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Synthesis of CdSe quantum dots via paraffin liquid and oleic acid*

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Abstract: This paper reported an efficient and rapid method to produce highly monodispersed CdSe quantum dots (QDs), in which the traditional trioctylphosphine oxide (TOPO) was replaced by paraffin liquid as solvent and oleic acid as the reacting media. The experimental conditions and the properties of QDs had been studied in detail. The resulting samples were confirmed of uniform size distribution with transmission electronic microscopy (TEM), while UV-vis absorption and photoluminescence (PL) spectra clearly indicated that such synthesized QDs had good fluorescence properties.

Key words: CdSe, Synthesis, Quantum dots (QDs), Fluorescence
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INTRODUCTION

Semiconductor quantum dots (QDs) are of considerable interest as their applications cover a broad spectrum, from optoelectronic to biomedical technology (Gao *et al.*, 2003). Until now, many work have been reported on synthesis of II-VI QDs, especially CdSe QDs fabricated by a high-temperature organometallic precursor route, which was first published by Murray *et al.*(1993). These QDs had a wide fluorescent emission spectra ranging from blue to red (Han *et al.*, 2001). They could also be easily coated with some other semiconductor materials such as ZnS or CdS to form a core/shell structure, which was confirmed more photochemical stable (Hines and Guyot-Sionnest, 1996). However, it was not easy to make CdSe QDs of high quality because the organometallic precursor route involved an important coordinating solvent named trioctylphosphine oxide (TOPO), which is dangerous, unstable, and environmentally unfriendly. Furthermore, TOPO is also extremely expensive for large-scale fabrication of CdSe QDs. Thus there was a need for a method that could provide rapid, safe and scalable production of highly monodispersed nanoparticles for practical use. Recently, a much cheaper and safer non-TOP-based route for large-scale synthesis of CdSe QDs was proposed by Deng *et al*.(2005). Paraffin liquid was used as solvent instead of TOPO, and high quality CdSe QDs were fabricated with very simple equipments. Here, we also prepared high quality CdSe QDs using oleic acid and paraffin liquid, similar to Deng's way. Moreover, the experimental conditions to control the size of the CdSe nanoparticles and the optical properties of the CdSe QDs were investigated in detail. The structures and properties of these CdSe QDs were characterized by using transmission electron microscopy (TEM), UV-vis absorption and photoluminescence (PL) spectrometers.

EXPERIMENTAL SECTIONS

The typical synthesis procedures (S-1) are as follows. First, 1.0 mmol Se powder was added into 50 ml paraffin liquid in a three-neck flask and heated carefully with stirring to 220 °C to form a bright

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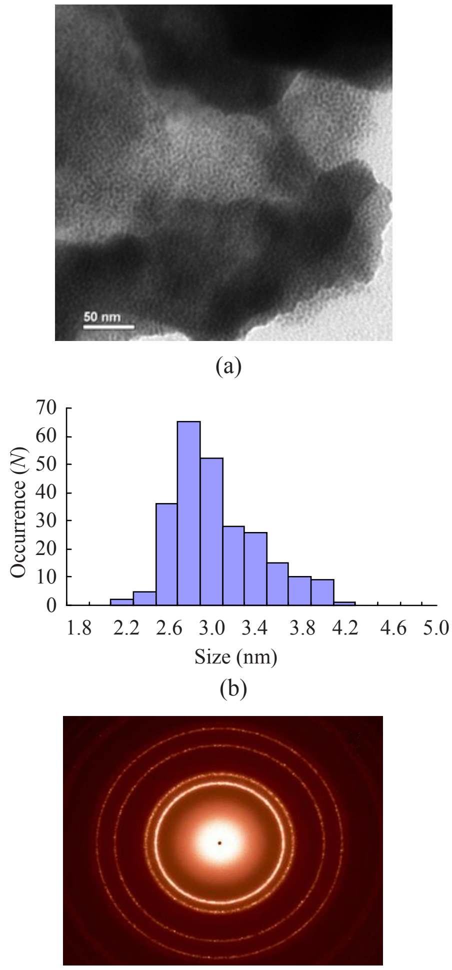
yellow solution (solution A, Se precursor). Second, 20 mmol CdO, 9.6 ml oleic acid and 40 ml paraffin liquid were injected into a flask. When the temperature slowly went up to 150 °C, a homogeneous dark red solution (solution B, Cd precursor) was formed. Then 5 ml of solution B (containing about 2 mmol Cd precursor) was quickly taken out and injected into solution A with continuously stirring. The temperature was restored at 220 °C for QDs' growth. Aliquots of the reaction solution were removed at regular intervals and cooled to room temperature. Methanol was added to precipitate CdSe QDs. The precipitated CdSe QDs were separated by centrifugation, further washed with methanol several times and dried under 50 °C for characterization or redispersed in ethanol for reservation.

