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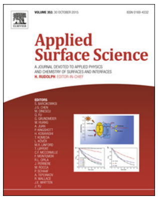

Prepare core–multishell CdSe/ZnS nanocrystals with pure color and controlled emission by tri-n-octylphosphine-assisted method

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ABSTRACT

Core–multishell semiconductor nanocrystals have great potential in light emitting devices (LEDs) display, fluorescent biomarkers and luminescent solar concentrators. However, their applications are strongly limited due to the wide full-width at half-maximum (FWHM), inaccurate controllable emission wavelength, and decreased quantum yield as the shell coverage growth. So there still remains a great challenge for improving the photoluminescence properties of core–multishell quantum dots. In this work, tri-n-octylphosphine (TOP) assisted method was used to prepare CdSe/ZnS QDs with narrow FWHM and controlled emission wavelength, the influence of experimental conditions on the photoluminescent properties of the core–multishell QDs were investigated. The experimental results indicated this is an effective method to prepare core–multishell QDs with pure color emission (FWHM value is smaller than 25 nm after coating with 3 monolayers of ZnS), accurately controlled emission and high QY (>95%). This is the smallest FWHM for core–multishell QDs. The emission wavelength of the as-prepared core–multishell QDs can be continuously tuned by simply varying the emission of the core nanocrystals. Furthermore, the knowledge gained in this study enabled us to better understand the mechanism of TOP-assisted method and provide a promise way for light emitting diodes-backlit display with high color saturation.

1. Introduction

Quantum dots (QDs) have been considered as an excellent material in light emitting diodes (LEDs) [1–4]. However, plain core QDs tends to photooxidation, coating a shell with wider band gap material (e.g. ZnS) is able to improve their photostability [5]. Furthermore, ZnS shell can improve the fluorescence quantum yield (QY) of the core material thought passivating the trap sites on their surface [6–8]. However, their photoluminescence QY decreased as the shell coverage further growth. Additionally, to be ultimately competitive in QD-LEDs, especially for QD-LED backlit and displays, QDs with narrow full-width at half-maximum (FWHM) and accurate tunable peak emission wavelength are urgent [9–11].

In order to meet the needs of application, many methods for preparing high-quality core–shell QDs have been continuously developed [6,12–15]. In particular, successive ionic layer adsorption and reaction (SILAR) is the most widely used method [7,16,17]. However, the intrinsic strain-induced formation of misfit dislocations and the defects within the shell cannot be avoided by SILAR method, which results in the decrease of QY as the shell thickness increasing [6,8,18]. Until now, many efforts have been paid to improve the QDs efficiencies [19,20], and these reported methods indeed can prepare core–shell QDs with high QY, but the FWHM increased sharply after high coverage of shell and the emission wavelength could not be controlled well, especially for the CdSe/ZnS. Therefore, synthesis core–multishell QDs with extremely improved FWHM and accurate controlled emission wavelength still remains a great challenge.

Our previous study [21] indicated that tri-n-octylphosphine (TOP) can improve the QYs of core–multishell CdSe/ZnS QDs. So in this study, we focused on improving the color purity of the prepared core–multishell QDs with controlled emission wavelength. We made a systematic study on the relationship between their color quality and the growth conditions of TOP-assisted method. Under the optimal conditions, the FWHM value for multi-color QDs can be maintained between 25 and 28 nm even after coating 3 monolayers of ZnS, and the emission wavelength can be accurately controlled

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in a wide range. Furthermore, the effect of TOP in improving the QY and FWHM value of the core–multishell CdSe/ZnS QDs were investigated. The knowledge gained in this study enabled us to better understand the mechanism of TOP-assisted method.

2. Materials and methods

2.1. Chemicals

Cadmium oxide (99.99%), selenium powder (99.5% powder), sulfur (99.5%, powder), zinc oxide (99.99% powder), oleic acid (OA, 90%), stearic acid (SA, 95%) were purchased from Sigma–Aldrich, USA. Trioctylphosphine oxide (TOPO, 95%), tri-n-octylphosphine (TOP, 97%), 1-octadecene (ODE, 90%), octadecylamine (ODA, 90%) and other organic solvents were obtained from J & K Chemical Reagent Company, China. All the chemicals were used as received without further purification.

2.2. Synthesis of CdSe quantum dots (QDs)

2.2.1. Synthesis of Se-rich CdSe core QDs

Highly fluorescent CdSe core with orange color were prepared by a modified procedure [16,22–24]. For a typical reaction, a mixture of 0.2 mmol of CdO and 0.8 mmol of stearic acid in a 25-mL three-neck flask was heated to about 220 °C under argon atmosphere to obtain a colorless clear solution. After cooling to room temperature, 2.16 g of ODA (ODA:Cd = 40:1) and 8 mL of ODE were added into the flask, and reheated to 270 °C under argon atmosphere. At this temperature, a selenium solution prepared by dissolving 2 mmol of Se in 2 mL of TOP was swiftly injected. The growth temperature was then reduced to 250 °C and maintained for 5 min. Finally, the reaction mixture was cooled to room temperature, and an extraction procedure was used to purify the nanocrystals from side products and unreacted precursors [16,23]. The prepared CdSe QDs is about 3.7 nm with a first absorption peak around 575 nm. CdSe core with different emission were prepared by different ODA:Cd ratio (12:1, 20:1, 30:1, 50:1, 60:1, 65:1, 70:1, 80:1 and 90:1). For instance, 0.65 g (ODA:Cd = 12:1) and 4.9 g (ODA:Cd = 90:1) of ODA were used to prepare green color CdSe core QDs with emission peak at 570 nm and red color CdSe core QDs with emission peak at 615 nm, respectively.

