Study on the Zn(II)-Doped CdS Luminescent Nanoparticles Formation on the Chelating Polymer Microsphere

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Summary: Highly photoluminescent hybrid Zn(II)-doped CdS nanocluster/copolymer nanocomposites latex were prepared by using the chelating copolymer, poly(methyl methacrylate-co-methyl acrylate-co-2-methyl acrylic acid 3-(bis-carboxymethyl amino)-2-hydroxyl-propyl ester), with in-situ chemical precipitation method. The morphology and photoluminescence property of the hybrid Zn(II)-doped CdS nanocluster/copolymer nanocomposites latex was examined by TEM and photoluminescence analyzer (PL), respectively. The photoluminescent intensity of the hybrid CdS nanocluster/copolymer nanocomposites could be enhanced by Zn(II) doped treatment from the PL measurement. Furthermore, these hybrid nanocomposite latex could be easily manufactured into the transparent nanocomposite membrane without losing their photoluminescence property as they were cured at 60 °C. Interestingly, the photoluminescence property of the hybrid Zn(II)-doped CdS nanocluster/copolymer nanocomposite membranes would be influenced by amino compounds due to the surface passivation effect. When the secondary amine compounds were used as the surface passivation materials, the photoluminescent intensity of the hybrid nanocomposite membrane would be enhanced. On the contrary, the hybrid nanocomposite membranes would descend their photoluminescent intensity as the primary amine compounds were used as surface passivation materials.

Keywords: chelating polymer; luminescence; nanocomposite; nanoparticle; passivation

Introduction

Nanocrystals of semiconductor composites are popularly interesting to the researchers because their photoluminescence properties can dramatically change due to quantum confinement effect.[1–4] For example, as the size of ZnS nanocrystalline is smaller than 50Å in diameter (i.e. the Bohr diameter), the band gap of ZnS will shift to the higher energies. In other words, the band gap energy of semiconductor has the crystalline size dependence and it increases with the decreasing of particle size.[5] Thus, the photoluminescence properties of semiconductor improved by the size reducing effect has been successively reported[6–11] recently. In fact, most of the researchers employed the soft chemical, such as the organic compounds, to stabilize and control the size of semiconductor nanoparticle. For example, Borse et al.[10] used mercapto-ethanol as a capping agent to obtain Pb-doped ZnS nanoparticle, Manziek et al.[11] employed the crosslinked acrylic microsphere as nanoreactors for the synthesis of inorganic material, including ZrO_2, CeO_2, $LiMn_2O_4$, and $Ba_2YCu_3O_7$. Farmer et al.[1] prepared the core/shell CdS/SiO_2 nanopar-

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ticles using an atom transfer radical polymerization (ATRP) system. Zhao et al.[2] prepared the nanocrystalline CdS using salt-induced block copolymer micelles. Wang et al.[3,4] employed block copolymer to control the size of CdS nanocrystals. Carrot et al.[4] used polymer chains with a thiol end group as a covalently attached colloidal stabilizer. Obviously, the soft chemical is a key factor to prepare and control the size of the semiconductor nanoparticles.

On the other hand, the incorporation of a luminescent center in the semiconductor (a dopant) is also a useful and traditional method to enhance the photoluminescence property. However, the thermal diffusion of dopant from a salt into semiconductor is impractical method for the nanometer-sized manufacture process due to the agglomeration of nanoparticle in high temperature environment. Fortunately, the chemical precipitation method can overwhelm this agglomeration problem for nanoparticle preparation.

In this study, the chelating copolymer, poly(methyl acrylates-co-2-methyl-acrylic acid 3-(bis-carboxymethylamino)-2-hydroxy-propyl ester), latex was successfully synthesized by using soap-free emulsion polymerization and used as a core template to obtain the hybrid high photoluminescent Zn(II)-doped CdS nanocluster/copolymer nanocomposites via in-situ chemical precipitation method. In addition, we found that the soft chemicals (organic compounds) not only can act as the stabile agent for CdS nanocluster, but also can passivate the surface of CdS nanocluster and further influence their photoluminescence property.[12] Consequently, some chelating compounds were further employed to study the relation of the photoluminescence property to the surface passivation of the hybrid nanocomposite membrane in this study.