In order to investigate the experimental conditions for the size of the nanoparticles: (1) The initial dosage of Se used (1.0 mmol) in the typical experiment was increased to 2.0 mmol (S-2), and reduced to 0.5 mmol (S-3), respectively; (2) The reaction temperature of the typical experiment was changed from original 220 °C (S-1) to 170 °C (S-4) and 250 °C (S-5) respectively.

All the products obtained were treated in the same way and dissolved in ethanol for UV-vis and PL characterization.

RESULTS AND DISCUSSION

A TEM image and a selected area electron diffraction (ED) image of a typical reaction product (S-1) were captured (Fig.1a and 1c) respectively. From the resulting TEM image (Fig.1a), the uniform particles could be clearly observed. On the basis of the TEM of this sample, we can obtain an average size of particles ranging from 2.6 to 4.0 nm through a statistical analysis (Fig.1b). The ED pattern depicted the polycrystalline nature of the as-synthesis nanocrystals, whose diffraction rings could be indexed to perfect multi-crystal diffraction patterns of CdSe QDs (Fig.1c), similar to the previous report (Golan *et al.*, 1992). Fig.2 displayed UV-vis and PL spectra of the typical sample (S-1). As could be seen in Fig.2, there was an apparently absorption peak at around 541 nm in the UV-vis spectrum, indicating a sufficiently narrow size. The normalized PL spectrum showed a fairly symmetric shape, further proving the uniformity of the QDs. The FWHM (full width at half maximum) of the PL spectrum was about 40 nm, which also illustrated that the as-synthesis CdSe QDs



(a)

(b)

(c)

Fig.1 (a) TEM image; (b) Size distribution chart; (c) ED pattern of the CdSe sample (S-1)

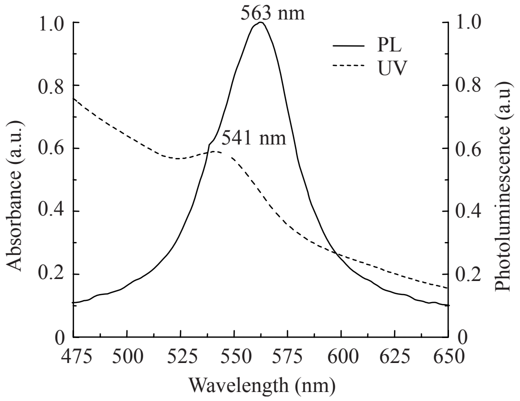


Fig.2 UV-vis absorbance and normalized photoluminescence (PL) spectra of the typical CdSe QD sample

were homogeneous and quite stable in PL emission peaks.

It is generally believed that QDs with larger average size have both UV-vis absorbance peak and PL emission peak at longer position in the wave band than the smaller ones. In this experiment, the effect of the quantity of the Se precursor on the size of final product was investigated firstly. Fig.3 displays typical UV-vis and PL spectra that are obtained at different concentration of Se precursor in the reaction mixture. We can clearly see that with the initial dosage of the Se powder increasing from 0.5 mmol to 2.0 mmol, the UV-vis absorbance peaks (dash lines) red-shifted from 534 nm to 557 nm, indicating that there was control over the population of particles throughout the reaction. On the other hand, all PL spectra (solid lines) of the three samples contained a fairly sharp feature and also red-shifted from 556 nm to 574 nm accordingly, depending on the concentrations of Se precursor. The sharp PL feature corresponded to the radiative recombination inside the CdSe nanocrystals. As the growth progressed, the band edge surface state emission intensity ratio increased in favor of the former, and the entire spectrum shifted toward longer wavelengths, indicating that the nanocrystals became larger (Mićić *et al.*, 1995; 2001).

