In-situ EXAFS study of nucleation process of CdSe nanocrystals

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Abstract. An in-situ EXAFS method is developed to study the nucleation and growth processes of nanocrystals by using a microfluidic reactor which converts the time-dependent kinetics to position-dependence. As an example, we measured the Se K-edge EXAFS spectra for CdSe nanocrystals along a microfluidic reactor channel and indicated strong time-dependence of the nucleation and growth at the beginning of the reaction. A rapid increase of the reaction yield within several seconds was observed. It is found that after injection of starting materials, the nucleation occurs abruptly and the CdSe nuclei concentration reaches the maximum and then declines rapidly.

1. Introduction

CdSe nanocrystals have attracted significant attention due to their size-tunable optical properties and promising applications in a variety of fields ranging from optoelectronic devices [1, 2] to biomedical tags [3, 4]. Colloidal chemical growth is one of the most important routes of synthesizing CdSe nanocrystals with low cost and good repeatability [5, 6]. Understanding the details of the process and parameters controlling the synthesis is essential for the growth of nanocrystals with the desired size and optoelectronic properties, especially the nucleation and growth processes are highly important issues [7].

Generally, in a colloidal chemical reaction of synthesizing CdSe nanocrystals, nucleation and growth processes occur simultaneously in a confined volume. However, in the initial stage of reaction, typically within tens of seconds, the nucleation process is abrupt and dominant over the slow growth process.

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2. Experiment

The synthesis of the CdSe QDs was modified from the original organometallic procedure [18] for utilization of the microfluidic reactor [9, 17, 19]. Three raw material stock solutions (Se source, Cd source and ligand solutions) were prepared under a dry nitrogen atmosphere. The selenium stock solution was prepared by dissolving 0.711 g of selenium powder in 33.4 g of trioctylphosphine (TOP), which was then diluted with 47.2 g of octadecene (ODE). The cadmium stock solution was prepared by heating a mixture of 0.480 g of Cd(CH₃COO)₂·2H₂O, 2.89 g of oleic acid and 76.6 g of ODE at 180 °C under Ar flow. The solution was then degassed at 100 °C for approximately 30 min. The surface ligand solution was prepared by dissolving dodecylamine (DDA) in ODE. These three stock solutions were loaded into three glass syringes separately and then mixed in the microfluidic mixer connected to a Kapton tube. In the mixed solution, the initial Se and Cd concentrations were [Se]₀=30 mM and [Cd]₀=6 mM, respectively, and the DDA concentration was 5 wt.%.

The mixed raw material solution was subsequently heated in the connected Kapton tube. The inner and outer diameters of the tube were 0.5 mm and 0.66 mm, respectively, and 70 mm of it was attached to a heating unit at a target temperature of 240 °C. The flow rate in the Kapton tube was controlled at 7.6mm/s by using a syringe pump. The reaction time can then be calculated from the length of the heating part of the microreactor channel and the flow rate. In-situ EXAFS spectra at Se K-edge were performed at beamline BL13B1 of Photon Factory (PF) of High Energy Accelerator Research Organization, Japan. The electron beam energy of PF was 2.5 GeV and the maximum stored current was about 450 mA. The water-cooled Si(111) plane double-crystal monochromator was used. The microreactor was mounted on a high precision XY stage on a goniometer (Huber 410) controlled by stepping motors. In order to cover a long stroke (80 mm) along the X-axis, a two-stage mechanism is used.

3. Results and discussions

Figure 1(a) shows the Se K-edge EXAFS functions χ(k) measured at points A through D, as well as those of the TOP-Se solution and CdSe powder measured at room temperature. The corresponding

![Graph](image)

**Figure 1.** (a) Se K-edge EXAFS functions χ(k) at points A, B, C, and D, along with those of the TOP-Se solution and CdSe powder measured at room temperature. (b) The corresponding Fourier transform magnitudes of the k²-weighted χ(k) functions.
Fourier transforms (FT) magnitudes of the $k^2$-weighted $\chi(k)$ functions in the $k$-range of 2–10 Å$^{-1}$ are shown in Fig. 2(b). In the FT for the starting TOP-Se, a prominent peak located at $R=1.6$ Å is attributed to the Se-P bond. For CdSe powder data, the strong peak at 2.5 Å is ascribed to the nearest Se-Cd bond, while a side lobe at 1.8 Å arises from the nonlinearity of the phase-shift of Cd scatterer [20]. The FT at point $A$ resembles that of TOP-Se, and no signal arising from Se-Cd bond can be observed. At point $B$, Se-P peak is still prominent, but a weak Se-Cd peak appears at 2.5 Å. This Se-Cd peak further increases in intensity at point $C$, and reaches the maximum at point $D$. An obvious reduction of the Se-P peak intensity is also evident at point $D$. Due to the limited heating time (<8.1 s) of reactants in the microreactor which is not enough for the long growth process lasting several hours [8], the Se-Cd bond can mostly originate from the initial CdSe nuclei. The observed position-dependence primarily reflects the time-dependent nucleation process of the CdSe nanocrystals within several seconds starting from the TOP-Se solution at 240 °C.

