Synthesis and Characterization of L-cysteine-modified ZnSe:Co/ZnSe Quantum Dots

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Abstract. In this paper, ZnSe:Co/ZnSe QDs were synthesized by co-precipitation technique in aqueous phase using L-cysteine as modifier, the experimental results were characterized by X-ray power diffraction (XRD), transmission electron microscope (TEM), infrared spectrum (IR) and photoluminescence spectrum (PL). The results showed that the ZnSe:Co/ZnSe QDs was spherical with diameter around 3.2nm, belonged to cubic sphalerite structure and had good fluorescent characteristics. The photoluminescence emission intensity of the L-cysteine modified ZnSe:Co/ZnSe core/shell QDs was enhanced by doping Co²⁺ and coating ZnSe shell to the core ZnSe. After doped with Co²⁺ and coated with ZnSe shell, the fluorescence quantum yields of the as-prepared ZnSe:Co/ZnSe QDs increased from 4.93% to 29.94%. The L-cysteine modified on the surface of ZnSe:Co/ZnSe renders the QDs water-soluble and biocompatible.

1. Introduction
Quantum dots (QDs) have attracted considerable attention in the field of biological analysis ascribing to their unique photochemical properties, such as wide absorption bandwidths, narrow and symmetry emission bandwidths and good photochemical stability [1-6]. The fluorescent properties of QDs can be adjusted and controlled by doped with transition metal ions. And the surface of the quantum dot was coated with a layer of suitable inorganic shells material to form a core-shell structure, which can reduce or eliminate the surface defects of the QDs and improve the fluorescence quantum yield and photochemical stability. The surface of QDs modified with appropriate organic small molecules control the size of the particles, enhance the dispersity of the QDs, and make the QDs water-soluble and biocompatible. Therefore, the synthesis of surface-modified doped QDs with core-shell structure are of great significance.

In 1996, Hines et al. [7] successfully prepared CdSe/ZnS core-shell QDs for the first time. Since then, progress has been made in the preparation of core-shell structure QDs, Cadmium doped core-shell QDs (such as CdS: Mn / CdS[8] and CdSe: Mn / CdS[9]) have been synthesized. However, intrinsic toxicity of such Cd-base QDs and the organic synthesis methods of the QDs limit the application of cadmium-base QDs. Compared with cadmium-base QDs, the toxicity of zinc-base QDs is reduced. ZnSe QDs with a band gap energy of 2.86eV have drawn special attention due to its applications in optoelectronics and biological analysis [10]. Nowadays, the ZnSe core/shell QDs doped with transition ions (such as ZnSe: Mn/ZnS[11], ZnSe: Cu/ZnS[12], ZnSe: Fe/ZnS[13]) have been reported. So far, there are only a few reports on the synthesis of ZnSe:Co QDs directly in the aqueous phase [14]. The low fluorescence quantum yield of ZnSe:Co QDs hinders its further application.

To the best of our knowledge, the water-soluble ZnSe:Co/ZnSe core-shell QDs synthesized directly in aqueous solution have not been reported. In this paper, we show a facile synthesis of ZnSe:Co/
ZnSe QDs in aqueous solution using L-cysteine as modifier. The fluorescence quantum yield of the ZnSe:Co/ZnSe QDs are improved effectively after Co$^{2+}$ doping and the epitaxial growth of ZnSe shell. Compared with the thioglycolic acid use as a modifier in literature [14], the L-cysteine used as a modifier in this paper is stable, cheap, non-toxic and biocompatible, L-cysteine has more active groups (such as mercapto, amino and carboxyl), which can be combined to biological molecules for its applicable in biological analysis.

2.Experimental

2.1 Reagents and instruments

NaBH$_4$, Se, Zn(Ac)$_2$·2H$_2$O, NaOH, C$_2$H$_5$OH, L-cysteine, CoCl$_2$·6H$_2$O are purchased from Guoyao Chemical Reagent. All reagents are used as received without any further purification.

The X-ray power diffraction (XRD) pattern was obtained on an X’pert-MPD X-ray powderdiffractometer (Philips, USA). The fluorescence spectra are recorded on a CARY ECLIPSEspectrofluorometer (Varian, USA). The morphologic images are obtained on FEITECNAI G2F20 high-resolution transmission electronmicroscope (USA). Infrared spectra are performed within AVATAR 360 FTIR spectrometer (Nicolet, USA).

2.2 Synthesis of ZnSe:Co/ZnSe QDs modified with L-Cysteine

Under a N$_2$ atmosphere, 0.0930g of L-cysteine, 0.1097g of Zn(Ac)$_2$, and 1mL of 0.01 mol/L CoCl$_2$ solution were dissolved in deionized water in a three-necked flask and the pH value of the solution was adjust to 10 by dropwise addition of 2.0 mol/L NaOH solution with magnetic stirring. The freshly prepared NaHSe solution ( NaHSe solution was prepared according to the procedure ffrom literature[15]) was injected into the reaction mixture followed by continuous stirring at 100°C in a oil bath with a slow N$_2$ flow for 1.0 hr. Subsequently, a transparent and stable L-cysteine-modified ZnSe:Co colloidal solution was obtained.

