Synthesis and Characterization of the Water-Soluble ZnSe:Fe/ZnS Core/Shell Quantum Dots

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Abstract-The synthesis and fluorescence properties of water-soluble ZnSe:Fe/ZnS core/shell quantum dots with L-cysteine as the stabilizer in aqueous solution are reported in this paper. The structure, component and fluorescence properties of quantum dots were characterized by X-ray powder diffraction (XRD),infrared spectrum(IR),UV-Vis absorption spectrum and photoluminescence(PL). XRD studies present that the L-cysteine modified ZnSe:Fe/ZnS core/shell quantum dots have a cubic zinc-blende structure. The photoluminescence emission intensity of the L-cysteine modified ZnSe:Fe/ZnS core/shell quantum dots is enhanced by coating ZnS shell on the surface of core d-dots. The PL intensity of the ZnSe:Fe/ZnS core/shell quantum dots increase at the beginning and decrease with further growth of the ZnS shell, which achieve the maximum when nshell/ncore=0.75:1. After doped with Fe^{2+} and coated with ZnS shell, the fluorescence quantum yields of the as prepared quantum dots increased from 10.83 % to 18.70%

Keywords: ZnSe:Fe/ZnS core/shell quantum dots; L-cysteine; synthesis; water-soluble; fluorescene

I. INTRODUCTION

Over the past decades, II-VI group semiconductor nanocrystals, also known as quantum dots(QDs), have been widely explored for their outstanding properties and potential application. Usually ,they have novel optical properties, such as narrow and size-tunable emission, broad absorption , high stability against photo and chemical radiation, long fluorescence lifetime, etc.[1,2] Therefore, the quantum dots have enormous wide potential applications in analysis. Much attention has been paid on the doped quantum dots, which means a small part of transition metal ions was added into quantum dots changing optical properties largely. In 1994, Bhargave's group[3] first reported ZnS:Mn quantum dots had a high PL quantum yield. In 2002, Cao's group[5] first reported the fluorescence of ZnS:Mn/ZnS doped quantum dots was enhanced by coating ZnS shell. Base on the appropriate selection of an inorganic shell material, the formation of a type elective surface passivation can be realized, and the good match between core and shell lattice constants, this will help the effective elimination of surface defects and improve the luminescence yield and stability of photochemistry. When modify the nanocrystal surface with small organic molecules can control the size of particle, prevent particle agglomeration, improve fluorescence properties and biocompatibility. [3-5]

Up to now, a large number of high quality QDs, especially cadmium chalcogenides, such as CdS, CdSe and CdTe and especially CdSe/ZnS core/shell q-dots have been successful synthesized. [6-8] However, the inherent toxicity of such q-dots containing cadmium limits their widespread application, especially for the applications directly related to biology. In comparison to Cd-based QDs, the toxicity of Zn-based QDs decreases dramically. ZnSe is a kind of material with a wide band gap of 2.7eV, and have been widely and deeply investigated as a leading candidate for fabrication of blue laser diodes, blue light-emitting diodes(LEDs) and biological labeling.[8-10] ZnSe is also a promising material for lenses, beam expanders, window and optically controlled switching, its visible transmission and high photosensitivity[11-13]. Because of the large band-gap energy of ZnSe quantum dots(2.7eV), transition-metal or impurities are usually doped into ZnSe quantum dots capping with ZnS shell to modulate their PL emission. The synthesis of Fe-doped ZnSe QDs have been reported. In 2013,Xie`s group[14] reported water-soluble Fe:ZnSe nanocrystals with mercaptoacetic acid(MAA) as stabilizer in aqueous solution. In 2012,Yang`group[15] reported microemulsion-mediated hydrothermal synthesis of ZnSe:Fe quantum dots. In2014, Yang`s group[16] reported ZnSe:Fe/ZnSe core/shell core/shell nanocrystals via a hydrothermal microemulsion technique. Up to now, the synthesis of L-cysteine-modified ZnSe:Fe/ZnS core/shell quantum dots in aqueous solution have not been reported .ZnSe:Fe/ZnS core/shell quantum dots is an attractive material ,which be operated at room temperature for application in medicine, environmental control.

