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Short communication

Intensification of nucleation stage for synthesizing high quality CdSe quantum dots by using preheated precursors in microfluidic devices

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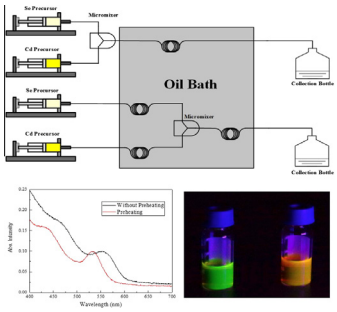
HIGHLIGHTS

- Nucleation stage was intensified by using preheated precursors in microfluidic devices.
- Small size CdSe QDs with green fluorescence can be synthesized.
- A method to synthesize monodispersed crystal seeds for further synthesis was developed.

GRAPHICAL ABSTRACT



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ABSTRACT

We developed a simple and facile microfluidic approach to continuously synthesize high quality CdSe quantum dots by using preheated precursors. The preheating process could intensify the burst of nucleation, and CdSe quantum dots with smaller size would be synthesized compared to previous methods using room-temperature precursors directly. Besides, a burst of nucleation stage and a stable growth stage without prolonged nucleation could reduce the size distribution of CdSe quantum dots through the preheating process. By this method, high quality quantum dots with small size or high quality crystal seeds could be synthesized easily, which is necessary for the synthesis of small core–shell quantum dots or large quantum dots with high monodispersity.

1. Introduction

Over the past decades, semiconductor quantum dots, especially CdSe quantum dots, which exhibit excellent size-tunable optical properties and soluble characteristics, have drawn great attention both in fundamental researches and practical applications [1–5]. Batch reactors were widely used for the synthesis of CdSe quantum dots [6–9]. However, due to the lack of rapid mass transformation and accurate temperature control in batch reactors, high-quality CdSe quantum dots were difficult to be synthesized. As the mass and heat transfer efficiency in microfluidic devices is much higher than that in batch reactors [10,11], many methods based on microfluidic devices for CdSe quantum dots synthesis have been developed [12–16]. For example, Bawendi et al. [12] used a continuous-flow microcapillary reactor to synthesize CdSe quantum dots and the absorbance peaks varied from 510 nm to 606 nm. It was achieved by changing Se precursors concentration, reaction temperature and residence time. Sargent et al. [13] separated the nucleation and growth stages to synthesize high quality PbS quantum dots by using a dual-temperature-stage flow in microfluidic devices and this method was suitable for the synthesis of other quantum dots like CdSe as well. Nevertheless, there still existed several limitations for the synthesis of CdSe quantum dots by using continuous-flow microfluidic devices [17]. One of them was the wide size distributions. To reduce the size distributions,

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the burst of nucleation stage is essential. An elevated temperature can promote the burst of nucleation stage [18–20]. The existing researches in continuous-flow microfluidic devices all used mixed room-temperature precursors and then raised the temperature to over 250 °C to synthesize CdSe quantum dots [12–16]. It would make the nucleation stage not only occur at the beginning but also during the growth stage, and as a consequence, additional crystal seed formed during the growth stage, which broadened the size distribution of CdSe quantum dots.

In this communication, the Cd precursor and Se precursor were preheated to reaction temperature. The adsorbed ligands on the precursors such as amines at room temperature would be desorbed at elevated temperature, so the chemical reactivity of precursors would increase [9,21]. When the preheated Cd and Se precursors are mixed in the micromixer, the burst of nucleation would occur instantly. So smaller CdSe quantum dots could be synthesized through the preheating progress. Besides, the size distribution of CdSe quantum dots would be narrowed as fewer additional crystal seeds would be formed during the growth stage.

To synthesize CdSe quantum dots, our microfluidic process was adapted from well-known batch mode synthesis methods [9,15,21]. For the Cd precursor, cadmium oleate and oleylamine were dissolved in 1-octadecene, and for the Se precursor, Se powder was dissolved in trioctylphosphine and 1-octadecene. As shown in Fig. 1, the Cd precursor and Se precursor were first preheated in oil bath before mixing in a micromixer. The mixed solution kept heated in microchannel by oil bath and then products were collected in the collection bottle. For the contrast experiments, precursors were mixed at room temperature before heating. The length of micro channels in which the mixed solution was heated was the same for both methods. CdSe quantum dots were purified by ethanol and dispersed in chloroform for UV–Vis. spectra, photoluminescence (PL.) spectra and HRTEM characterisation. The specific information about materials, precursor solutions preparation, experimental microfluidic devices and characterisation method could be found in Supporting Information.

