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In situ extended x-ray absorption fine structure study of initial processes in CdSe nanocrystals formation using a microreactor

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The nucleation process of CdSe nanocrystals is studied by fluorescence-detected extended x-ray absorption fine structure (EXAFS) using a microreactor and synchrotron radiation. Detailed analysis of in situ Se K-edge EXAFS data measured along a microreactor channel revealed a strong position-dependence which displays a rapid increase in the CdSe phase with time at the initial stage. The results indicate that the CdSe nucleation completes within several seconds starting from trioctylphosphine Se solution and dodecylamine surfactant at 240 °C. This shows the promising capability of in situ EXAFS combined with a microreactor to investigate the nucleation process of nanocrystals synthesized in a solvent. © 2009 American Institute of Physics.

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CdSe nanocrystals attract much attention owing to their promising applications in optoelectronic devices and biomedical tags.1–3 This is due to the fact that CdSe nanocrystals with a narrow size distribution and controllable optical properties can be easily prepared.4,5 Colloidal chemical synthetic methods are widely used to synthesize CdSe nanocrystals with controlled particle size, and the nanocrystals are typically stabilized with ligand molecules as surfactants. Understanding the roles of stabilizing ligands6–10 and details of the nucleation and growth processes11 is essential for growing nanocrystals with desired size and optoelectronic properties. In an initial stage of a reaction, typically within tens of seconds, the dominant process is nucleation, which is also accompanied by a slow growth process.12 Although the growth process has been extensively studied and its mechanism is well understood,12,13 it is rather challenging to probe the quick nucleation process.14

In this letter, in situ extended x-ray absorption fine structure (EXAFS) technique is employed for studying the CdSe nanocrystals nucleation process by using a microreactor. The basic idea is to let the reaction solution flow along a microreactor channel at a constant flow rate15 and to measure the EXAFS spectra at different positions after the start of the reaction. In situ measurements along a microreactor channel converts time dependence to position dependence, and therefore this makes it feasible to observe various chemical reaction dynamics or phase transform processes within a confined volume over a long distance. As compared with time-resolved EXAFS measurement, this method has the advantage that data accumulation for measurements at a fixed position is possible. Thus it allows improving the signal-to-noise ratio for the dilute solution. In addition, this method does not require sophisticated improvement of the EXAFS beamline and detector electronics.

The CdSe nanocrystal preparation method reported by Peng and Peng4 was modified for the present microreactor system. We prepared three stock solutions, Se source, Cd source, and amine solution. Se powder was dissolved in trioctylphosphine (TOP) to prepare a TOP-Se stock solution, which was then diluted in octadecene (ODE). The cadmium stock solution was prepared by heating a mixture of Cd(CH3COO)2, oleic acid, and ODE at 180 °C. Dodecylamine (DDA) was dissolved in ODE. These three stock solutions were mixed in the microfluidic mixer connected to the heated 70-mm-long reactor channel (Kapton tube). Se and Cd concentration in the mixed solution were 30 and 6 mM, respectively. The inner and outer diameters of the tube were 0.5 and 0.66 mm, respectively, and it was attached to a heating unit kept at a temperature of 240 °C. The flow rate in the Kapton tube was controlled at 7.6 mm/s by using a syringe pump. The heating time can be calculated from the length of the heating part of the microreactor channel and the flow rate. A schematic representation of the in situ microreactor EXAFS system is shown in Fig. 1(a).

In situ EXAFS spectra at Se K-edge were performed at beamline BL13B1 of the Photon Factory (PF) of High Energy Accelerator Research Organization, Japan. The electron beam energy of PF storage ring was 2.5 GeV, and the maximum stored current was about 450 mA. The water-cooled Si(111) double-crystal monochromator was used.16 The microreactor was mounted on a high precision XY stage on a goniometer (Huber 410) controlled by stepping motors. The beam position and temperature distribution were monitored by closed-circuit television (CCTV) and infrared television.
accompanied by an obvious reduction of the Se–P peak intensity. Because of the limited heating time (<8.1 s) of the reactants in the microreactor, which appeared not long enough for the slow growth process, the Se–Cd bond can mostly originate from the initial CdSe nuclei formed from the TOP-Se solution at 240 °C. The strong position-dependence indicates a rapid increase in the reaction yield to CdSe nuclei along the microreactor channel.