Traditional quantum dots were carried out using organic route with toxic reagent, these doped quantum dots are neither water-soluble nor suitable for biological applications. The ZnSe:Fe/ZnS core/shell quantum dots which are synthesis directly via an aqueous route have water-soluble, biocompatible and high PL fluorescence quantum yields become a hot research topic.

In this work, L-cysteine modified ZnSe:Fe/ZnS core/shell QDs are successfully synthesized in aqueous solution. Compare to mercaptoacetic(MAA)[16], L-cysteine is cheaper, less toxic and more stable. The L-cysteine modified on the surface of ZnSe:Fe/ZnS core/shell QDs renders the quantum dot water soluble, biocompatible and the ability to couple with biomacromolecules and applications in biosystem. The fluorescence intensity of ZnSe doped with Fe^{2+} and coated with ZnS shell enhanced, and the fluorescence quantum yield of the as prepared quantum dots increased from 10.83 % to 18.70%

II. EXPERIMENTAL

A. Apparatus and Material

Powder X-ray diffraction patterns(XRD)were carried out with a Philips X′ pert-MPD diffractionmeter. UV-Vis absorption spectra(UV) were recorded with a Varion Cary 50 UV-Visible spectrometer. Fluorescence experiments were performed on a F-1000 spectrometer photometer. Transmittance IR spectra were measured with a UV analyzer.

$NaBH_4$, Se, $Zn(Ac)_2{\cdot}2H_2O$, NaOH, C_2H_5OH, L-cysteine, $FeCl_2{\cdot}4H_2O$ were purchased from Guoyao Chemical Reagent. All reagents were used as received without any further putification.

B. Synthesis of the L-cysteine modified ZnSe:Fe/ZnS core/shell quantum dots

ZnSe:Fe/ZnS core/shell quantum dots were prepared via the chemical precipitation method. Under a N_2 atmosphere, a certain amount of L-cysteine, $Zn(Ac)_2$ and 1ml 0.01mol/L $FeCl_2$ solution were added into deionized water in turn. and the PH value of the solution was adjusted to 10 by dropwise addition of 2.0 M NaOH solution with stirring. The freshly prepared NaHSe solution was added through a syringe into the N_2-saturated solution after 30 minutes at room temperature. The reaction was heated at 100°C for 1h. Then the prepared solution was added 15 ml $Zn(Ac)_2$ solution and 5 ml Na_2S solution. The reaction was heated at 70°C for 1h .The L-cysteine modified ZnS:Fe/ZnS core/shell d-dots were obtained. The obtained L-cysteine modified ZnS:Co/ZnS core/shell d-dots was separated by centrifugation and decantation prior to further purification. The as-obtained powders were washed 3 times with methanol and distill water to remove the remnant substances.

III. RESULTS AND DISCUSSION

A. Structural characterization

The XRD pattern of L-cysteine modified ZnS:Fe/ZnS QDs is shown in Fig. 1 The tree broad peaks (Fig.1) with 2θ values of 27.45°, 46.07° and 54.21° corresponding to the(111)(220)(311)planes, respectively, which reflected that ZnSe:Fe/ZnS core/shell QDs have a cubic zinc blende structure and match well with the standard card(JCPDS NO.05-0566). It can be found that the L-cysteine modified ZnSe:Fe/ZnS core/shell QDs keep the zinc blende structure unchanged.No diffraction peaks from Fe-relate impurity phase are detected, furthermore, it can be concluded that doping Fe^{2+} into the host QDs does not generate a phase transformation of the crystal structure. The diffraction peak positions of the ZnSe:Fe/ZnS core/shell QDs exhibit a slight shift to higher angles toward pure ZnS quantum dots, that could indicate the formation of ZnS shell. The obvious broadening of the diffraction peaks is attributed to their small size effect of nanostructure, and it can be utilized to calculate their average crystallite size by means of Scherrer`s formula. The estimated average crystallite size is near 4 nm.

