

Structure Evolution of CdSe Nanocrystals During Ripening Process Studied by XAFS

Xinfeng Zhang, Feng Wei, Wensheng Yan, and Shiqiang Wei*

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

Abstract. The structure evolution of CdSe nanocrystal with different grown sizes (1.9, 2.7 and 3.1 nm, respectively) obtained by size-selective method from colloidal solution is investigated by XAFS. By such purposeful design of samples, we have investigated the isolated ripening process effect on the structure of nanocrystals. The Se K-edge XAFS results of CdSe nanocrystals show that structure disorder of nanocrystal increases from $0.0046 \text{ \AA}^2$ to $0.0053 (0.0072) \text{ \AA}^2$ while its size grows from 1.9nm to 2.7 (3.1) nm during the ripening growth process. We propose that during ripening process the growth of CdSe nanocrystal is through the deposition of Cd and Se ions on the surface of CdSe nucleate, and as a consequence, the defects on the nucleate surface lead to larger structural disorder of the resulting CdSe nanocrystal.

Keywords: CdSe nanocrystal, XAFS, ripening process.

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INTRODUCTION

CdSe is one of the most studied nano-materials because it has remarkable size-dependent optical properties due to quantum confinement effects.[1] High quality CdSe nanocrystals with very narrow size-distribution(<5%) could be obtained by colloidal chemistry methods and the band emission ranges the whole visible light spectrum(420–660nm).[2] These nanocrystal-based emitters can be used for many purposes, such as optoelectronic devices and biomedical tags, etc.[3,4]

It is well known that optical properties of a nanocrystal are greatly affected by its structures. For nanocrystal grown from colloidal chemistry methods, the growth conditions determine its structures, thus its properties. So a better understanding of growth process and growth mechanism will benefit the accurate control structures and properties of nanocrystals.[5] Typically, colloidal growth of nanocrystal involves both ripening process and crystallization process. Recently, Chen et al reported the investigation of the crystallization process of 2 nm CdSe nanocrystals. They found that the initially formed amorphous nanoparticles become well-crystallized during the crystallization process.[6] However, to our best knowledge, no report has been presented on the ripening process.

In this work, we will study the structure evolution of CdSe nanocrystal during ripening process by using

XAFS. We used size-selective method to obtain three CdSe samples with different sizes prepared under the same experimental conditions in order to exclude effect of crystallization. This facilitates the isolated studied of the ripening process and how it effects the atomic structure. From our EXAFS results, a new phenomenon about Oswald ripening is found.

EXPERIMENT

CdSe nanocrystals were synthesized according to literature methods with slight modifications.[3,7] Briefly, the freshly prepared NaHSe solution was quickly injected in to the Cd^{2+} solution under fast stirring. Then a series of CdSe nanocrystals with different sizes were obtained by size-selective method. High-resolution transmission electron microscopy (HR-TEM) was recorded by a JEOL-2010 electron microscope operating at 200 kV. X-ray powder diffraction (XRD) was carried out using a Siemens D5005 diffractometer.

The X-ray absorption spectra of Se *K*-edge were collected at the beamline of U7C of National Synchrotron Radiation Laboratory (NSRL). The storage ring of NSRL was operated at 0.8 GeV with a maximum current of 300 mA. The hard x-ray beam was from a three-pole superconducting Wiggler with a magnetic field intensity of 6 T. The fixed-exit Si(111) flat double crystals were used as monochromator. Three CdSe NCs samples of different sizes in aqueous

solution were measured. The XAFS spectra were recorded in a transmission mode with ionization chambers filled with Ar/N₂ at room temperature, using Keithley Model 6517 Electrometer to collect the electron charge directly. XAFS Data were analyzed by USTCXAFS data analysis package compiled by Wan and Wei according to the standard procedures.[5]

RESULTS

XRD Analysis

Fig. 1 shows XRD patterns of three CdSe powders obtained by size-selective process. All three samples have the same diffraction pattern. These diffraction features appearing at about 25.3°, 47.8°, and 56.3° correspond to the (111), (220), and (311) planes of the zinc-blende phase of CdSe (JCPDS file No.19-0191). The average particle size, estimated from the broadening of XRD patterns with Scherrer formula, was 1.9, 2.7, and 3.1nm, respectively.

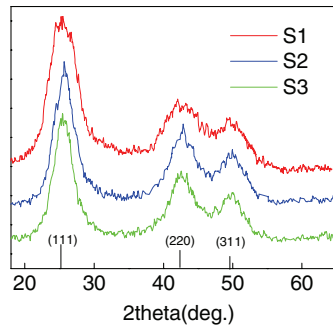


FIGURE 1. XRD pattern of CdSe Nanocrystal.

HR-TEM Analysis

The HR-TEM image of 1.9 nm sample is shown in Fig. 2. Nearly spherical nanocrystals are clearly visible as dark spots with radius close to 2 nm and nearly uniform in size. The existence of lattice planes on the HR-TEM image confirms the crystallinity of CdSe NCs. This result is consistent with Rogach's report.[7]

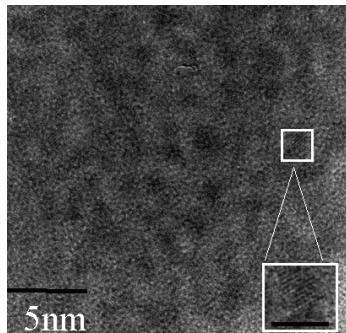


FIGURE 2. HR-TEM of CdSe Nanocrystal. Inset bar:2nm.