We also performed an ex situ UV-visible absorbance measurement, using the same reaction conditions as in the in situ EXAFS experiment. Figure 3(a) displays the UV-visible absorption spectra as a function of time after injection. No excitonic transition can be detected until at 2.6 s, a broad absorption band peaked at 460 nm appears, which was subsequently redshifted to 472 nm at 4.0 s and to 498 nm at 8.1 s. Following Yu et al., we estimated the average diameters of the CdSe nanoparticles to be 2.0, 2.1, and 2.3 nm at 2.6, 4.0, and 8.1 s, respectively. This gradual average particle size increase indicates a slow growth process following the initial nucleation.

Amine-capped CdSe nanoparticles have been studied by many researchers. In comparison with the conventional TOP-triocetylphosphine oxide (TOPO) method, the addition of primary amine (such as DDA, hexadecylamine) as a surfactant leads to improvements in both the size distribution and photoluminescence quantum efficiency. The benefits of amine over TOP-TOPO have been attributed to the higher packing densities due to the less sterically hindered
structure of amine and the strong chemical bond between the amine and the surface cadmium atoms. As a result, most of the Se atoms at the surface of CdSe nanocrystals are not linked to either DDA or TOP, or may be unpassivated. This is also supported by the absence of Se–N signal in the EXAFS spectra.

We estimated the consumed TOP-Se as a function of time from the Se–P peak intensities at different points, which reflects the initial nucleation rate. The observed Se–P bond in Fig. 2(b) primarily comes from the unreacted TOP-Se. Due to the large excess of TOP-Se to the Cd precursor, the Se–P peak is dominant over Se–Cd peak in the EXAFS spectra. The remaining amount of TOP-Se is proportional to the Se–P peak intensity, therefore the consumed TOP-Se at different points could be evaluated from the Se–P peak intensities by assuming that no TOP-Se is consumed at point A. After correcting the pileup effect of CdSe nanocrystals on the tube surface, the obtained fraction of the consumed TOP-Se in the nucleation process is shown in Fig. 3(b) which demonstrates the trend that the nucleation process is very quick within the first 1–3 s after the starting of reaction at 240 °C.

The growth of CdSe nanoparticles in hot oleic acid/ODE/DDA provides an ideal model system for studying the kinetics of nucleation and growth in solution. According to Ref. 25, the Cd concentration in the initial nucleation and growth process obeys the following equation:

\[
\frac{d[Cd]}{dt} = -kA(t)[Cd]N(t),
\]

where [Cd] is the concentration of available Cd at time \( t \), \( A(t) \) is the surface area of each particle, \( N(t) \) is the number of particles, and \( k \) is an interfacial rate constant. Here the CdSe nanoparticles are assumed to be spherical in shape, so \( A(t) = 4\pi r^2 \) and

\[
N(t) = \frac{1}{[Cd]_0} \frac{d[Cd]/dt}{4\pi kr^2}.
\]

[ Cd] as a function of \( t \) could be estimated from the consumed TOP-Se since the ratio of consumed Se and Cd was approximately 1:1, which then allowed us to calculate \( -d[Cd]/dt/[Cd] \), as shown in Fig. 3(b). Strikingly, there is a maximum in the \( -d[Cd]/dt/[Cd] \) curve near point B, after that \( -d[Cd]/dt/[Cd] \) decreases rapidly with time. The red-shift of the UV-visible absorption spectra with time [Fig. 3(a)] indicates that the radius \( r \) of CdSe nanoparticles increases with time. Therefore, it can be deduced from Eq. (2) that the number of CdSe particles \( N(t) \) reaches a maximum at around 1.4 s and then declines rapidly. This demonstrates the existence of a critical nuclei density at the initial nucleation stage, beyond which the size grows at the expense of nuclei density. Finally we note that in our experiment, nuclei appeared in a homogeneous solution without any seed for heterogeneous nucleation (e.g., dust particles or bubbles). The conditions of homogeneous nucleation were fulfilled and the nuclei were formed via a burst homogeneous nucleation process. Immediately after the burst nucleation, the density of nuclei became large which made reacting materials (especially Cd precursor) deficient and therefore the growth was hindered.

In summary, we developed an in situ EXAFS method aiming at the study of nucleation and growth progresses by using a microreactor. We measured the Se K-edge EXAFS spectra for CdSe nanoparticles as a model system along the microreactor channel and found strong time-dependence of the initial nucleation progress. 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.

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\[ \text{Eq. 1} \]

\[ \text{Eq. 2} \]