Preparation and Fluorescence Property of Water-dispersible 
ZnSe:Co/ZnSe/ZnS Quantum Dots

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Abstract. In this paper, water-dispersible, L-cysteine-capped Co-doped ZnSe/ZnSe/ZnS core/shell/shell quantum dots are prepared via a simple epitaxial growth approach by depositing ZnS on the superficial layer of the Co-doped ZnSe/ZnSe core/shell QDs. The crystal structure as well as fluorescence performance of the as-prepared Co-doped core/shell/shell QDs have been testified through X-ray power diffraction, infrared spectrum, ultraviolet-visible spectrum and photoluminescence spectrum. The results exhibit that the Co-doped ZnSe/ZnSe/ZnS core/shell/shell quantum dots have a cubic sphalerite crystal and the size about 3.4nm. After coating ZnS shell with appropriate thickness around the Co-doped ZnSe/ZnSe core/shell QDs, the fluorescence intensity of Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs has been improved greatly.

1. Introduction
Semiconductor fluorescence quantum dots, or simply “quantum dots (QDs)” for short, are compounds mainly consisted of II-VI group and III-V group compounds[1]. When the size of QDs is closer to or smaller than its exciton Bohr radius, the QDs exhibit unique physical and chemical properties distinguish from that of conventional bulk-sized materials, including a broad and continuous absorption spectrum, a narrow, adjustable and symmetric emission spectrum, admirable anti-optical and chemical stability, etc[2]. Due to their outstanding optical properties, such QDs have been vastly exploited in light emitting diode, sensing element, especially in fluorescent marking in versatile biological and biomedical application[3]. Doping with intention impurities (such as Mn, Cu or Fe ) in parent core as the dopant emissive center can modulate fluorescent emission of core QDs; In addition, coating on the surface of the QDs with a suitable shell to form a core-shell QDs, which is an important strategy for improving the fluorescence intensity of QDs by improving the surface defects states.

At present, plenty of high quality Cadmium-based QDs, such as classic cadmium chalcogenides CdE (E=S,Se,Te) and especially their core/shell QDs, have been synthesized by the organinc-phase growth or the aqueous synthesis. Nevertheless, the intrinsic poisonousness of Cadmium-based QDs restrict their further application directly relate to human health[4]. But better than Cadmium-based QDs, the poisonousness of Znic-based QDs is drastically decreased. ZnSe, as a typical low-toxic, wide-bandgap (2.69eV) II-VI Zn-based blue semiconductor material, have been developed as a host material for doping various metal ions[5]. Until now, there have been few reports on the prepare of water-dispersible Co-doped ZnSe QDs directly in aqueous phase[6,7]. In 2011, Zhang et al. synthesized Co-doped QDs with thioglycolic acid as the stabilizer in aqueous phase[6]. In 2013, Ram group prepared Co-doped QDs using polyvinyl alcohol as a stabilizer in aqueous solution[7]. And later our...
research group reported the prepare of hydro-soluble ZnSe:Co/ZnSe core/shell QDs with L-cysteine as modifier in aqueous solution[8]. Furthermore, it is well known that encapsulate the parent core QDs by a shell with wider band gap, can increase the fluorescence quantum yield and stability against photo-oxidation[9]. In 2012, Niu et al. prepared Cu-doped ZnSe/ZnSe/ZnS core/shell/shell QDs by using wider band gap ZnS as outer shell for improving the fluorescence quantum yield (QYs) of the QDs[10].

By now, there is no report regarding prepare L-cysteine-capped, Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs (i.e. ZnSe:Co/ZnSe/ZnS QDs) in aqueous phase. In this paper, water-dispersible Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs are prepared direct in aqueous phase with L-cysteine as stabilizer through epitaxial growth method. Compared with thioglycolic[5] or polyvinyl alcohol[7] used as stabilizer to prepare ZnSe:Co QDs, using L-cysteine as stabilizer to prepare Co-doped ZnSe/ZnSe/ZnS QDs is cheaper, more stable and non-toxic. After coating ZnS shell around the ZnSe:Co/ZnSe QDs, the fluorescence quantum yield of ZnSe:Co/ZnSe/ZnS QDs has been enhance greatly.

2. Experimental

2.1 Instrument and reagents

The X-ray power diffraction patterns were performed by using a X’pert-MPD Model(USA, Philips). The Ultraviolet-visible(UV-Vis) spectra were obtained by a Varion Cary 50 UV-Visible spectrometer(USA, Varian). Fluorescence spectra experiments were carried out by using a F-1000 spectrometer photometer(JPN, Hitaciji). IR spectra were measured with a UV analyzer.

