



Research Article

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In situ studies on aqueous synthesis of Cd doped ZnSe quantum dots

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ABSTRACT

The growth mechanism of Cd doped ZnSe quantum dots (QDs) obtained from the aqueous synthesis method is studied by *in situ* X-ray absorption fine structure (XAFS), UV-vis absorption spectra and photoluminescence (PL). Detailed analysis reveals that just after the injection of Cd ions into ZnSe QDs precursor, the Cd ions are immediately deposited on the surfaces of the ZnSe QDs, and enter the lattice of ZnSe QDs, cause the distortion of lattice. With heating, the surface defects remove from the QDs, but the distortion of Cd doped ZnSe QDs lattice still aggravates in the initial 30min. After 120min of heating, the surfaces of the Cd doped ZnSe QDs are well passivated by glutathione capping, and the lattice defects of the QDs also decrease along with further growth of the QDs.

Key words: XAFS, Quantum dots and Aqueous synthesis.

INTRODUCTION

Semiconductor quantum dots which exhibit excellent optical properties have attractive application prospect in many fields such as optoelectronic devices and biomedicine [1-3]. ZnSe is an important wide-band gap semiconductor material with an emission band covering blue-violet light spectra, and can acquire wider tunable fluorescence emission range, longer excited state lifetime and more stable photochemical properties by doping [4-5].

Aqueous synthesis of semiconductor QDs has gained more and more attention recently because simple process, low cost and that the products can be used for biomedical tags directly [6-7]. Ying and coworkers reported the aqueous synthesis of glutathione capped Cd doped ZnSe QDs, the fluorescence emissions of which are tunable between 360 and 500nm [8]. Zhang et al synthesized a series of ZnSe QDs in aqueous solution with different pH value, and found that the PL quantum yield of ZnSe QDs reaches the maximum when pH is 11.5 [9].

In order to understand the evolution rules of optical properties and structure of Cd doped ZnSe QDs in aqueous synthesis, and then realize the controllable synthesis of QDs, the absorption and PL spectra Cd doped ZnSe QDs are measured, and *in situ* XAFS techniques are employed to investigate the growth mechanism associated by XRD.

EXPERIMENTAL SECTION

Cd doped ZnSe QDs are obtained by adding Cd ions into ZnSe precursor [10]. 20mL of freshly prepared 0.02M NaHSe solution is incorporated into 100mL solution containing 1mmol ZnCl₂ and 1.2mmol GSH at a pH of 11.5 with vigorous stirring. The resulting mixture is heated to 80 °C for 30 min. 10mL solution containing 1mmol CdCl₂ and 1mmol GSH is introduced into this ZnSe precursor solution. After adapting pH to 11.5, the mixture is heated to 80 °C for 120min. The whole process is under protection of N₂ gas.

The as-prepared Cd doped ZnSe QDs are precipitated and washed several times with 2-propanol, then dried at room temperature in vacuum overnight. Powder X-ray diffraction (XRD) pattern of the powder obtained is collected on Rigaku D/MAX-RA X-ray diffractometer with Cu K α radiation ($\lambda = 1.5045\text{\AA}$). The composition of the Cd doped ZnSe QDs is confirmed as Zn_{0.43}Cd_{0.57}Se by ICP-MS element analysis.