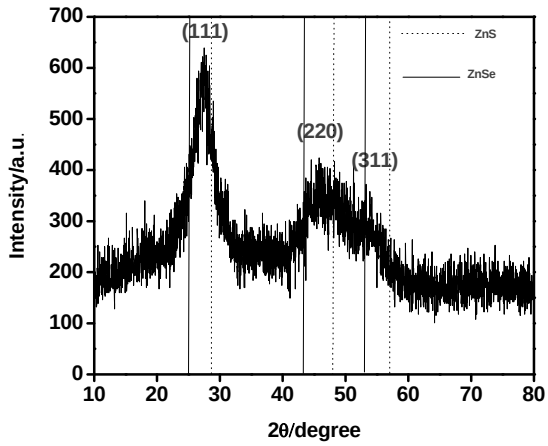

Fig. 1 XRD pattern of ZnSe:Fe/ZnS core/shell QDs

B. Opticall characterization

1) IR analysis

IR measurements on pure L-cysteine and as-prepared L-cysteine-modified ZnSe:Fe/ZnS QDs are shown in Fig.2. It is found the spectrum of pure L-cysteine exhibits a number of characteristic spectral bands such 1588 cm^{-1} (C=O),1302cm^{-1}(C=O),1200c m^{-1}(C-O),3449cm^{-1},3171cm^{-1}(O-H), 2083cm^{-1} (N- H), 2971cm^{-1} (N-H), 1075cm^{-1} (C-NH_2), 639cm^{-1} (C-S), 2561cm^{-1} (S-H).However, no S-H bond stretching appears at 2561 cm^{-1} in the spectrum of L-cysteine-modified ZnSe:Fe/ZnS core/shell quantum dots, which implied that hydrosulphonyl (-SH) has bonded to Zn^{2+} or Fe^{2+} ions. The above data indicates that the ZnSe:Fe/ZnS core/shell quantum dots were capped by L-cysteine.

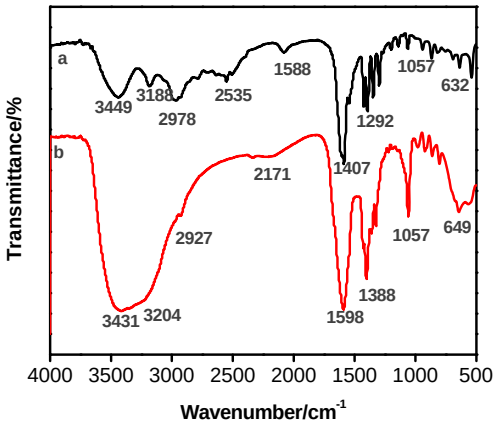

Fig. 2 IR spectra of the L-cysteine(a) and L-cysteine-modified ZnSe:Fe/ZnS(b) QDs

2) Absorption

Fig. 3 prensents the UV-Vis spectra of L-cysteine-modified ZnSe:Fe(a) and ZnSe:Fe/ZnS(b) QDs. It can be seen from the Fig.3 that the absorption have a blue shift compared to that of cubic bulk ZnSe (460nm) at room temperature[17], which provides evidence for the quantum confinement. Compared to ZnSe:Fe QDs , ZnSe:Fe/ZnS core/shell QDs absorption edge has a obvious red shift, which due to the size effect induced by the shell cap. This phenomenon could demonstrate the overcoating reaction of the ZnS shells on the ZnSe:Fe d-doped cores.

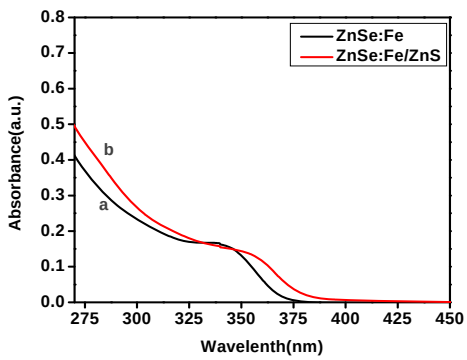

Fig. 3 UV-Vis absorption spectra of L-cysteine-modified ZnSe:Fe(a) and ZnSe:Fe/ZnS(b) QDs

3) Photoluminescene

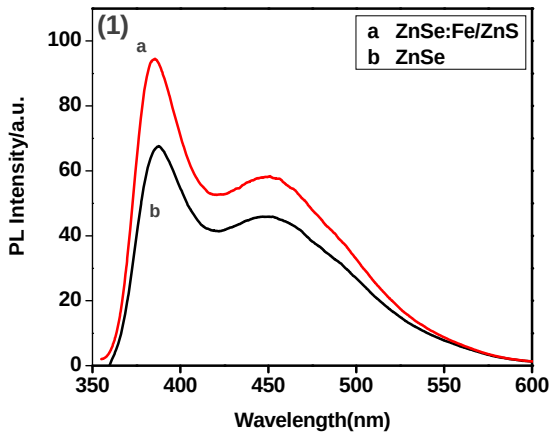

Fig4. PL spectra of L-cysteine-modified ZnSe and ZnSe:Fe/ZnS QDs.