Then, 15mL of 0.01 mol/L Zn(Ac)$_2$ solution and 0.6 ml NaHSe solution were added into the ZnSe:Co colloidal solutions at 70°C with a slow nitrogen flow for 1.0 hr to acquire a brown and transparent L-cysteine-modified ZnSe:Co/ZnSe QDs colloidal solution. The crude solution was concentrated by a rotary evaporator. The purified ZnSe:Co/ZnSe powder was obtained through the ethanol precipitation procedure.

3.Results and discussion

The XRD pattern of L-cysteine-modified ZnSe:Co(a),ZnSe:Co(b) and ZnSe:Co/ZnSe (c)QDs were shown in the Fig.1. From the Fig.1, the diffraction peaks of ZnSe QDs at 2θ =27.36°, 46.11°and 54.25°, according to the standard cubic ZnSe (JCPDS NO. 37-1463), the three diffraction peaks correspond to (111), (220), and (311) planes of ZnSe, respectively, which indicated that the as-prepared ZnSe QDs belong to the cubic zinc blende structure. The positions of the three diffraction peaks of L-cysteine-modified ZnSe:Co QDs at 2θ =$27.66°$, 46.25° and 54.68°, exhibited a little shift compared with the pattern of ZnSe QDs, which indicated that the concentration of Co$^{2+}$ is so low that it had little effect on the ZnSe:Co QDs. The diffraction peaks of ZnSe:Co/ZnSe QDs shift toward 2θ = 27.78°, 46.37° and 54.83°, which proved that ZnSe is epitaxial growth on the surface of ZnSe:Co to form ZnSe:Co/ZnSe QDs[16].The broadening in the three diffraction peaks of the QDs due to the small size effect of nanostructure can also be observed from this pattern.
The HRTEM image of ZnSe:Co/ZnSe are shown in Fig. 2. From Fig. 2, The shape of the particles is spherical shape with good dispersity and nearly uniform size. The particle diameter is about 3.2 nm.

The IR spectra of the L-cysteine (a) and ZnSe:Co/ZnSe (b) QDs modified by L-cysteine in the range of 4000 to 500 cm\(^{-1}\) are shown in Fig. 3. In Fig. 3(a), 1589 cm\(^{-1}\)(C=O), 1390 cm\(^{-1}\)(C=O), 1291 cm\(^{-1}\)(C-O), 3439-3181 cm\(^{-1}\)(O-H), 2965 cm\(^{-1}\)(N-H), 2076 cm\(^{-1}\)(N-H), 1070 cm\(^{-1}\)(C-NH\(_2\)), 635 cm\(^{-1}\)(C-S), 2553 cm\(^{-1}\)(S-H) are found. In Fig. 3 (b), the 2553 cm\(^{-1}\) (S-H) characteristic peak disappears, which indicates that the sulfur atom in mercapto group of L-cysteine is coordinated with Zn\(^{2+}\) ions on the surface of the QDs, resulting in the formation of L-cysteine-modified ZnSe:Co/ZnSe QDs.
The fluorescence spectra of ZnSe (a), ZnSe:Co (b) and ZnSe:Co/ZnSe (c) QDs are shown in Fig.4. It can be seen that the PL emission of ZnSe QDs show two distinct emission bands. Two emission bands can be assigned to the bandgap emission (around 390 nm) and surface-defect emission (around 460 nm) of ZnSe QDs, respectively. The emission intensity of ZnSe:Co QDs is stronger than that of ZnSe QDs, which indicates that the Co$^{2+}$ ions were doped into the ZnSe:Co QDs. The fluorescence intensity of ZnSe:Co/ZnSe QDs is stronger than that of ZnSe:Co QDs, and the emission peak position of ZnSe:Co/ZnSe QDs have a slight red shifted compared with the emission peak position of ZnSe:Co QDs, which indicates ZnSe is epitaxial growth on the surface of the ZnSe:Co to form ZnSe:Co/ZnSe QDs. The increase in the fluorescence intensity of ZnSe:Co/ZnSe core-shell QDs can be attributed to the overcoating of ZnSe shell, which can efficiently confine the excitation to core, eliminating nonradiative relaxation pathways and preventing photochemical degradation.$^{[17,18]}$. The fluorescence quantum yields of ZnSe, ZnSe:Co and ZnSe:Co/ZnSe QDs are 4.93%, 13.19% and 29.94%, respectively. The fluorescence quantum yield of ZnSe:Co/ZnSe QDs is increased greatly after doped with Co$^{2+}$ and coated with ZnSe shell.

4 Conclusions
The ZnSe:Co/ZnSe QDs were synthesized in aqueous solution by using L-cysteine as a modifier. The results showed that the ZnSe:Co/ZnSe QDs was spherical with diameter around 3.2nm, belonged to
cubic sphalerite structure and had good fluorescent characteristics. After doped with Co$^{2+}$ and coated with ZnSe shell, the fluorescence quantum yields of the as-prepared ZnSe:Co/ZnSe QDs increased from 4.93% to 29.94%. The L-cysteine modified on the surface of ZnSe:Co/ZnSe QDs rendered the quantum yields of the as-prepared ZnSe:Co/ZnSe QDs increased from 4.93% to 29.94%. The L-cysteine modified on the surface of ZnSe:Co/ZnSe QDs rendered the QDs water-soluble and biocompatible, and provided the possibility of –NH$_2$ and –COOH groups of L-cysteine interacting with various molecules for applications in biological fluorescence analysis.

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