

Research Article

Aqueous Synthesis of ZnSe/ZnS-2-R-Benzothiazole Nanocrystals with White Emission

Ying-Fan Liu,^{1,2} Yan-Hui Zhang,¹ Guo-Qing Wang,¹ Kai-Ming Mao,¹ Shao-Ming Fang,^{1,2} Zhang-Di Li,¹ and Hong-Duo Tang¹

¹Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, No. 166, Science Avenue, Zhengzhou 450001, China

²Henan Collaborative Innovation Center of Environmental Pollution Control and Ecological Restoration, Zhengzhou University of Light Industry, No. 166, Science Avenue, Zhengzhou 450001, China

Correspondence should be addressed to Ying-Fan Liu; yfliu@zzuli.edu.cn and Shao-Ming Fang; mingfang@zzuli.edu.cn

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We prepared water-soluble white light-emitting ZnSe/ZnS-2-R-benzothiazole nanocrystals (NCs), R = 2-hydroxy-5-(2,5-dimethylthienyl)-phenyl. The penicillamine (Pen) capped ZnSe/ZnS NCs were firstly prepared with high photoluminescence quantum yields (PL QY) of 40%. Then they bond to 2-R-benzothiazole molecules, resulting in white light-emitting ZnSe/ZnS-2-R-benzothiazole NCs with QY of 75% over a 375 to 650 nm range of emission, which can be applied to white light-emitting diodes. The ZnSe/ZnS-2-R-benzothiazole NCs with two emission bands at around 451 and 557 nm were discussed and the possible mechanism of the interaction of ZnSe/ZnS NCs with 2-R-benzothiazole was also proposed.

1. Introduction

The investigations on semiconductor nanocrystals (NCs) in the last two decades have opened the perspectives for the design and synthesis of new multifunctional materials. The wide interest in NCs arises from their unique optical and electrical properties, including broad absorption and narrow emission spectra, strong resistance to photobleaching, long fluorescence lifetime, and size-tunable emission [1–3]. These properties have created many applications of NCs for LEDs, lasers, barcoding, and biological and chemical sensing [4–8]. However, the band gap of most emissive semiconductors is either too high or low to easily make visible emitting NCs.

Until recently, there are mainly two methods to tune PL emission wavelength of the NCs: the first one is realized by size change of a few NCs, such as CdTe quantum dots (QDs), where PL is size-tunable from 400 to 700 nm [9, 10]. Although CdTe NCs exhibit high and size-tunable luminescence, the toxicity of cadmium will limit the use of these NCs, especially for bioapplications. Another method is used by doping technique. It is well-known that, as nontoxicity

NCs, ZnSe NCs having greater band gaps of 2.7 eV are one of blue emitting semiconductors with 450 nm [11–13]. Hines and Guyot-Sionnest were the first to report the synthesis of luminescent TOP/TOPO-capped ZnSe NCs [14]. Due to the large band gap energy of ZnSe NCs, transition-metal Cu or Mn impurities are usually introduced into NCs to modulate their PL emission region to the UV-visible band, such as Mn doped ZnSe NCs with 590 nm and Cu doped ZnSe NCs with 500 nm [15–21]. Although size-tunable synthetic strategies and nucleation-doping technologies have been proved to be promising, more technologies need to be explored to further improve the PL QY, color tunability, and stability of the NCs.

How to control simultaneously with the emitting wavelength and intensity of the NCs may still be urgent. The organic molecules stabilizing the QD dispersion largely influence the colloidal properties of the NCs, such as the hydrodynamic size, charge, and PL QY. Hydrophilic thiols bind to QD surface atoms and simultaneously stabilize QD dispersions in polar solvents and are responsible for the surface-related optical properties of the QDs [22–25]. Using mercaptopropionic acid (MPA) as stabilizer, Lan et al.

synthesized ZnSe QDs in aqueous solution, the QY of the as-prepared ZnSe QDs improved from 8.1% to 44% under UV irradiation [26]. Wang et al. have reported the synthesis of MPA-capped ZnSe:Mn QDs [27]. Using MPA as stabilizer reagents, Fang et al. [28] have described the preparation of ZnSe:Mn/ZnS in aqueous media. However, the as-prepared QDs still possess weak luminescence, blocking their applications. Thus, it is still a great challenge to synthesize highly luminescent water-soluble ZnSe NCs.

In our previous works [29, 30], owing to outstanding thermal stability of Pen, we successfully synthesized Ag and Ag₂S NCs with good biocompatibility and low cytotoxicity by using Pen as stabilizer. In this work, using Pen as stabilizer reagents, we prepared ZnSe/ZnS NCs with QY of 40%. Furthermore, the prepared NCs can be bond to organic fluorescent chromophore benzothiazole derivatives 2-hydroxy-5-(2,5-dimethyl-thienyl)-phenyl-benzothiazole (2-R-benzothiazole), resulting in PL white emitting from 375 to 650 nm with as high as QY of 75%. This observation creates inroads towards the development of novel white light-emitting diodes as discussed in the following.

2. Experimental Section

2.1. Chemicals. All materials used in this work were analytical reagents. Penicillamine (also named β,β -dimethylcysteine, 99%, Pen), Se, and NaBH₄ (96%) were obtained from Sigma, Inc. Thioacetamide (TAA) and Zn(Ac)₂ were obtained from Shanghai Chemical Reagents Company. 2-Hydroxy-5-(2,5-dimethyl-thienyl)-phenyl-benzothiazole (2-R-benzothiazole) was provided by Dr. Xiao-Chun Li from Henan Normal University. High purity deionized water (>18.3 M Ω /cm) was produced by Millipore A10 Milli-Q.