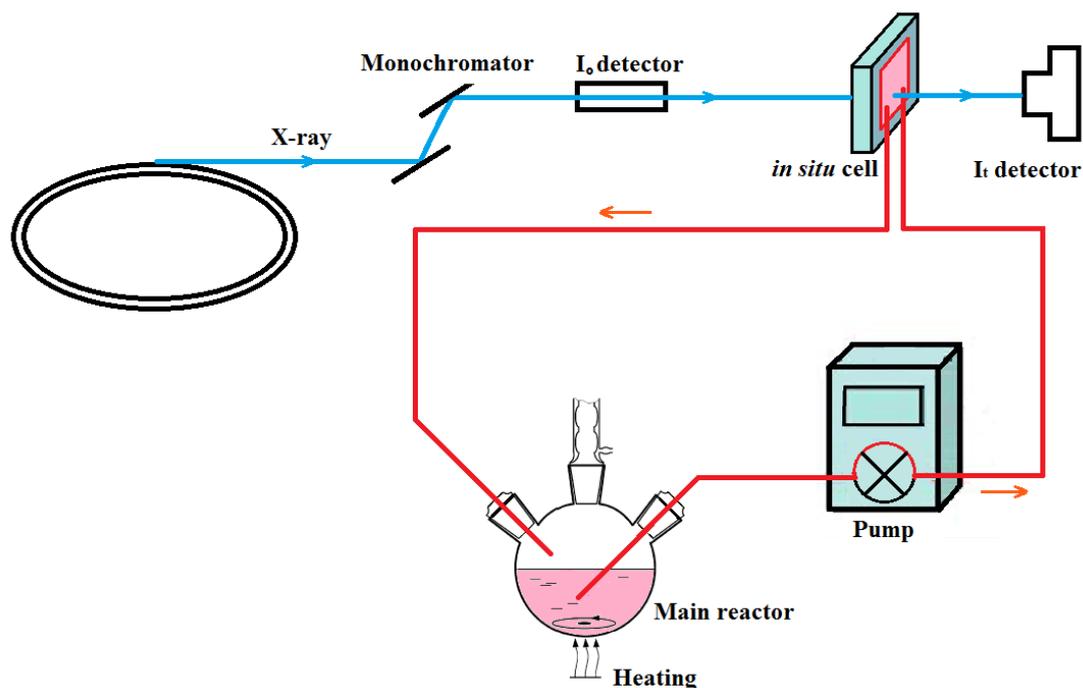


Figure-1 Schematic Representation of the *In Situ* XAFS System

Figure-1 shows the schematic representation of the *in situ* XAFS system. The reaction solution in the main reactor is circulated rapidly and constantly into the sample cell by a pump [10]. The Se *K*-edge XAFS spectra are measured at the 1W1B beam line of Beijing Synchrotron Radiation Factory (BSRF). The storage ring of BSRF is operated at 2.5 GeV with a maximum current of 250mA. The luminous flux at the sample is about 10^{11} photons/s/0.1%BW. XAFS spectra are recorded before and 0, 30, 120 minutes after the injection of Cd ions by utilizing quick-XAFS technique, the data of one spectrum are collected within 60 seconds.

UV-vis absorption spectra are recorded with Shimadzu UV-2450 UV-vis spectrophotometer and PL measurements are performed using Edinburgh FLS920 spectrofluorimeter at room temperature. The samples for optical measurements are extracted from the main reactor before and 0, 30, 120 minutes after the addition of Cd ions.

RESULTS AND DISCUSSION

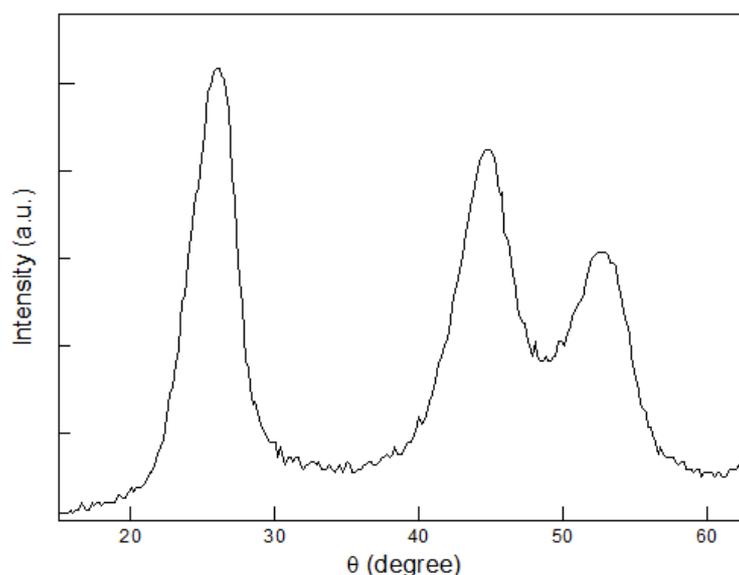


Figure-2 XRD Pattern of $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{Se}$ QDs

XRD pattern (Figure-2) reveals that the as-prepared $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{Se}$ QDs have a zinc blende cubic crystal structure, and the XRD peak positions of the QDs are quite close to those of CdSe crystal. According to Scherrer equation, the grain size of $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{Se}$ QDs is calculated to be 2.6nm from the (111) peak width.