Amine-capped CdSe nanocrystals have been studied by many researchers [12, 21-27]. In comparison with the conventional TOP-TOPO method, the addition of primary amine (such as DDA, hexadecylamine) to the growth solvent as stabilizing ligands leads to improvements in both the size distribution and photoluminescence quantum efficiency [21, 22, 27]. The benefits of amine over TOP and TOPO as stabilizing ligands have been interpreted by the higher packing densities due to the less sterically hindered structure of amine and the strong chemical bond between amine and the surface cadmium atoms [21, 22, 27]. As a result, most of the Se atoms at the surface of CdSe nanocrystals are not linked to either DDA or TOP [24], or may be unpassivated [28].

The observed Se-P bond in Fig. 1(b) primarily comes from the unreacted TOP-Se. Due to the large excess of TOP-Se to the Cd precursor, at each point the Se-P peak is always dominant over Se-Cd peak in the EXAFS spectra. At point $A$, no TOP-Se has been consumed to form CdSe nanocrystals. At other points, Se-Cd peak appears, indicating the formation of CdSe nuclei. The Debye-Waller factors and bond lengths of Se-P bonds at these points could be regarded as equal, since the temperatures were very close. Therefore, the Se-P peak intensity is proportional to the amount of unreacted TOP-Se. By examining the fluorescence intensity of repeated scans, we noted a weak pileup of CdSe nanocrystals on the capillary inner wall at point $D$ which reduced the contribution of Se-P and a correction was therefore made.

The growth of CdSe nanocrystals in hot oleic acid/ODE/DDA provides an ideal model system for studying the kinetics of nucleation and growth in solution [10, 12]. According to Ref. [10], the Cd concentration in the nucleation process obeys an equation of the form:

$$\frac{d[\text{Cd}]}{dt} = -kA(t)[\text{Cd}], N(t),$$  \hspace{1cm} (1)

where $[\text{Cd}]$ is the concentration of available Cd at time $t$, $A(t)$ is the surface area of each particle at time $t$, $N(t)$ is the number of particles at time $t$, and $K$ is an interfacial rate constant that reflects the rate determining steps during deposition. As usual, the CdSe nanocrystals are assumed to be spherical in shape, so $A(t)=4\pi r^2$, and

$$N(t) = -\frac{d}{dt} \frac{1}{4\pi Kr^2}.$$  \hspace{1cm} (2)

The temporal evolution of $[\text{Cd}]$, could be estimated from the consumed TOP-Se, which then allows us to calculate $-d[\ln([\text{Cd}])]/dt$ as shown in Fig. 3(b). Strikingly, there is a maximum in the $-d[\ln([\text{Cd}])]/dt$ curve; from point $B$, $C$, to $D$, $-d[\ln([\text{Cd}])]/dt$ rapidly decreases with time. It is well known that the radius $r$ of CdSe nanocrystals increases with time, especially at the initial stage after injection [10, 12, 29]. This is also confirmed by the red-shift of our UV-vis absorption spectra with time (Fig. 2).

4. Conclusions

We developed an in-situ EXAFS method aiming at the study of nucleation and growth progresses of
nanocrystals by using a microfluidic reactor. We measured the Se $K$-edge EXAFS spectra for CdSe nanocrystals along the reactor channel and found strong time-dependence of the nucleation and growth at the beginning of the reaction. A rapid increase of the reaction yield of CdSe nanocrystals within several seconds was observed. It is found that after injection of starting materials, the nucleation occurs abruptly and the CdSe nuclei concentration reaches a maximum and then declines rapidly. The results show the promising capability of in-situ EXAFS combined with a microfluidic reactor for investigations of nucleation and growth processes of various nanocrystals synthesized in solution.

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