2.2. Synthesis of Pen Capped ZnSe NCs. All the solutions were freshly prepared with deionized water prior to the synthesis. The synthesis of ZnSe NCs was performed according to [26] with some modification. Typically, ZnSe NCs were prepared by using the reaction between Zn²⁺ and NaHSe solution. Under vigorous stirring, the oxygen-free 0.08 mmol of NaHSe solution was prepared by the reaction of Se and NaBH₄ in aqueous solution. The concentrations of Zn²⁺ and the molar ratio of Zn²⁺ : HSe⁻ : Pen were set as 1.6 mM and 1 : 0.5 : 2, respectively. Under a robust flow of argon, 1.6 mL (0.1 M, 0.16 mmol) of ZnAc₂ was dissolved in 100 mL of Milli-Q water, and 47.8 mg (0.32 mmol) of pure Pen was added. Dropwise addition of 0.5 M NaOH was then used to adjust the pH to 10.5 under vigorous stirring. The resulting mixture solution between Zn²⁺ and NaHSe was heated to 100°C under open-air conditions and refluxed for 1 h. 2-Propanol was added to the as-prepared ZnSe NCs colloid solution. ZnSe NCs were precipitated from the solution and collected by centrifugation. Finally, the obtained ZnSe NCs were dried at room temperature in vacuum overnight.

2.3. Synthesis of ZnSe/ZnS Nanocrystals. 70.0 mL of the as-prepared ZnSe core NCs solution was placed in a 100 mL three-necked bottle. 25.1 mg (0.17 mmol) of D-penicillamine,

0.84 mL of Zn(OAc)₂ solution (0.1 M), and 0.84 mL of thiourea (0.1 M) were added to ZnSe NCs aqueous solution. Then the solution was heated to 100°C under open-air conditions and refluxed from 1 h to 50 h. 2-Propanol was added to the as-prepared ZnSe/ZnS NCs colloid solution. ZnSe/ZnS NCs were precipitated from the solution and collected by centrifugation. Finally, the obtained ZnSe/ZnS NCs were dried at room temperature in vacuum overnight.

2.4. Synthesis of ZnSe/ZnS-2-R-Benzothiazole Nanocrystals. The ZnSe/ZnS NCs precipitation was dissolved in PBS buffer solution (pH = 7.4) to produce ZnSe/ZnS PBS buffer solution. To obtain ZnSe/ZnS-2-R-benzothiazole NCs, 0.1~0.8 mL of the ethylene glycol solution of 2-hydroxy-5-(2,5-dimethyl-thienyl)-phenyl-benzothiazole (2-R-benzothiazole) was injected into 2 mL of freshly prepared ZnSe/ZnS PBS buffer solution. The concentrations of ZnSe/ZnS NCs and 2-R-benzothiazole were 1×10^{-6} mol·L⁻¹ and 5×10^{-5} mol·L⁻¹, respectively. 2-Propanol was added to the as-prepared ZnSe/ZnS-2-R-benzothiazole NCs colloid solution. ZnSe/ZnS-2-R-benzothiazole NCs were precipitated from the solution and collected by centrifugation. Finally, the obtained ZnSe/Zn-2-R-benzothiazole NCs were dried at room temperature in vacuum overnight.

2.5. Characterization. UV-vis absorption and photoluminescence (PL) spectra were measured at room temperature with a Shimadzu UV-3600 spectrophotometer and a Hitachi 7000 fluorescence spectrometer, respectively. Time-resolved luminescence measurements were carried out on an Edinburgh FLS 980 spectrofluorometer with LED lamp as light source. The excitation wavelength was 360 nm. Ludox was applied for PL lifetime measurement in order to eliminate the influence of light scattering (i.e., excitation and emission). For all structural characterization, ZnSe (A) and ZnSe/ZnS (B) samples were obtained after heating for 1 and 4 h, respectively. Powder XRD measurements were taken on a Philips X'Pert PRO X-ray diffractometer. High-resolution transmission electron microscopy (HRTEM) was performed on a Philips FEI Tecnai G² 20 S-TWIN.

3. Results and Discussion

3.1. XRD, TEM, and XPS Characterization. The powder XRD patterns for the ZnSe and ZnSe/ZnS-2-R-benzothiazole NCs (2-R-benzothiazole = 2-hydroxy-5-(2,5-dimethyl-thienyl)-phenyl-benzothiazole) are depicted in Figure 1. The XRD patterns were obtained from ZnSe and ZnSe/ZnS-2-R-benzothiazole powders, which were precipitated from aqueous solution with an excess of 2-propanol and the precipitate was isolated by centrifugation and dried at vacuum. The characteristic zinc blend planes of 111, 220, and 311 locating at 24.04°, 45.33°, and 53.80° for ZnSe and at 27.80°, 46.23°, and 54.55° for ZnSe/ZnS-2-R-benzothiazole in the 2 θ range of 10 to 60° have been observed. The position of the XRD peaks of ZnSe cores matched well with those of bulk ZnSe cubic structure (JCPDS no. 37-1463). After growth of ZnS shell on ZnSe core, peak position shifted to higher angles towards the

