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Preparation and Characterization of Water-soluble ZnSe: Fe/ZnSe Quantum Dots

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Abstract. Water-soluble Fe-doped ZnSe/ZnSe quantum dots (ZnSe: Fe/ZnSe QDs) were prepared through a facile, low-cost and effective strategy in aqueous solution using L-cysteine (L-cys) as modifier. X-ray diffraction (XRD) studies showed that the prepared ZnSe: Fe/ZnSe QDs belonged to zinc blende crystal structures. Transmission electron microscopy (TEM) exhibited that the average diameter of ZnSe: Fe/ZnSe QDs was about 2.9 nm. Infrared spectrum (IR) exhibited that the L-cys has been successfully modified to QDs. The tests of Ultraviolet-visible (UV-vis) spectrum exhibited that the absorption edge position of ZnSe: Fe/ZnSe QDs had a slight red shift with the deposition of ZnSe shell. The fluorescence properties of obtained ZnSe: Fe/ZnSe QDs were investigated through photoluminescence (PL) spectrum. The results exhibited that the PL intensity of ZnSe: Fe/ZnSe QDs has been improved obviously compared with ZnSe: Fe QDs.

1. Introduction

Luminescent quantum dots (QDs), also called semiconductor nanocrystals, have attracted especially attention owing to their novel physical and chemical properties. Usually, the fluorescence QDs have widely potential applications in the field of biological analysis, such as biological labeling^[1], fluorescent probes^[2,3], biosensors^[4], and so on. Doping with transition metals (such as Cu, Mn, Ni, Fe or Co) in parent core QDs can adjust fluorescence characteristic of parent core QDs; Coating with a suitable shell on the surface of the bare core QDs to form core/shell QDs can improve the PL intensity of QDs. Therefore, the study of doped core/shell QDs will play an important role in the field of biological application.

Currently, the commonly used core/shell II-VI group QDs are mainly based on heavy metal Cd-based (i.e., CdS: Ag/ZnS^[5], CdS: Mn/CdS^[6] and CdSe: Mn/CdS^[7]), which are toxic to the biological system and environment, thus restricting their applications in the area of biomedical.^[8] Compared with the Cadmium-based QDs, zinc selenide (ZnSe) QDs, as a blue semiconductor luminescent material with wide/direct band gap and lower toxicity have attracted a great interest of researchers. Moreover, the water soluble of QDs is also an important requirement for bioapplications. The preparation of QDs with organometallic strategies usually requires hard conditions such as high temperature, toxic solvents and reagents, and the as-prepared QDs have hydrophobicity, so the synthesis of water-soluble QDs via aqueous route is beginning to receive more and more attention. Until now, the synthesis of water-soluble Cu, Mn-doped ZnSe core/shell QDs such as ZnSe: Cu/ZnS^[10], ZnSe: Mn/ZnO^[9] and ZnSe: Mn/ZnS^[11] core/shell QDs in water phase have been numerous reported. The synthesis of water-soluble Fe-doped ZnSe QDs directly in aqueous phase have been few reports^[12,13]. In 2013, Xie's group^[12] reported water-soluble ZnSe:Fe nanocrystals with mercaptoacetic acid (MAA) as stabilizer in



aqueous solution. In 2018, Ehsan group^[13] prepared water-soluble ZnSe(S): Fe/ZnSe(S) core/shell QDs with N-acetyl-L-cysteine as stabilizer. Compared with mercaptoacetic acid^[12] choosed as stabilizer to modify ZnSe: Fe QDs, L-cysteine is more stable, cheaper and non-toxic. In addition, L-cys has amino, carboxyl and mercapto group, which could be better connected with intention molecules for its applications in the field of biological analysis.

In this article, an effective and facile synthesis of ZnSe: Fe/ZnSe core/shell QDs in aqueous solution using L-cys as modifier have been reported. The as-prepared ZnSe: Fe/ZnSe QDs are water-soluble and biocompatible becuae of the L-cys as a surface modifier. Compared with bare core ZnSe: Fe QDs, the PL intensity of ZnSe: Fe/ZnSe core/shell QDs has been improved obviously.

2. Experimantal section

2.1. materials and instruments

Zinc acetate dihydrate, Selenium, L-cysteine, sodium brohydride, Sodium hydroxide, Anhydrous ethanol and Ferrous sulfate dihydrate were obtained from Guoyao Chemical Reagent and used as received.

IR spectra were detected by an AVATAR 360 FTIR spectrometer (Nicolet, USA). The UV-Vis spectra were carried out by a Varion Cary 50 UV-Visible spectrometer (USA, Varian). PL experiments were obtained by a F-1000 spectrometer photometer (JPN, Hitacji). Powder X-ray diffraction patterns were measured with using a X'pert-MPD Model (USA, Philips). Morphological image is obtained with FEITECNAI G2F20 high-resolution transmission electronmicroscope (USA) operating at 200 kV.