2.2.2. Synthesis of CdSe core QDs with different Cd:Se ratio

Four representative reactions were carried out by using the same manner as for the orange color QDs except the initial Cd:Se molar ratio of the precursors was varied from 5:1 to 1:5.

2.3. Synthesis of the core–shell QDs

2.3.1. A typical TOP-assisted process for preparing CdSe/ZnS core–shell QDs with emission peak at 590 nm

High quality CdSe/ZnS core–shell QDs was prepared according to our previous research [21]. The synthesis process is presented graphically in Scheme 1. For a typical reaction, the orange-colored CdSe QDs (3.7 nm in diameter, 7.7×10^{-5} mmol of particles) dissolved in 2.5 mL of hexanes were mixed with 0.8 g of ODA and 4.0 mL of ODE in a 25-mL three-neck flask. The flask was pumped down at room temperature with a mechanical pump for 30 min to remove the hexanes and at 100 °C for another 10 min to remove any residual air from the system. Subsequently, the system was switched to argon atmosphere and heated to 140 °C for the injections.

For in-situ growth of the buffer layer, 0.4 mL of TOP solution was injected as an activator and the reaction mixture was further maintained at 200 °C for 30 min. Then, 0.33 mL of Zn solution (0.1 M) was injected and maintained at 200 °C for 20 min.

After that, without further purification, the reaction temperature was decreased from 200 °C to 180 °C. Then 0.33 mL of S precursor solution was added into the reaction flask via syringe and the temperature was increased to 220 °C immediately, for the growth of ZnS outer-layers. After 60 min, the first ZnS monolayer was grown in-situ, and then the temperature was decreased to 140 °C.

After 0.4 mL of fresh TOP solution was injected, the temperature was increased immediately to 180 °C. The Zn and Se precursor solutions (0.46 mL each) were added consecutively via syringe to the reaction flask at the interval of 10 min for the growth of second ZnS monolayer. Cycling of injection and growth continued for both the increased monolayers of ZnS shell, the amounts of subsequent injection solutions were calculated using the method described in our previous work [21]. The reaction was terminated by allowing the reaction mixture to cool. The final product was diluted by hexanes followed by a methanol extraction. The extraction procedure was repeated for three times, and the top hexane layer was stored. If necessary, heating or further addition of ODE can be used for the better extraction. The nanocrystals were further purified by precipitating with acetone or methanol. Highly pure nanocrystals were obtained by repeating the above purification procedure for several times. The emission wavelength of the final orange colored CdSe/ZnS core–shell QDs is 590 nm.

Green and red colored core–shell QDs were prepared by the same procedures as above, except for the bare CdSe cores and the amounts of precursor for shell growth was different.

2.3.2. Large-scale synthesis of orange colored CdSe/ZnS core–shell by TOP-assisted method

The TOP-assisted procedure was readily extended for large-scale preparation. The procedures were the same as described in Section 2.3.1 except for the amounts of cores and shell precursors. The quality of the resulting nanocrystals was similar to that of the small scale synthesis.

2.3.3. Synthesis of CdSe/ZnS core–shell QDs with different initial Cd:Se ratio of precursors

CdSe/ZnS core–shell QDs with different initial Cd:Se ratio of precursors (5:1, 2:1, 1:2, 1:5) were carried out by using the same method described in Section 2.3.1.

2.3.4. Synthesis of buffer layer coated core–shell emitter with different initial Cd:Se ratio of precursors

As for XPS measurement, ten times scale of core–shell QDs was prepared. In a typical large-scale synthesis, calculated amount of CdSe core prepared by different Cd:Se ratio was dissolved in 30 mL of hexanes and mixed with 8 g of ODA and 40 mL of ODE in a 250 mL threeneck flask. Then the flask was pumped down at room temperature with a mechanical pump for 40 min to remove the hexanes and at 100 °C for another 10 min to remove any residual air from the system. Subsequently, the system was switched to argon atmosphere and the reaction mixture was heated to 140 °C before the injections.

For the in-situ growth of buffer layer, 4 mL of TOP solution was injected as an activator, and the reaction mixture was maintained at 200 °C for another 20 min. After the activation, 4 mL of 0.1 M Zn injection solution was injected and maintained for 30 min at 210 °C to allow the growth of buffer layer. Purification of the nanocrystals was carried out by using the same method as described in Section 2.3.1.