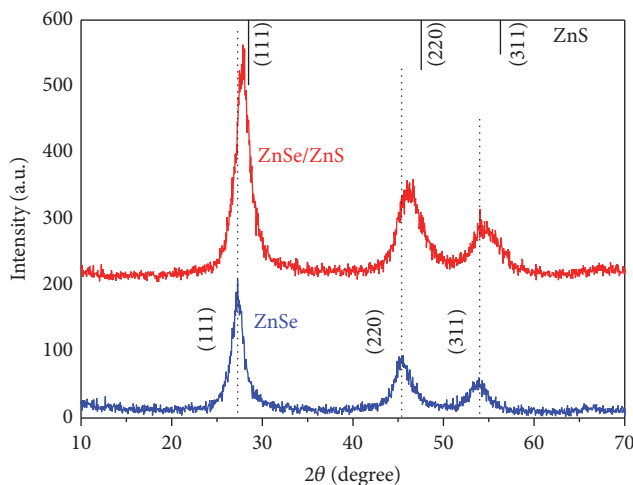


FIGURE 1: XRD patterns of ZnSe and ZnSe/ZnS-2-R-benzothiazole NCs.

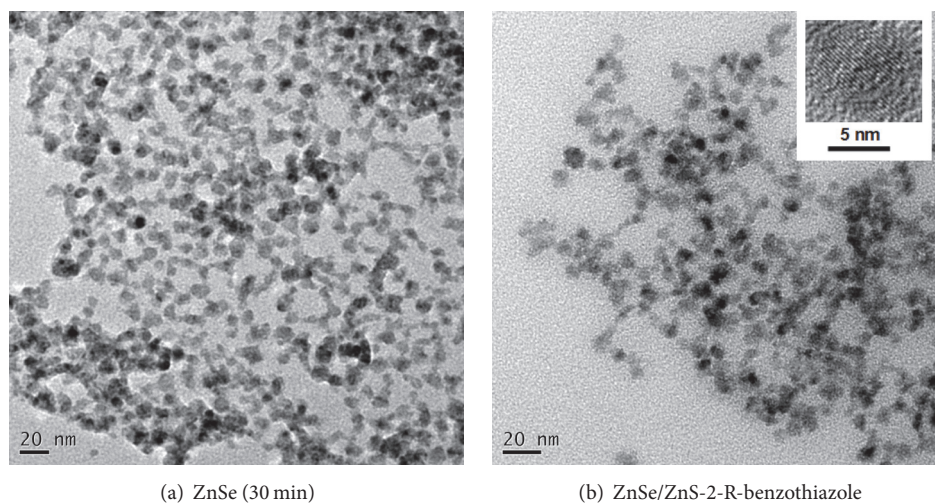


FIGURE 2: TEM images of ZnSe and ZnSe/ZnS-2-R-benzothiazole NCs. The scales bars are 20 nm in (a) and (b). Inset: HRTEM image with a scale bar of 5 nm.

positions of bulk ZnS cubic structure peaks (JCPDS no. 05-0566), which proved the formation of ZnSe/ZnS NCs and agreed with the values reported in the literature [31].

Figure 2 shows TEM images of ZnSe and ZnSe/ZnS-2-R-benzothiazole NCs. As can be seen, the as-prepared NCs are quasispheres with average size of 5.0 ± 0.3 nm and 6.0 ± 0.3 nm, respectively, when 200 NCs were counted. The size increase of the NCs is 1 nm, which is mainly caused by the formation of ZnS layers outside the NCs. From the EDS results in Figure 3, it can be seen that Zn, Se, and S are uniformly distributed in the ZnSe and ZnSe/ZnS-2-R-benzothiazole NCs. The S/Zn and Se/Zn of the NCs before and after core-shell formation increased from 0.14 to 0.18 and decreased from 0.43 to 0.36. A full survey scan and Zn, Se, S photoelectron spectra of the ZnSe NCs, and ZnSe/ZnS-2-R-benzothiazole NCs are displayed in Figure 4. Besides the Zn2p core levels, the spectra are dominated by the Cls and Ols signals stemming from the capping agent. XPS spectra

of ZnSe NCs in Figure 4 show that Zn2p, Se3d, and S 2p are 1021.40 and 1044.61; 53.50, 63.17; and 159.73 eV, respectively, while the binding energies of Zn2p, Se3d, and S 2p for ZnSe/ZnS-2-R-benzothiazole NCs are 1021.74 and 1044.88; 53.65, 63.37; and 161.25 eV, respectively. Compared with ZnSe core, there is lower content of Se on ZnSe/ZnS surface. The peak at 161.25 eV is mainly attributed to S^{2-} in the ZnS shell [32]. The intensity of S2p binding energy (161.25 eV) increased after ZnS formation on the ZnSe NCs surface. These data of X-ray photoelectron spectroscopy (XPS) provide the direct evidence of the formation of ZnSe/ZnS NCs.