2.2. prepared of L-Cys Modified ZnSe: Fe/ZnSe QDs

Under N₂ flow, deionized water, 0.0930g of L-cys, 0.1097g of Zn(Ac)₂·2H₂O and 1ml of FeSO₄·2H₂O were sequentially loaded into a 250 ml three-neck flash under magnetic stirring. After 30 minutes, the temperature of oil bath was heated at 100 °C, and then 1.5 mL of fresh NaHSe solution prepared from Se powder and NaBH₄ was quickly injected into the pH=10 of the mixture solution, which was adjusted by adding NaOH (2.0 M) solution. After the reaction solution vigorous stirring 1 h, the L-cys-capped ZnSe: Fe QDs crude solution were obtained. In order to obtained L-cys-capped ZnSe: Fe/ZnSe core/shell QDs, the solution was then cooled to 70 °C .

Under the N₂ atmosphere, 15 ml of Zn(Ac)₂·2H₂O solution was slowly added into the ZnSe: Fe crude reaction solution. After the mixture were stirred for 30min, 0.6 ml of a freshly prepared NaHSe solution was added to above reaction system, and then the mixture was agitated for 1h to form an ZnSe: Fe/ZnS QDs crude colloidal solution. The crude colloidal solution of containing QDs was separated by reprecipitation with ethanol and centrifugation to purification. The final products dried in a vacuum at 60 °C for 10 h.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the obtained Fe-doped ZnSe core QDs and Fe-doped ZnSe/ZnSe core/shell QDs are shown in Figure 1. The pattern indicates that Fe-doped ZnSe core QDs has a zinc blende crystal structures with three diffraction peaks at $2\theta = 28.31^\circ$, 46.15° and 52.60° , corresponded to (111), (220), (311) planes of the cubic crystalline ZnSe (JCPDS NO.37-1463), respectively. Impurities affect on crystal structure can be neglected due to contained Fe²⁺ is so low , thus the ZnSe: Fe/ZnSe QDs is still cubic zinc blende. Compared with ZnSe: Fe QDs, the three peaks of the ZnSe: Fe/ZnSe QDs shift a slight toward higher 2θ value, which confirming the formation of ZnSe shell. Furthermore, note that the diffraction peaks of above QDs apparent broadening, which is attributed to the small size effect.

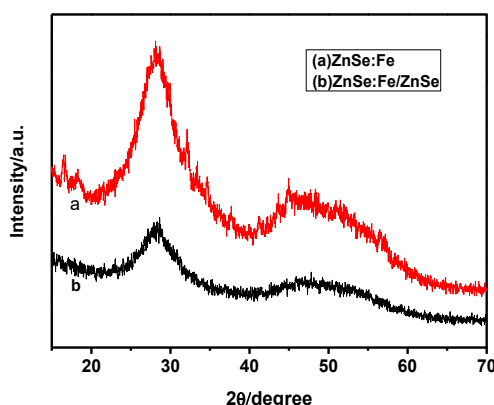


Figure 1. XRD patterns of the ZnSe: Fe and ZnSe: Fe/ZnSe QDs.

3.2. TEM analysis

Figure 2. shows the TEM image of the ZnSe: Fe/ZnSe QDs. As can be seen, the shape of ZnSe: Fe/ZnSe QDs is spherical shape with good dispersity. The average diameter of the particles is about 2.9 nm.

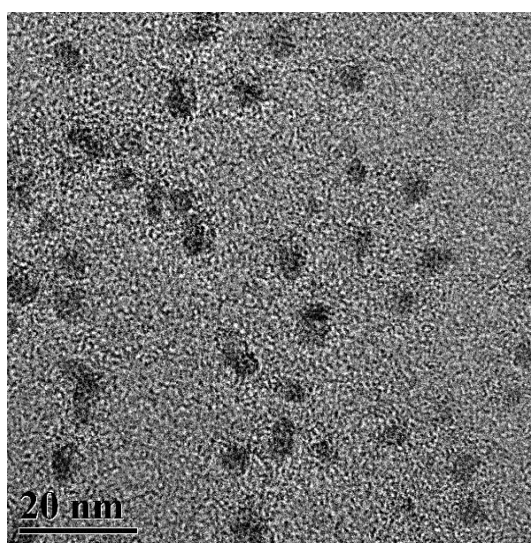


Figure 2. TEM of the ZnSe: Fe/ZnSe QDs.

3.3. IR spectrum analysis

Figure 3. shows the IR absorption spectra of L-cys molecule and the as-prepared L-cys-capped ZnSe: Fe/ZnSe QDs. The IR absorption spectrum of L-Cys is presented in Figure 3(a), it can be observed that 3434cm^{-1} (O-H), 1582cm^{-1} (C=O), 1294cm^{-1} (C-O), 1071cm^{-1} (C-NH₂), 2079 and 2967cm^{-1} (N-H), 2552cm^{-1} (S-H) and 634cm^{-1} (C-S). From Figure 3(b), it can be concluded that the S-H of L-cys coordinates with the Zn^{2+} or Fe^{2+} ion on the surface of ZnSe: Fe/ZnSe QDs, due to most of the characteristic peaks of L-cys of L-cys-capped ZnSe: Fe/ZnSe QDs just slightly shifted, and the characteristic peak of 2552cm^{-1} (S-H) disappear.

