSA molecules (one –SH and two –COOH groups), which is an important aspect of the processing of QDs with narrower size distribution. The position of the PL maximum of the smallest (2.1 nm) CdSe QDs is located at 495 nm (green emission), whereas the largest (2.6 nm) CdSe QDs obtained emits in yellow-green with a PL maximum at 545 nm. The PLQY of as-synthesized CdSe QDs depends on the particle size, and they are calculated to be 3.2, 7.9, 12.6, 19.8 and 32.4%, respectively. Furthermore, these QDs were very stable in the dark under ambient conditions. After kept for 2 months, their absorption and PL spectra almost had no change, and no obvious precipitations were observed.

X-ray powder pattern was recorded from powder of QDs, and the patterns are shown in Figure 1b. The three broad, distinct peaks at $2\theta = 25$, 43, and 50 correspond to (111), (220), and (311) Miller indice of cubic zinc blende structure.¹⁶ The absence of reflections at $2\theta = 35$ and 46 due to (102) and (103) is an indication that the wurtzite CdSe structure is absent and the QDs possess purely zinc blende structure.¹⁷ In comparison, the zinc blende structure is a more stable form at lower temperature, while the wurtzite structure prefers to form at higher temperature (above 260 °C). The main reason for the formation of the zinc blende structure is that our reaction occurred at a comparative low temperature (100 °C).

TEM measurements were carried out to study the size and

morphology of CdSe QDs. As can be seen in Figure 2, the particles are spherical in shape and show good homogeneity in the particle size distribution. The presence of clear lattice planes in the high resolution image (Figure 2(b) inset) confirms that the QDs have good crystallinity, which is further supported by the SAED pattern (given in the same Figure as an inset).

A simple and rapid method has been developed for the synthesis of CdSe QDs under ambient atmospheric conditions. It is found that the obtained CdSe QDs are homogeneous and spherical. The CdSe QDs prepared by our method show very narrow and symmetric PL spectra with the FWHM of the PL peaks about 35 nm and the maximum PLQY of 32.4%.

Acknowledgments. The present work was supported by the Scientific Research Fund of the Education Department of Guangxi Zhuang Autonomous Region (2013YB014) and the Foundation of College Student Experimental Skills and Innovation Ability Training of Guangxi University (SYJN20130313).

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