3.2. Optical Properties. As found in the original reports by Fang et al. [31] and Zheng et al. [33], because superior ligand glutathione was used in the synthesis of ZnSe and ZnSe/ZnS NCs, the resulting ZnSe and ZnSe/ZnS QDs possessed high PL QY up to 20% and 60%, respectively. The PL of the water-soluble ZnSe NCs capped with other thiols ligands such as

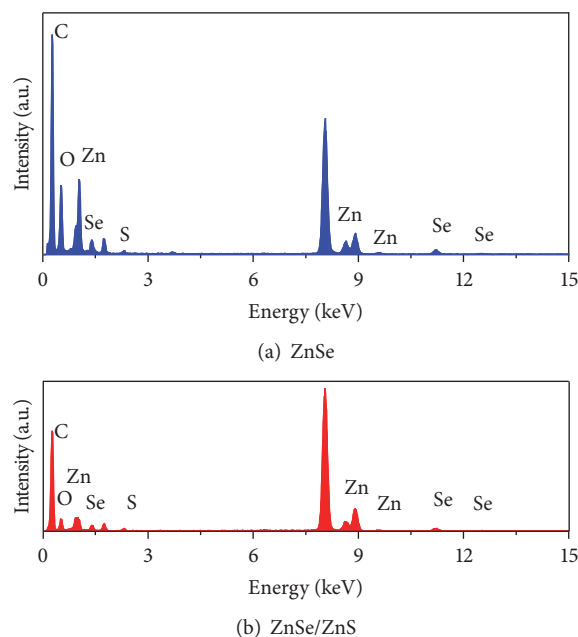


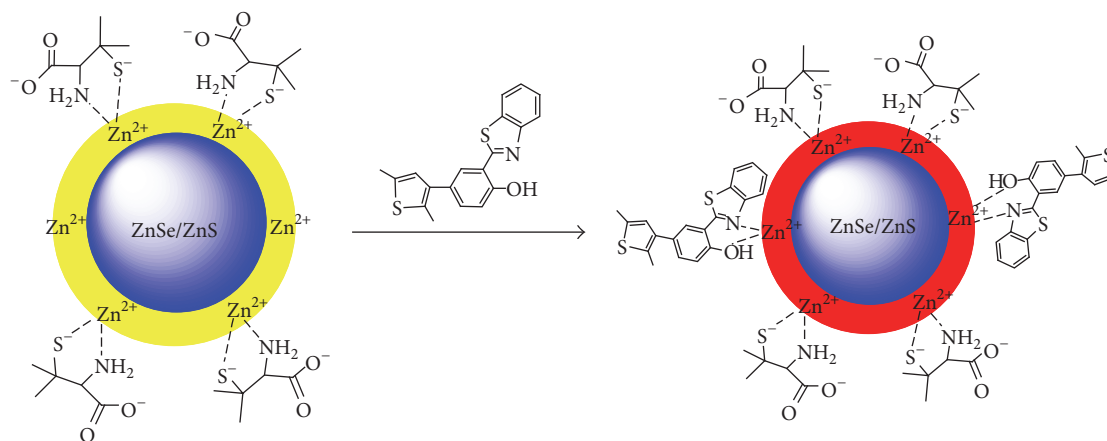
FIGURE 3: EDS spectra of ZnSe and ZnSe/ZnS-2-R-benzothiazole NCs: (a) ZnSe NCs; (b) ZnSe/ZnS-2-R-benzothiazole NCs.

thioglycerol, thioglycolic acid, and 3-mercaptopropionic acid usually is negligible and mainly shows a broad emission in the range of 400–600 nm. Alternatively, ligand Pen was used in the synthesis of aqueous ZnSe and ZnSe/ZnS NCs, because Pen molecule structure contains $-SH$, $-NH_2$, and $-COOH$ group, which is similar to that of glutathione. With the introduction of $Zn(OAc)_2$, capping reagent Pen, and sulfur source thiourea into the as-prepared ZnSe NCs reaction solution, the ZnS shell formed gradually and deposited around the ZnSe core to form the ZnSe/ZnS core/shell nanostructures.

Figure 5 shows the temporal evolution of the UV-vis absorption and PL emission spectra of the ZnSe/ZnS core/shell NCs together with the initial ZnSe core NCs. All of the samples showed a sharp well-resolved first excitonic absorption onset from 300 to 450 nm, which should be attributed to the electronic transition of $1S(e)-1S_{3/2}(h)$. The absorption onsets of the ZnSe/ZnS did not obviously shift to longer wavelength compared to that of the initial ZnSe core NCs, while the absorptivity of the ZnSe/ZnS increased when the heating time was increased from 0 to 9 h, which demonstrated the growth of the ZnS shell around ZnSe cores. However, at longer reaction time from 20 to 50 h, the absorptivity of the NCs decreased perhaps due to that the concentration of the NC solution decreased originating from the aggregation of a few NCs. As shown in Figure 5(b), after heating for 1, 9, 20, 25, 35, and 40 h, the PL intensity of the NCs first increased gradually and then decreased. The PL peak position could approach to 437 nm in a period of 35 h growing time from the original 427 nm corresponding to the ZnSe core NCs. Figure 5(b) showed that the band-edge emission of the ZnSe/ZnS NCs improved 36-fold and reached to the maxima after 35 h refluxing at $100^\circ C$. The luminescence QYs were measured by an absolute method using an integrating sphere and amounted to 40%. The observed PL enhancement

is caused by passivation of surface trap states due to dual protection of both the ZnS shell and Pen stabilizer reagents. It was noted that the $-NH_2$ and $-SH$ of the Pen molecules simultaneously binding to Zn^{2+} on the surface of the NCs could efficiently eliminate dangling bonds, resulting in high PL QY.