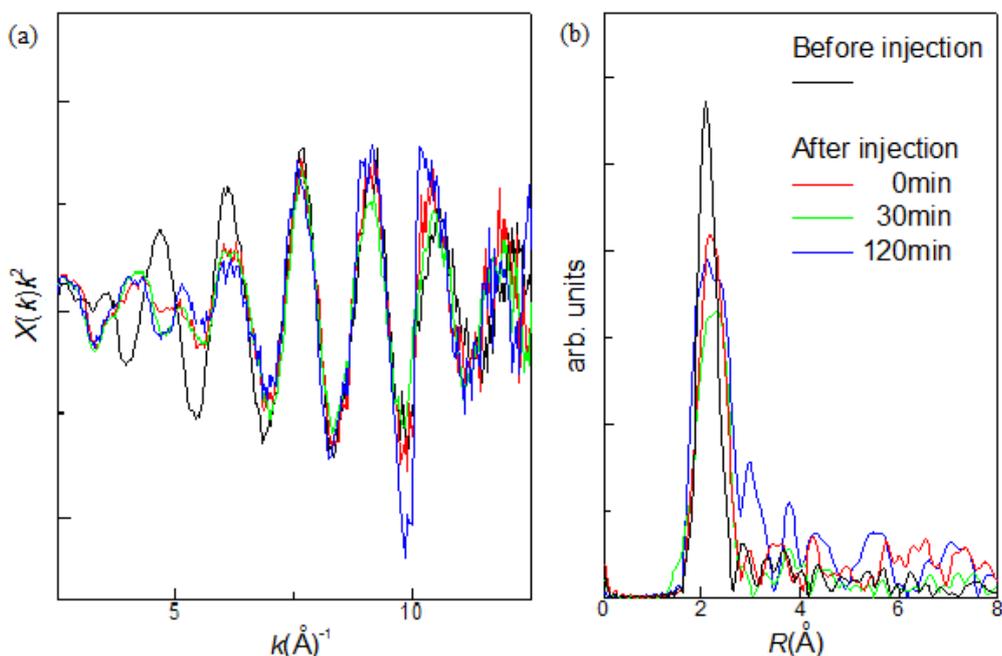


Figure-3 $\chi(k)k^2$ Spectra (a) and Radial Structural Functions (b) of Cd Doped ZnSe QDs

Figure-3(a) demonstrates the Se K -edge normalized XAFS functions $\chi(k)k^2$ of Cd doped ZnSe QDs, Figure-3(b) shows the radial structural functions (RSFs) around Se atoms by Fourier transforming the $\chi(k)k^2$ functions. The RSFs curves have only one peak around 2.2 \AA corresponding to the first shell atoms in Cd doped ZnSe with zinc blende structure. Just after the injection of Cd ions, the peak of the first coordination shell shifts from 2.08 \AA to 2.18 \AA , meaning the increase of bond length compared to ZnSe QDs, meanwhile the intensity of coordination peak reduces, indicating the increase of structural disorder of the QDs. In the initial 30min of heating after the addition of Cd ions, the bond length and structural disorder of Cd doped ZnSe continue to increase. This might be because Cd atoms enter the lattice of ZnSe QDs, cause the distortion of lattice, and then lead to the increase of bond length and structural disorder. However, after 120min of heating, the peak of the first coordinate shell shifts back to 2.08 \AA , and the intensity increases, at the same time a shoulder peak appears. The first coordination shell of Se atoms ought to constitute of Zn-Se and Cd-Se sub shells, and with further growth, the lattice defects of Cd doped ZnSe QDs decrease, lead to the decrease of structural disorder and bond length.

