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In-Situ XAS Study on Initial Growth of CdSe Nanocrystals Using Microfluidic Cell

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Introduction

CdSe nanocrystals attract much attention owing to their promising applications in optoelectronic devices and biomedical tags. For applications, monodisperse and highly crystalline NCs are needed. This demands a complete understanding of the details of their nucleation and growth processes. But it is still challenging due to the short nucleation time and lack of information on the initial stage.[1] In this report, We used an in-situ EXAFS method for studying the nucleation as well as growth progresses by using a microfluidic cell.[2] We find that initial nucleation burst is associated with a rapid particle size increase, and after that the growth rate is slowed. [3]. At the same time, we also find that the initial nucleation stage is significantly accelerated by the presence of DDA, but the growth rate of nanocrystals is also reduced.[4]

Experimental

CdSe nanocrystals (NCs) were prepared in a microfluidic cell (Kapton tube) at 513 K. The inner and outer diameters of the tube were 0.5 and 0.66 mm. The flow rate in the Kapton tube was controlled at 7.6 mm/s by using a syringe pump.

The Se K-edge XAFS spectra of CdSe NCs samples were measured at the beamline BL-13B of Photon Factory and NW-2A of Photon Factory - Advanced Ring for Pulse X-rays, High Energy Accelerator Research Organization (KEK). The Fluorescence x-ray signal was detected by a compact silicon drift diode detector.

Results and Discussion

Figure 1 shows the Se K-edge Fourier transforms (FTs) and UV-vis absorbance spectra of the CdSe NCs. It can be readily observable from FTs and UV-vis absorbance spectra that the initial nucleation stage is significantly accelerated by the presence of DDA: without addition of DDA the nucleation took about 5 s, while it was shortened to within 1 s with the presence of 5 wt.% and 10 wt.% DDA.

Figure 2 shows the temporal evolution of CdSe NCs in the presence of 5 wt.% and 10 wt.% DDA: (a) diameter, (b) particle concentration. As seen from Figure 2a, the addition of DDA affects the reaction in two distinct ways. First, in the presence of DDA with higher concentration (10 wt %), the CdSe nanocrystals size is larger within the first 4 s, especially the detectable starting particle size is much larger (1.9 vs 1.4 nm). Second, after 4 s of reaction, the CdSe nanocrystals size for 10 wt % DDA becomes smaller and at the same time the growth rate is considerably lower. it is evident that DDA accelerates the initial surface reaction in the nucleation stage but retards the subsequent particle growth if too much DDA is added. Figure 2b is a plot of the particle concentration $N(t)$. The addition DDA led to a burst of nucleation28 of CdSe NCs after heating the reaction solution. Within 2.4 s, the particle concentration for 10 wt % DDA was somehow smaller than the value at the same reaction time for 5 wt % DDA, suggesting that too higher DDA concentration reduced the initial nuclei density. Therefore, we purpose that addition of DDA plays two competitive roles, namely, accelerating the initial nucleation by activating the precursors and delaying the subsequent growth of the NCs.

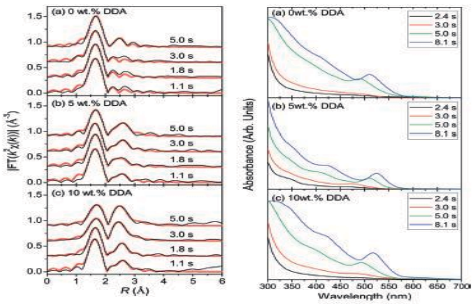

Figure 1. Fourier transform (FT) and UV-vis absorbance spectra of CdSe nanocrystals.

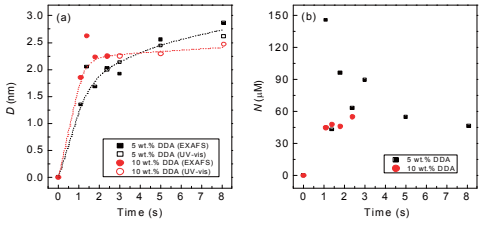

Figure 2. Temporal evolution of CdSe nanocrystals in the presence of 5 wt.% and 10 wt.% DDA: (a) diameter, (b) particle concentration.

Reference

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