Figure 6 shows the fluorescence change of the ZnSe/ZnS NCs in PBS solution upon interaction with different concentrations of 2-hydroxy-5-(2,5-dimethyl-thienyl)-phenyl-benzothiazole (2-R-benzothiazole) for a fixed time interval of 5 min. When 0.1 mL of 2-R-benzothiazole was added into ZnSe/ZnS NCs solution, a new PL peak was appeared at 557 nm and the PL of NCs solution displayed a broad double peaks character. It was evident that the PL intensity of the system was increased along with adding of the volumes of 2-R-benzothiazole (QY 51%) and arrived maximum (QY 75%) up to additions of 0.8 mL of 2-R-benzothiazole. Further adding 2-R-benzothiazole to 1.0 mL (Figure 6(g)), the PL of the NCs was almost constant. The observed fluorescence band centered 451 nm was attributed to the recombination of the charge carriers within surface states and 557 nm was originated from 2-R-benzothiazole-Zn complex. It was noted that the PL wavelengths of ZnSe/ZnS-2-R-benzothiazole NCs covered from 375 to 650 nm, which made NCs available as a white LED material. Scheme 1 gives the conjugation of ZnSe/ZnS NCs and 2-R-benzothiazole. As shown in Scheme 1, when 2-R-benzothiazole was added into ZnSe/ZnS NCs solution, the N and O atoms of the 2-R-benzothiazole molecules could bind to excess Zn^{2+} ions on the surfaces of the NCs to form 2-R-benzothiazole-Zn complex. When the 2R-benzothiazole was added into ZnSe/ZnS NCs solution, the energy from Zn-2R-benzothiazole complexes can be transferred to ZnSe/ZnS NCs in composite NCs, which usually trends to PL quenching of the QDs. However, there



SCHEME 1: The possible mechanism of the interaction of ZnSe/ZnS NCs with 2-R-benzothiazole.

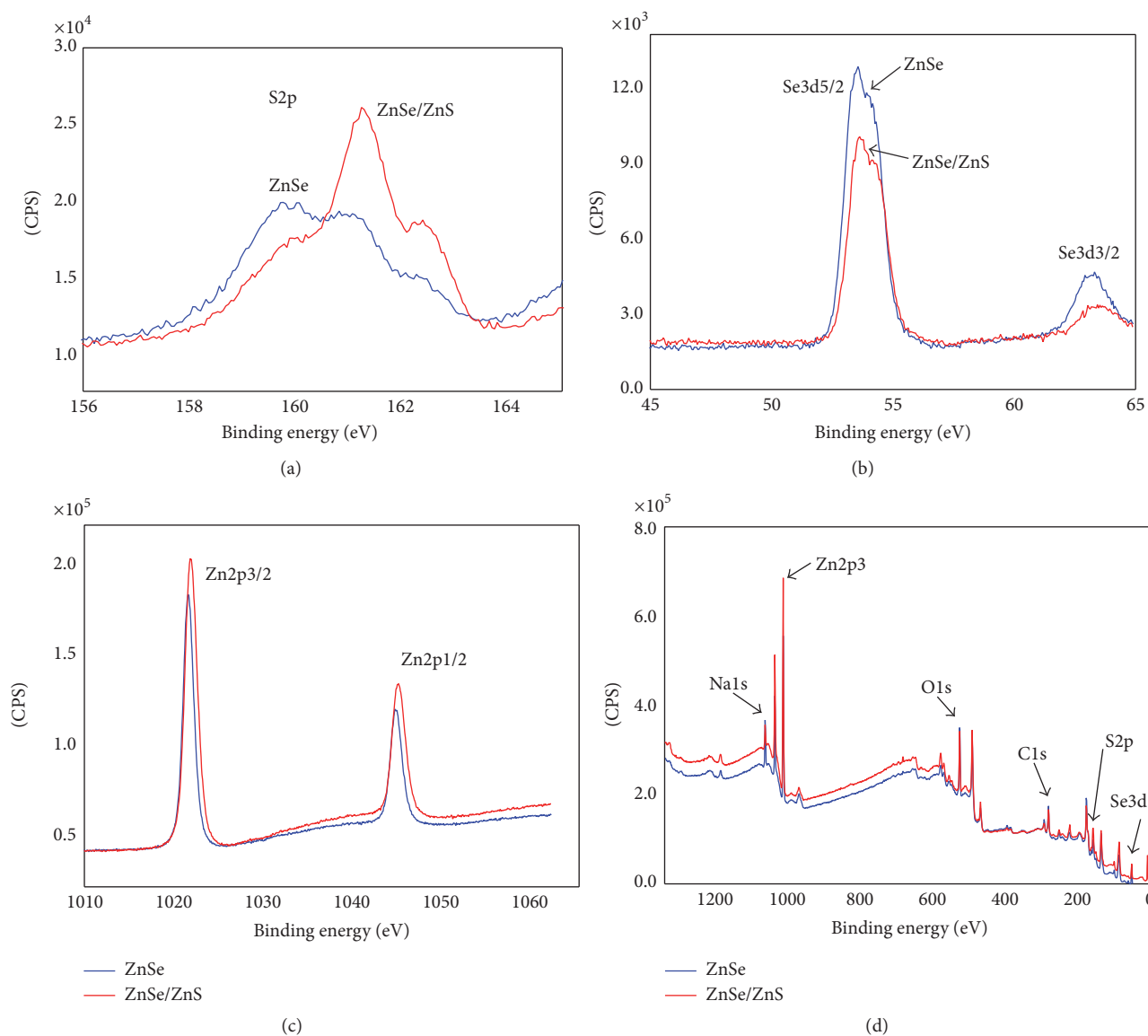


FIGURE 4: XPS spectra of ZnSe and ZnSe/ZnS-2-R-benzothiazole: (a) S 2p, (b) Se 3d levels of ZnSe and ZnSe/ZnS, (c) Zn 2p levels of ZnSe/ZnS-2-R-benzothiazole, and (d) total XPS spectra of ZnSe/ZnS-2-R-benzothiazole (top) and ZnSe (bottom) NCs. The ratios of S/Zn and Se/Zn of ZnSe and ZnSe/ZnS-2-R-benzothiazole are from 0.79 and 0.55 to 0.91 and 0.32.