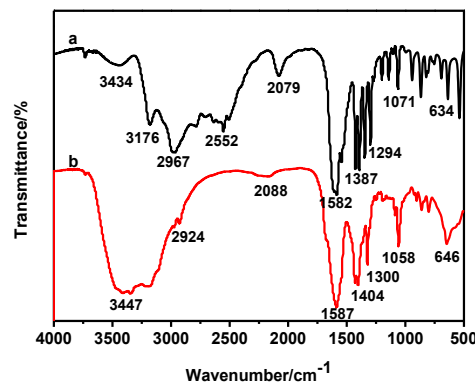


Figure 3. IR absorption spectra of L-cys molecule (a) and L-cys-capped ZnSe: Fe/ZnSe (b) QDs.

3.4. UV-Vis absorption spectrum analysis

The UV-Vis absorption spectrum of the obtained Fe-doped ZnSe core QDs and Fe-doped ZnS/ZnSe core/shell QDs are presented in Figure 4. As can be seen, compared to cubic bulk ZnSe at 460nm^[14], the above QDs exhibit an obvious blue shift in the position of the absorption edge, which is attributed to the small size effect^[15]. As the growth of ZnSe shell on the surface of ZnSe: Fe QDs, the ZnSe: Fe/ZnSe QDs shows a red shift in the absorption edges, which further certified the formation of core/shell structure.

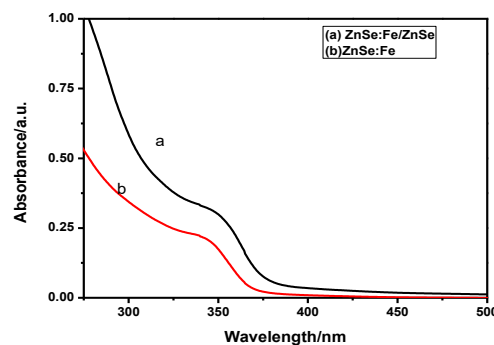


Figure 4. UV-Vis absorption spectra of ZnSe: Fe and ZnSe: Fe/ZnSe QDs.

3.5. Fluorescent spectrum analysis

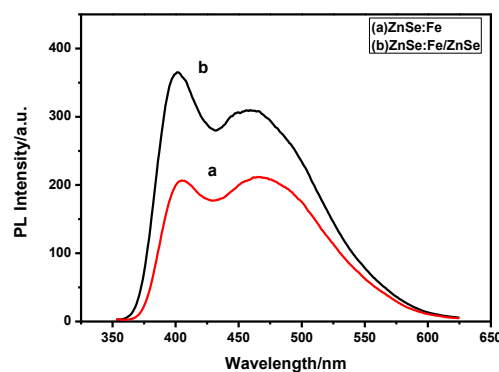


Figure 5. fluorescence spectra of ZnSe: Fe (a) and ZnSe: Fe/ZnSe (b) QDs.

The fluorescence spectra of Fe-doped ZnSe core QDs and Fe-doped ZnS/ZnSe core/shell QDs are presented in Figure 5. Figure 5(a). shows that ZnSe: Fe QDs have two distinct fluorescence emission peaks, including a sharp band-edge emission peak at around 410 nm and a wide emission peak at around 460 nm caused by surface defects emission. As exhibited in Figure 5(b), the PL intensity of ZnSe: Fe/ZnSe QDs enhanced obviously, along with slight red-shift in emission wavelength of ZnSe: Fe/ZnSe QDs, which are caused by the coating of ZnSe layer. The coating of ZnSe shell not only can cause increase of size, but also passivate surface of defect and block its photochemical degradation. Therefore, the change of PL spectra reveals ZnSe is deposited on the surface of ZnSe: Fe QDs to obtain core/shell structure.

4. Conclusions

In summary, the water-soluble Fe-doped ZnSe/ZnSe core/shell QDs using L-cys as modifier are successfully prepared via facile, low-cost and effective strategy in aqueous solution. The as-prepared core/shell QDs have a zinc blende crystal structures, and average diameter is about 2.9 nm. A layer of ZnSe was employed around the surface of Fe-doped ZnSe core QDs, compared to the uncoated ZnSe: Fe QDs, the PL intensity of ZnSe: Fe/ZnSe core/shell QDs is improved obviously. Additionally, the L-cys modified on the surface of Fe-doped ZnSe/ZnSe QDs renders the QDs water-soluble, which will play an important role in the field of biological application.

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