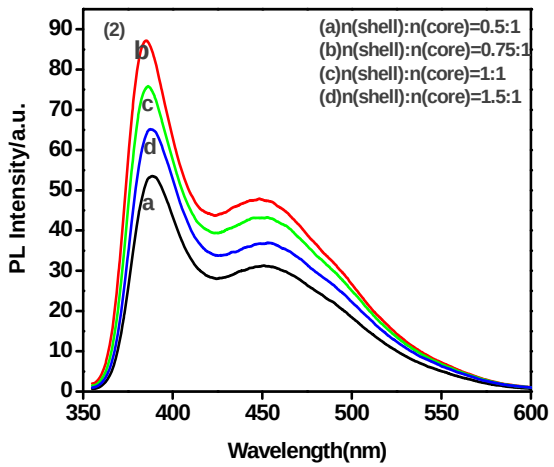

Fig5. PL spectra of L-cysteine-modified ZnSe:Fe/ZnS QDs with ZnS shells of different thickness

The fluorescene properties of L-cysteine-modified ZnSe and ZnSe:Fe/ZnS core/shell d-dots are illustrated in Fig4. It is observed that there are two emissions in the semiconductor nanocrystals—band-edge and surface-defect luminescence. It is found that the band-edge emission is sharp and is located near the absorption edge of the quantum dots, while the surface-defect emission is broad. The ZnSe:Fe/ZnS max emission peak at 385 nm can be assigned to a band-edge emission ,whereas the peak at 450nm is related to surface-defect emission. Compare to ZnSe quantum dots, the intensity of fluorescence is obvious increased. The fluorescence quantum yield of the as prepared quantum dots increases from 10.83% to 18.70% after doped with Fe^{2+} and coated with ZnS shell.

Layers of ZnS shell are found to play a critical role in determining the properties of the resulting ZnSe:Fe/ZnS core/shell d-dots. PL spectra of L-cysteine-modified ZnSe:Fe/ZnS core/shell d-dots with varying thickness of ZnS shells are presented in Fig.4(2).It shows that PL intensity first increases progressively as the growth of ZnS shell continues, and reaches its maximum value for n(shell)/n(core)=0.75:1 and then decreases as the shell

further thickening. Since this is a wide band gap for the outer ZnS shell, both electrons and holes were confined in the core, and the ZnS shell reduced the surface defects of the cores, an radiative recombinations were improved, consequently, the PL intensity of the quantum was enhanced. Moreover, when it was deposited on the surface of ZnSe:Fe cores, the ZnS shell physically separated the surface of the optically active core from its surrounding medium ,contributing to the enhancement of the PL emission.[18] However, with the further thickening of the ZnS shell, the lattice mismatch between the ZnS shell and the ZnSe:Fe cores usually generated some defects, resulting in the nonradiative recombination which led to the decrease of the emission.

IV. CONCLUSION

In summary, water-soluble L-cysteine-modified ZnSe:Fe/ZnS core/shell DQs were synthesized via a simple green method in aqueous solution. Experimental results show that the ZnSe:Fe/ZnS core/shell QDs have cubic zinc blende structure. PL intensity of the as prepared quantum dots increases sharply originally and reaches it maximum when x=n(shell/core)=0.75:1 and decreases slowly with the additional of ZnS shells, which achieve the maximum when nshell/ncore=0.75:1. The L-cysteine modified on the surface of ZnSe:Fe/ZnS core/shell QDs renders the quantum dot water-soluble and biocompatible. This study will promote the further studies of ZnSe:Fe/ZnS in molecular assembly and biological fluorescence analysis.

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