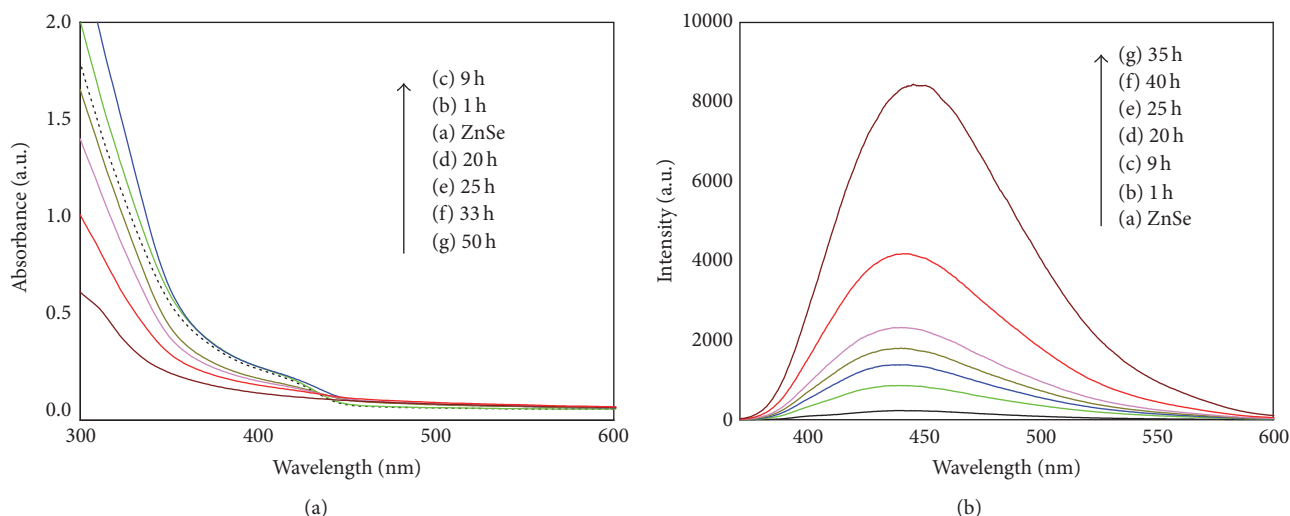


FIGURE 5: Typical temporal evolution of the absorption (a) and corresponding emission (b) spectra of ZnSe and ZnSe/ZnS NCs. Curve a represents the absorption (a) and corresponding emission (b) spectra of ZnSe NCs. Curves b~g represent the absorption (a) and corresponding emission (b) spectra of ZnSe/ZnS NCs obtained for heating for 1, 9, 20, 25, 35, and 40 h, respectively; the excitation wavelength was 360 nm.

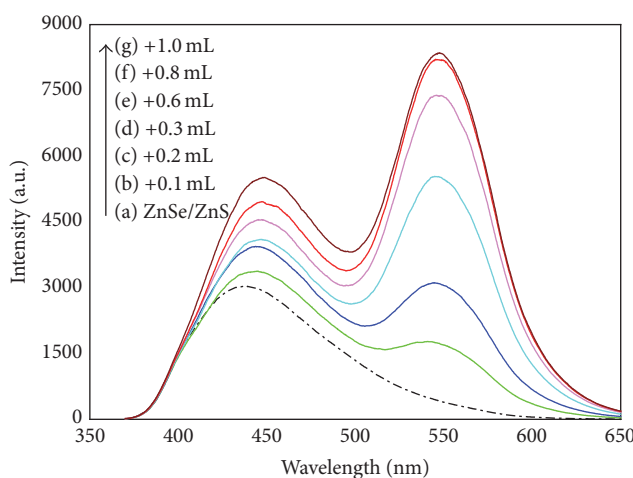


FIGURE 6: The fluorescence change of ZnSe/ZnS-2-R-benzothiazole NCs in the presence of variable volumes of 2-hydroxy-5-(2,5-dimethylthienyl)-phenyl-benzothiazole (2R-benzothiazole): (a) 0, (b) 0.1 mL, (c) 0.2 mL, (d) 0.3 mL, (e) 0.6 mL, (f) 0.8 mL, and (g) 1.0 mL for a fixed time interval of 5 min. All measurements were performed in a 50 mmol/L PBS buffer solution (pH = 7.4). The concentrations of ZnSe/ZnS NCs and 2-R-benzothiazole were $1 \times 10^{-6} \text{ mol L}^{-1}$ and $5 \times 10^{-5} \text{ mol L}^{-1}$, respectively. The excitation wavelength was 360 nm.

is no evidence of PL quenching of QDs in our system, which may be due to the complex formation resulting in two emission peaks and one of the peaks is overlapped with that of the ZnSe/ZnS NCs.