The typical UV–Vis. spectra and PL. spectra of CdSe quantum dots synthesized by two methods are shown in Fig. 2a. Two samples were synthesized at 270 °C and the residence time was 40 s. Firstly, the first band-edge excitation peak was sharp by using preheated precursors, while wide absorption peak was observed for the samples prepared with room temperature precursors. This indicated CdSe quantum dots with fewer structure defects were synthesized after the burst of nucleation stage. Moreover, blue shift of the first excitation peak was observed in the UV–Vis. spectra while the precursors were preheated before reaction, which indicated that the size of CdSe quantum dots become smaller.

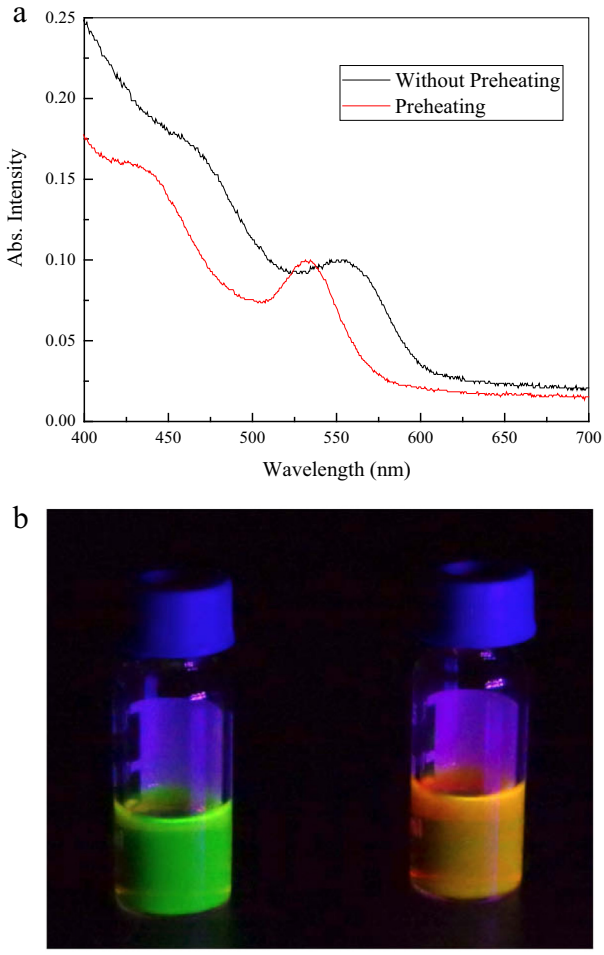

Fig. 2. CdSe quantum dots synthesized at 270 °C for 40 s with or without the preheating process. (a) UV–Vis. spectra and PL. spectra of the two samples. (b) A photograph of these two samples under a UV lamp. The left one was synthesized from preheated precursors, and the right one was synthesized from room-temperature precursors.

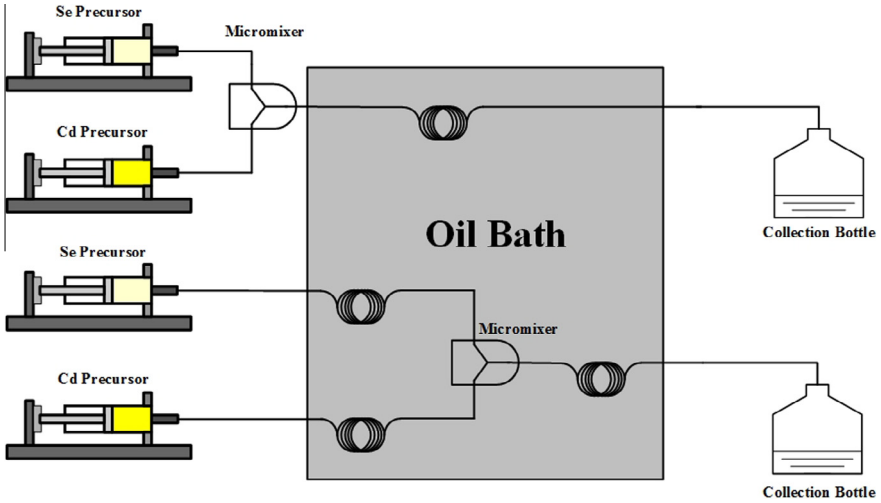

Fig. 1. Schematic diagram of two microfluidic methods for CdSe quantum dots synthesis.