All the chemicals including Selenium(Se, ≧99.0%), sodium brohydride(NaBH₄, ≧99.0%), Zinc acetate dihydrate(Zn(Ac)₂·2H₂O, ≧99.0%), L-cysteine(L·Cys, ≧98.5%), Sodium hydroxide(NaOH, 96.0%), Anhydrous ethanol(C₂H₅OH, ≧99.7%), Cobalt chloride hexahydrate(CoCl₂·6H₂O, ≧98.0%), Sodium sulfide nonahydrate(Na₂S·9H₂O, ≧98.0%) were purchased from Guoyao Chemical Reagent and used as purchased without further refinement.

2.2. Synthesis of L-Cysteine Modified Co-doped ZnSe/ZnSe/ZnS core/shell/shell Quantum Dots

The ZnSe:Co/ZnSe/ZnS quantum dots were prepared by the methods as follows: Firstly, under a N₂ atmosphere, 0.50 mmol Zn(Ac)₂·2H₂O, 0.77 mmol L-cysteine was sequentially added to distilled water in a 250 ml three-neck flash with vigorously magnetic stirring, and 1ml of 0.01mol/L CoCl₂·6H₂O solution was added into above reaction solution. After 30 min reaction, the pH of the above solution should be set to 10.0 with dilute NaOH (0.2 mol/L), and a transparent solution was obtain. In the state of stirring, a freshly prepared NaHSe solution was injection into above reaction mixture. The reaction solution was heated up to 95-100°C in an oil bath with a N₂ atmosphere for 1h to obtain a transparent, L-cysteine-capped Co-doped ZnSe crude solution.

Then, a certain amount of 0.02mol/L Zn(Ac)₂·2H₂O solution were slowly added into L-cysteine-capped Co-doped ZnSe solution under a N₂ flow. The reaction was heated at 70°C. After 30 min moderate stirring, 0.6 ml of a freshly prepared NaHSe solution was injection into above reaction mixture. The reaction mixture was heated up to 70°C and with a nitrogen-saturated for 1h to obtain a transparent, L-cysteine-capped Co-doped ZnSe/ZnSe core/shell crude solution.

Finally, a certain amount of 0.05 mol/L Zn(Ac)₂·2H₂O solution and 0.05 mol/L Na₂S·9H₂O solution were dropwise added alternately into L-cysteine-capped Co-doped ZnSe/ZnSe mixture under a N₂ flow. The reaction mixture was heated up to 70°C in an oil bath with a nitrogen-saturated for 1h to obtain a transparent, L-cysteine-capped Co-doped ZnSe/ZnSe/ZnS core/shell/shell colloidal solution. The as-prepared crude colloidal solution is further purified by multiple concentration, precipitation and centrifugation.

3. Results and discussion

3.1 XRD analysis
The XRD patterns of the obtained Co-doped ZnSe/ZnSe, Co-doped ZnSe/ZnSe/ZnS QDs are presented in Figure 1. For the Co-doped ZnSe/ZnSe, the location of the three diffraction maximum with 2θ = 27.780°, 46.370°, and 54.830° orient along the (111), (220), and (311) directions of the cubic crystalline ZnSe (JCPDS NO.37-1463), which indicated that Co-doped ZnSe/ZnSe QDs owe to a cubic sphalerite structure. The diffraction peaks of the Co-doped ZnSe/ZnSe/ZnS shift a slight toward higher 2θ value in comparison to that of Co-doped ZnSe/ZnSe, which confirm that ZnS is epitaxial growth on the surface of Co-doped ZnSe/ZnSe to form Co-doped ZnSe/ZnSe/ZnS, and the Co-doped ZnSe/ZnSe/ZnS is still cubic zinc blende[11]. There is no diffraction peak from cobalt impurities, due to the trace amounts of Co$^{2+}$ producing no change of crystal structure[12]. Furthermore, the broadening of three peaks of above QDs is attributed to the small size effect of nano-structure. In addition, the average crystallite size of ZnSe:Co/ZnSe/ZnS QDs was calculated using Debye-Scherrer formulate: $D=0.94\lambda/(\beta\cos\theta)$[13]. The average particles diameter is approximately 3.4 nm.