XAFS Analysis

Figure 3 (a) shows the Se *K*-edge EXAFS functions ($\chi(k)$) for three CdSe samples of different growth stages. All three samples have the same pattern of oscillation, but with slight differences in their amplitudes. It can be seen that sample of 1.9 nm has the largest amplitudes, which decreases as the size of CdSe nanocrystals increase to 2.7 nm and 3.1nm.

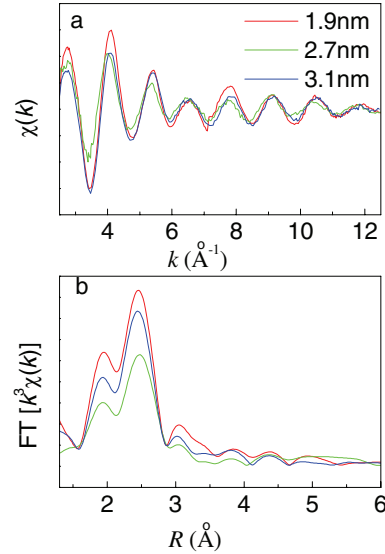


FIGURE 3. EXAFS (a) and RSF (b) of CdSe Nanocrystal.

In order to illustrate more clearly the local structure change for the different CdSe samples, the radial structure distribution functions (RSF) of Se were obtained by Fourier transform of the k^3 -weighted EXAFS functions, as shown in Fig. 3 (b). The RSFs of CdSe nanocrystal has only one coordination peak at 2.45 Å corresponding to the first shell of cubic CdSe. It can be clearly seen that the magnitude of Se-Cd peak decreases when the size of the nanocrystal grows. The local structure parameters were obtained from the least-squares curve fitting in R-space by using theoretical amplitude and phase shift functions generated with FEFF 8 code. The curve-fitting results are summarized in Table 1. All three samples have the same coordination number $N=4$ within the error bar of 5% for the Se-Cd pair. The mean squared relative displacement σ^2 is 0.0046 Å² for 1.9 nm samples and increases to 0.0053 and 0.0072 Å² for 2.7 and 3.1 nm nanocrystals, respectively.

TABLE 1. Results of fits to CdSe nanocrystal.

Sample	Bond type	R(Å)	$\sigma^2(10^{-3}\text{Å}^2)$
1.9nm	Se-Cd	2.590±0.004	4.6±0.1
2.7nm	Se-Cd	2.591±0.004	5.3±0.1
3.1nm	Se-Cd	2.606±0.003	7.2±0.1

DISCUSSION

From results of EXAFS, we can clearly see that the structure disorder of CdSe nanocrystal increases as the particle size increases. Surface reconstruction and the interior structure defects can both bring disorder to nanocrystal. Surface reconstruction by which the surface atoms of nanocrystal decrease surface free energy would increase disorder.[8] But such effect will make smaller particles more disordered, which can not explain our results. So the evolution of structure disorder in our CdSe samples is generated by the interior defects within particle rather than by surface reconstruction.[9] Namely, along with the growth of particles, the arrangement of atoms become more disordered, and the structure defects increase. Impurity doping, crystallization processes and ripening processes are the main factors influencing the interior structural defects of nanocrystals. Typically, impurity doping is only of minor percentage and its random distribution could not cause the evolution of structure defects of different-sized samples. Nanocrystal grown from colloidal solution is also accompanied by crystallization process. As our samples were obtained by size-selective method from the same batch colloidal solution, the reaction conditions, such as temperature, time, and surfactant, which greatly affected the crystallization process were the same. So we believe that crystallization process is not the reason of structure evolution. Thus we conclude that ripening process causes more disorder and structure defects when particles grow in size. The growth of CdSe nanocrystals is through the deposition of Cd and Se ions on the surface of CdSe nucleate.[10] and as a consequence, the defects on the nucleate surface lead to larger structural disorder of the resulting CdSe nanocrystal.

Generally, nanocrystals from colloidal growth have three different evolution types of disorder along with their growth: increased, decreased, and unchanged. It is the outcome of competition between crystallization processes and ripening processes. By delicate design of samples, we have investigated the isolated ripening process effect on structure of nanocrystals. Our EXAFS analysis clearly indicates that ripening process leads to the increase of structure defects of nanocrystal along with growth in size. We propose the as-prepared CdSe nanocrystals have such structure: the inner part is highly crystallized, while the outer layer becomes more and more disordered.

The synthetic conditions such as concentration of precursor, temperature and time, surfactant can influence both ripening and crystallization processes. As mentioned above, ripening will increase disorder while crystallization decreases disorder. So a more careful choice of the synthetic conditions will be

helpful to control the two competing processes and thus modulate the properties of nanocrystals. Zhang et al reported synthesis of CdTe nanocrystals using the same routes as ours but under hydrothermal conditions and found that the crystallinity of thiol-capped CdTe nanoparticles improved significantly.[11] Better control over the ripening and crystallization must be investigated further in order to better modulate the structures and properties of nanocrystals.

CONCLUSIONS

In summary, we have investigated ripening effects on structure of colloiddally grown nanocrystals by using EXAFS. It was found that the structural disorder of nanocrystals increased from $0.0046 \text{ \AA}^2$ to $0.0053 (0.0072) \text{ \AA}^2$ when their size grew from 1.9 nm to 2.7(3.1) nm during the ripening process. We propose that the growth of CdSe nanocrystals is through the deposition of Cd and Se ions on the surface of the CdSe nucleate, and as a consequence, the defects on the nucleate surface lead to larger structural disorder in the resulting CdSe nanocrystal.

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