To further prove the possible mechanism of the interaction of ZnSe/ZnS NCs with 2-R-benzothiazole, 0.2 mL of the ethylene glycol solution of 2-R-benzothiazole ($5 \times 10^{-5} \text{ mol L}^{-1}$) was added into 2 mL of the aqueous solution of Zn^{2+} ($5 \times 10^{-6} \text{ mol L}^{-1}$), resulting in the formation of 2-R-benzothiazole-Zn complex. Figure 7(a) gives the absorption spectra of 2-R-benzothiazole with maximum peak at 355 nm. Figure 7(b) shows PL emission spectra of the 2-R-benzothiazole and 2-R-benzothiazole-Zn complex. It was evident that the PL peak of the 2-R-benzothiazole was at

561 nm and split into two peaks at 450 and 548 nm after solvent of the 2-R-benzothiazole changed from the ethylene glycol solution to the mixture of ethylene glycol and water solution, and further 2-R-benzothiazole-Zn complex formed, which was agreed with the interaction of 2-R-benzothiazole with ZnSe/ZnS NCs.

The ZnSe/ZnS-2-R-benzothiazole NCs were further studied by time-correlated single-photon counting (TCSPC) experiments. The decay profiles were recorded at the emission maxima of the NCs, at 451 and 557 nm, upon excitation at 360 nm, respectively, as presented in Figure 8. These PL decay curves at peak of $\text{Em} = 450 \text{ nm}$ and $\text{Em} = 557 \text{ nm}$ ($\lambda_{\text{ex}} = 360 \text{ nm}$) can be well fitted by a biexponential equation $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ [34–36]. The observed lifetimes

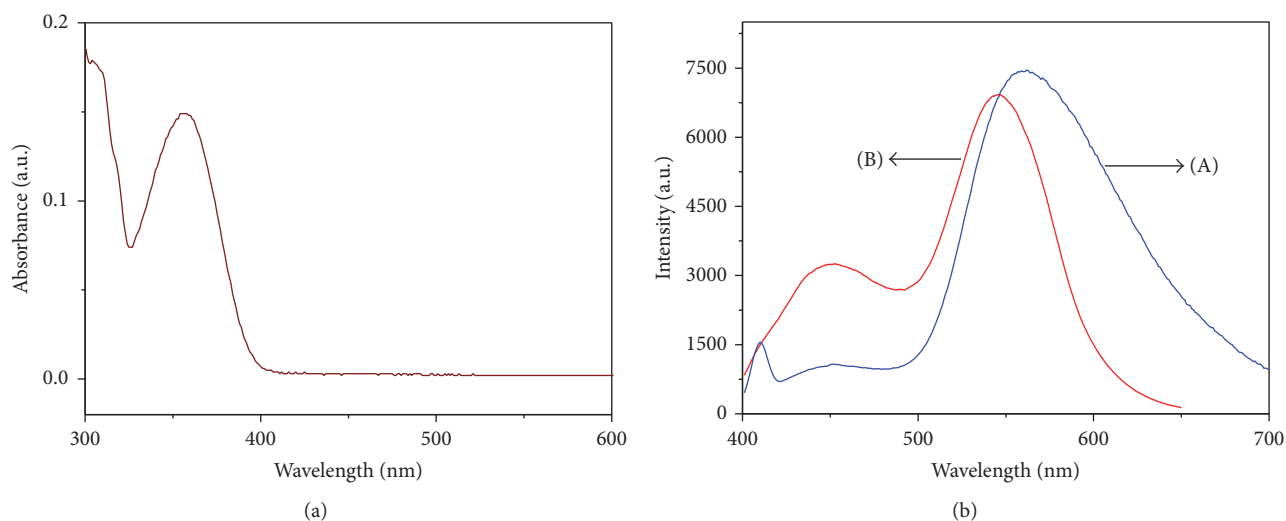


FIGURE 7: The absorption (a) of 2-R-benzothiazole and PL emission spectra (b) of 2-R-benzothiazole (A) and 2-R-benzothiazole-Zn complex (B). The concentrations of the 2R-benzothiazole and the 2-R-benzothiazole-Zn complex were $1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$.