![XRD patterns of the Co-doped ZnSe/ZnSe and Co-doped ZnSe/ZnSe/ZnS Quantum Dots.](image)

**Figure 1.** XRD patterns of the Co-doped ZnSe/ZnSe and Co-doped ZnSe/ZnSe/ZnS Quantum Dots.

### 3.2 Ultraviolet-visible absorption spectrum analysis

Figure 2. presents the Ultraviolet-Visible absorption spectra of the as-prepared Co-doped ZnSe, Co-doped ZnSe/ZnSe core/shell and Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs. It can be observed from the Figure 2, comparing with cubic bulk ZnSe(460nm)[14], the absorption edge of above quantum dots have an obvious blue shift, which ascribed the size quantization effect[15]. As the deposit of ZnSe and ZnS shells, it can observe that the absorption edge of the core/shell and the core/shell/shell QDs are moved to long wavelength, sequentially. The shell of ZnS deposit on the ZnSe shell of ZnSe: Co/ZnSe were explicitly reflected in the red shift of the absorption spectra, which further certified the formation of ZnSe:Co/ZnSe/ZnS core/shell/shell structure[16,17,18].
3.3 Infrared analysis

Figure 3. displays the Infrared spectra of L-cysteine and the as-prepared L-cysteine-capped Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs. The Infrared spectrum of L-cysteine is shown in Figure 3(a), it is found that 1583 cm\(^{-1}\)(svC=O), 1292 cm\(^{-1}\)(wvC-O), 3441-3184 cm\(^{-1}\)(mvO-H), 2073 and 2974 cm\(^{-1}\)(mvN-H), 1069 cm\(^{-1}\)(mvC-NH\(_2\)), 636cm\(^{-1}\)(wvC-S) and 2553 cm\(^{-1}\)(vS-H).

The Infrared spectrum of L-Cysteine-capped Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs is shown in Figure 3(b). From Figure 3(b), it can be observed that most of the peaks only slightly shifted, but the characteristic vibration peak of S-H of thiol disappear, which indicated that the thiol (-SH) of L-cysteine coordinates with the metal ion on the surface of Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs\(^{[19]}\). The results demonstrate that the L-cysteine has been successfully modified to Co-doped ZnSe/ZnSe/ZnS QDs.
3.4 Fluorescent spectrum analysis

Figure 4. Fluorescence spectra of Co-doped ZnSe (a), Co-doped ZnSe/ZnSe (b) and Co-doped ZnSe/ZnSe/ZnS (c) QDs.

Figure 5. Fluorescence spectra of Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs with different thickness of ZnS.

Figure 4. shows the changes of fluorescence properties after coating of ZnSe and ZnS shells. It can be seen that there are two distinct emissions of the Co-doped ZnSe core-shell system, include a pronounced, relatively narrow band-edge emission peak (around 390 nm) and surface-defect emission (around 460 nm) from trap sites. It is observed that the fluorescence emission peaks of Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs show a slight red shift in comparison with that of Co-doped ZnSe and Co-doped ZnSe/ZnSe core/shell QDs. In addition, the fluorescence intensity of Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs is stronger than that of Co-doped ZnSe and Co-doped ZnSe/ZnSe core/shell QDs, which reveals ZnS is deposited on the surface of Co-doped ZnSe/ZnSe. The enhanced of the fluorescence intensity of Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs can be ascribe the coating of ZnS layer, which can block non-radiative recombination centers and prevent photochemical degradation[20,21].

Figure 5. presents the fluorescence spectra of Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs with varying thickness of ZnS shell. As exhibited in Figure 5, the fluorescence intensity first increased markedly as the growth of ZnS shell, and reaches its maximum when the ratio of n(ZnSe: Co /ZnSe) to n (ZnS ) is 1:0.2, and then slowly decrease as the further growing of ZnS shell. The above phenomenon can be explained as follows: The coating of ZnS shell with appropriate thickness can better reduce the surface defects of the QDs, thus reducing the probability of non-radiated transition, and improving the fluorescence efficiency of the Co-doped ZnSe/ZnSe/ZnS QDs.

4 Conclusions
To summarize, water-dispersible Co-doped ZnSe/ZnSe/ZnS core/shell/shell QDs are successfully synthesized via a simple process in aqueous solution. The crystalline structure was confirmed by using XRD. The deposit of the ZnS layers was monitored by observing the red shift in Ultraviolet-visible spectra and fluorescence spectra. The water solubility will be enhanced with L-cysteine modified on the surface of the core/shell/shell QDs. After coating ZnS shell with appropriate thickness around the ZnSe:Co/ZnSe QDs, the fluorescence intensity of ZnSe:Co/ZnSe/ZnS QDs has been increased greatly.

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