We also did similar experiments with the same dosage of each reagent in the reaction mixture but changing the growing temperature from 170 °C to 220 °C and 250 °C, respectively. Interestingly, Fig.4 clearly shows that the growing temperature played an important role for the final product. When the growing temperature was maintained at 170 °C, both UV-vis and PL spectra were very weak, indicating few QDs were obtained. However, when the growing temperature was maintained at 220 °C, the product showed stronger UV-vis absorption and a very sharp PL peak, meaning large quantity of CdSe QDs formed. Moreover, with the temperature increasing to 250 °C, the UV-vis absorption peak (dash lines) red-shifted from 541 nm to 546 nm, while the corresponding PL peaks (solid lines) red-shifted from 563 nm to 569 nm. Therefore, we could confirm that QDs seldom grew at temperature below 170 °C, and would grow larger at higher temperature.

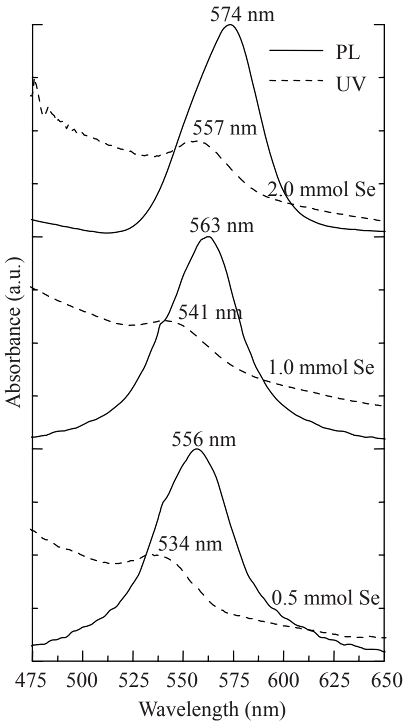


Fig.3 A compound image for the UV-vis absorbance and PL spectra of the CdSe QDs synthesized with different dosage of the Se powder. The dosage were 0.5 mmol, 1.0 mmol and 2.0 mmol from bottom to top

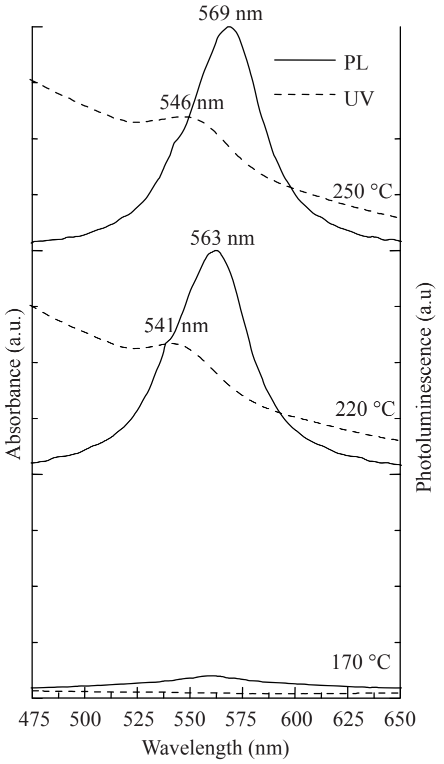


Fig.4 A compound image for the UV-vis absorbance and PL spectra of the CdSe QDs synthesized under different temperature. From bottom to top, the temperatures were 170 °C, 220 °C and 250 °C

CONCLUSION

High quality CdSe QDs could be easily obtained with paraffin liquid as solvent and oleic acid as the reacting media. The quantity of the Se powder used and the growing temperature in the reaction system played an important role for the size control of the final product. UV-vis absorption and PL spectra of the product would red-shift with increasing quantity of Se powder used and growing temperature, corresponding to the size of product growing. Little CdSe QDs could be formed at temperature below 170 °C.

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