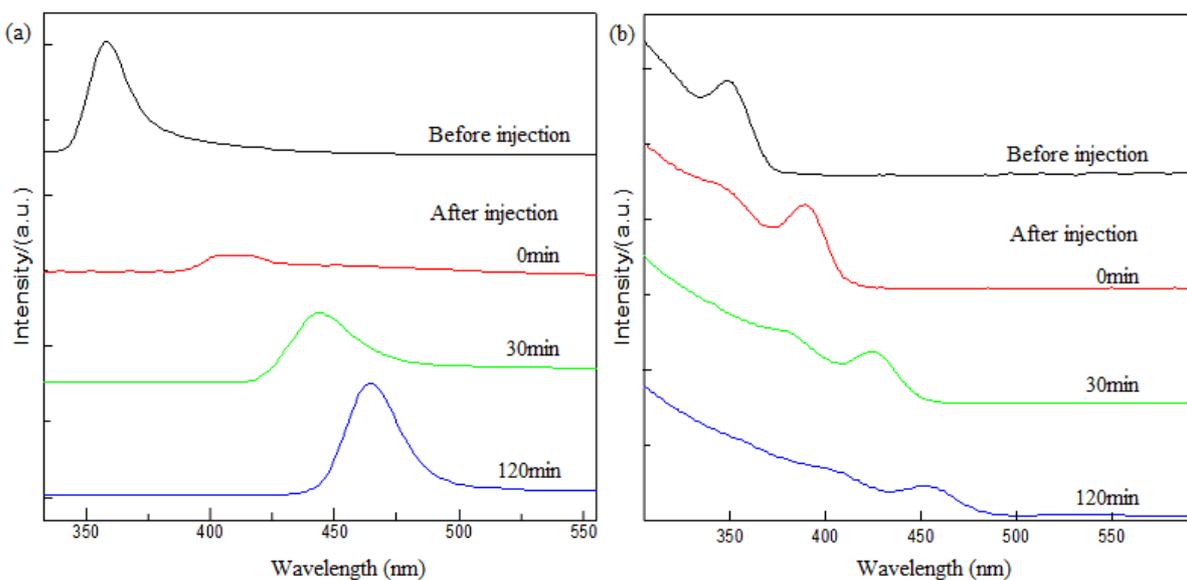


Figure-4 PL (a) and Absorption (b) Spectra of the Cd Doped ZnSe QDs

Figure-4 shows the evolution of the PL (a) and absorption (b) spectra of the Cd doped ZnSe QDs during the aqueous synthesis. After injection, the Cd ions are immediately deposited on the surfaces of the ZnSe QDs due to the higher association constant of CdSe compared to ZnSe, which results in the generation of defects on the surface of the ZnSe precursor, so most of the fluorescence of the ZnSe QDs is quenched. With further heating, the fluorescence emission shifts to long wave and the fluorescence intensity gradually increases with the removal of surface defects from the QDs. After 30 min of heating, the fluorescence emission peak further shifts to 443 nm, and the spectrum becomes dominated by band-edge emission. After 120min of heating, the fluorescence emission peak shifts to 464 nm, and the broad trap-emission tail at the longer wavelength almost disappears, indicating that the surfaces of the QDs are well passivated by glutathione capping [11]. In absorption spectrum, the absorption peak undergoes a red-shift, shifts from 348nm to 389nm and then 451 nm, illustrating that the size of the Cd doped ZnSe QDs grows [12].

CONCLUSION

The as-prepared Cd doped ZnSe QDs has a zinc blende cubic crystal structure. Just after the injection of Cd ions into ZnSe QDs precursor, the Cd ions are immediately deposited on the surfaces of the ZnSe QDs, causes the quenching of the fluorescence of the QDs; also Cd atoms enter the lattice of ZnSe QDs, cause the distortion of lattice, and then lead to the increase of bond length and structural disorder. Along with heating, the fluorescence intensity gradually increases with the removal of surface defects from the QDs, but the distortion of Cd doped ZnSe QDs lattice still aggravates in the initial 30min of heating, results in the increase of structural disorder. After 120min of heating, the surfaces of the Cd doped ZnSe QDs are well passivated by glutathione capping, and the lattice defects of QDs also decrease with further growth.

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