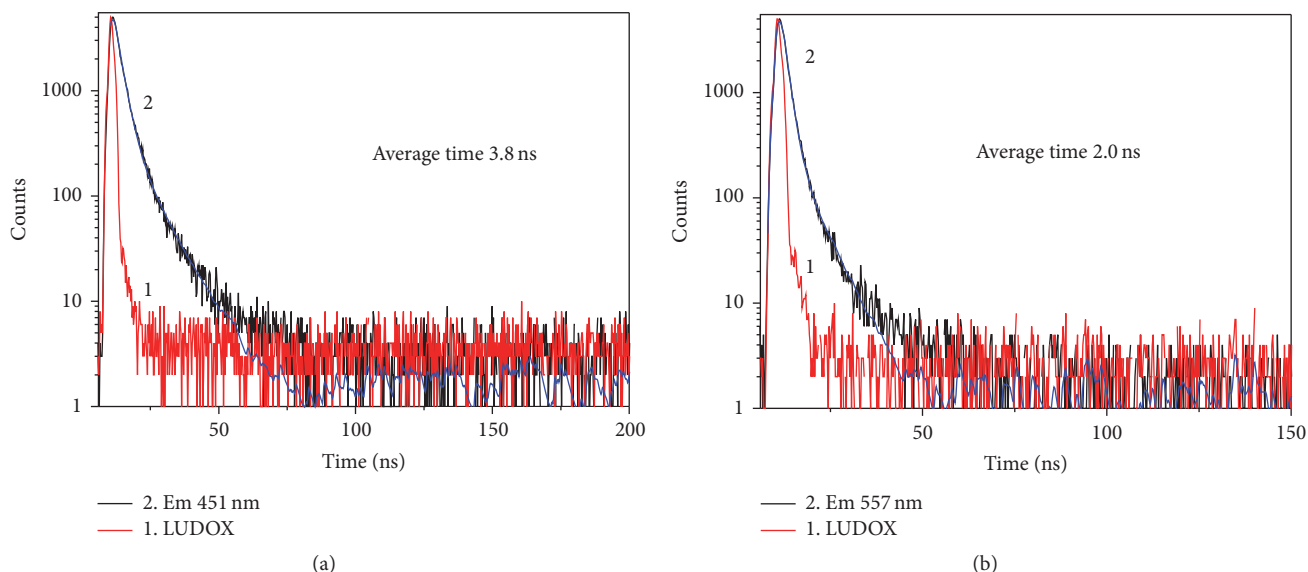


FIGURE 8: PL decay spectra of the ZnSe/ZnS-2-R-benzothiazole NCs at the emission maxima of the conjugation system, at 451 nm (a) and 557 nm (b), upon excitation at 360 nm, respectively.

were $\tau_1 = 2.42 \text{ ns}$ (Rel: 78.2%), $\tau_2 = 8.63 \text{ ns}$ (Rel: 21.8%), and $\chi^2 = 1.27$ for 450 nm peak, whereas $\tau_1 = 1.37 \text{ ns}$ (Rel: 85.2%), $\tau_2 = 5.83 \text{ ns}$ (Rel: 14.8%), and $\chi^2 = 1.06$ for 557 nm peak. The average lifetimes of both peaks were 3.80 ns and 2.00 ns, respectively. Obviously, the average emission lifetime of the latter was shorter than that of the former. The former was mainly attributed to the electron-hole pair recombination emission process of ZnSe/ZnS NCs, whereas the latter was due to the bipolar charge (electron and hole) transport of 2-R-benzothiazole-Zn complex.

Figure 9 shows the Commission Internationale de l'Eclairage (CIE) color coordinates of the ZnSe/ZnS NCs, dye (2-R-benzothiazole), and ZnSe/ZnS-dye hybrid NCs. As

shown from Figure 9, ZnSe/ZnSNCs emit blue light with CIE coordinates of (0.19, 0.20), dye is 2-R-benzothiazole, which emits orange-red light with coordinates of (0.41, 0.47), and ZnSe/ZnS-dye is of a hybrid of dye and ZnSe/ZnS NCs, which emits whit light with CIE coordinates of (0.31, 0.34).

To date, using ZnSe NCs with blue emitting as basis material, there were two methods of synthesizing of white LED material in the relevant literatures [32, 37]. One method was used by Mn-doping technique, and another was adopted by Se of ZnSe NCs binding to Eu complex. Here, we presented the novel method of preparing of white LED material, which was obtained by Zn of ZnSe/ZnS NCs binding to dye. Particularly, the prepared NCs of ZnSe, ZnSe/ZnS,

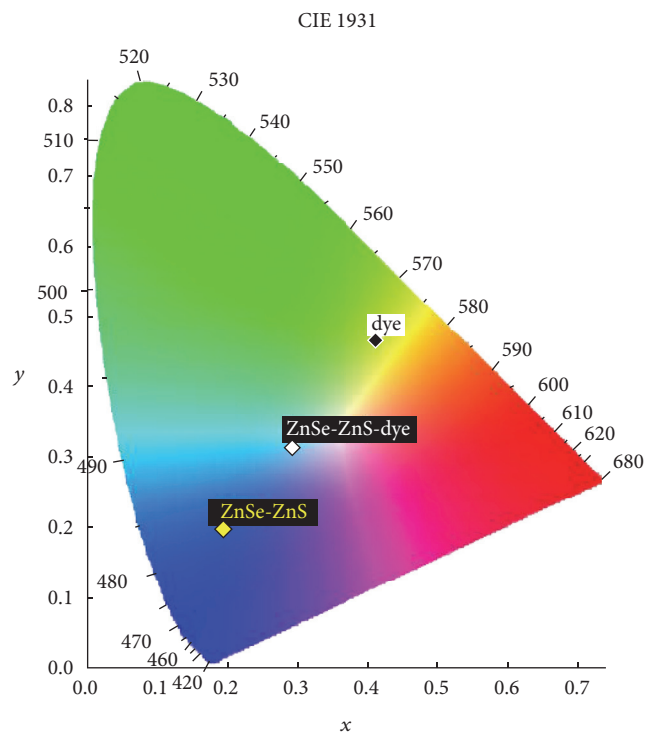


FIGURE 9: CIE color coordinates of the of ZnSe/ZnS NCs, dye (2-R-benzothiazole), and ZnSe/ZnS-dye hybrid NCs. The corresponding CIE coordinates are (0.18, 0.19), (0.41, 0.47), and (0.31, 0.34). The concentrations of ZnSe/ZnS NCs and dye were 1×10^{-7} mol L $^{-1}$ and 5×10^{-5} mol L $^{-1}$, respectively.

and ZnSe/ZnS/2R-benzothiazole have all excellent colloidal and photostability over two months of study in ambient conditions.

4. Conclusions

Highly luminescent water-soluble NCs were synthesized by a facile and reproducible procedure in water. The penicillamine was used as a capping ligand and the formation of ZnSe/ZnS NCs with 450 nm PL emission, which possesses a ZnS rich surface, was observed. This ZnS covering protects the NCs from nonradiative trapping and as a consequence, high QY were observed (40%). Moreover, the PL QY of ZnSe/ZnS-2-R-benzothiazole NCs improved greatly up to 75% and their wavelength covered from 375 to 650 nm, making NCs available as a white LED material.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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