Experimental Parts

Preparation of Nanocomposite

Methyl acrylate (MA), methyl methacrylate (MMA) and glycidyl methacrylate (GMA) (Aldrich Co.) were purified by distillation method. Reagent-grade iminodiacetic acid (IDA) (Aldrich Co.) was used as received. Chelating monomer (2-Methyl acrylic acid 3-(bis-carboxymethyl amino)-2-hydroxyl-propyl ester) (GMA-IDA) were prepared by following our previous study.[13] The soap-free emulsion polymerization was conducted in an 1 L, five-necked Pyrex kettle equipped with a stirrer, condenser, nitrogen inlet and thermister. Poly(MA-co-MMA-co-GMA-IDA) microspheres in latex form were used as the micro-template to in-situ form the Zn(II)-doped CdS nanocluster on the surface of polymer microsphere by chemical deposition method. The hybrid Zn(II)-doped CdS nanocluster/poly(MA-co-MMA-co-GMA-IDA) particle was prepared as below: Firstly, 0.07 g $Cd(OH)_2$ and 0.001g $ZnCl_2$ were added into 50 g poly(MA-co-MMA-co-GMA-IDA) latex and magnetically stirred for 4 hrs at 30 °C controlled by thermostatic water bath. During the stirring process, the adsorption of Cd(II) and Zn(II) on the chelating group gave a $–N(CH_2OO^-)_2Me^{2+}$ complexes on the surface of the copolymer microsphere. Next, H_2S gas with N_2 as a carrier was bubbled through the reaction flask to in-situ form the Zn(II)-doped CdS nanocluster on the surface of the copolymer microsphere. While, H_2S was generated by reaction of 30 mL of 0.05 M Na_2S with 10 mL of 0.1M HCl under N_2 atmosphere.

Surface Passivation

When $ZnCl_2$ was added to the hybrid CdS nanocluster/copolymer latex, the Zn(II) would displace precisely one monolayer of Cd(II) from the surface according to the method reported by Mews and co-workers.[14] In addition, the different kinds of chelating compounds, including iminodiacetic acid (IDA), ethylene diamine (EDA), tetraethylene tetraamine (TETA), tetraethylene pentaamine (TEPA), succinimide, imidazole and ammonia (NH_4OH), were also used as surface passivation solution for the Zn(II)-doped CdS nanocluster/poly(MA-co-MMA-co-GMA-IDA) membrane in this study, respectively.

Characteristic of the Hybrid Nanocomposite

Fourier transfer infrared spectrophotometry (FTIR, Nicolet NEXUS) was used to identify the chelated copolymer. The size of the Zn(II)-doped CdS nanocluster were characterized by obtaining TEM (Hitachi Model HF-2000 Field Emission transmission electron microscopy) and photoluminescence (PL) spectra (Hitachi F4500 spectrofluorimeter), respectively.

Results and Discussion

Characterization of Polymer Microsphere

Polymer material is a suitable material to act as a microtemplate for nanoparticle formation due to its well tunable physical properties. The soap-free emulsion polymerization was used to prepare uniform polymer microsphere which was further used as a microtemplate for obtaining the Zn(II)-doped CdS nanocluster on the surface of microsphere in this study. The chelating monomers, GMA-IDA, which contain an anionic chelating group, iminodiacetic acid, not only can replace the emulsifier to stabilize the polymer lattice, but also can strongly adsorb Cd(II) and further form CdS nanocluster in-situ on the surface of polymer microsphere. In addition, methyl acrylate polymer has a low transition temperature ($T_g \sim -5\,^\circ C$) and MMA has a high transition temperature ($T_g \sim 105\,^\circ C$). Therefore, one can tune the Tg of the polymer via the different recipe of MA and MMA to obtain polymer membrane.

Figure 1 shows the FTIR spectra of the chelating copolymer microsphere and membrane. One can observe the IR spectra of the chelating copolymer microsphere (Figure 1(a)) and membrane (Figure 1(b)) display the absorption band at 1725 cm^{-1} which is attributed to the stretching vibrations of the ester carbonyl groups. A strong band is observed at 1633 cm^{-1} and 1399 cm^{-1}, which is assigned to the asymmetric and symmetric stretching of C=O in carboxylate ($-COO^-$). Notably, the absorption intensity of 1633 cm^{-1} of copolymer membrane is smaller than that of polymer microsphere because Figure 1(b) is an IR-ATR spectrum. However, both templates have the chelating group, GMA-IDA, which is an important group to in-situ prepare the Zn(II)-doped CdS nanocluster on the surface of polymer particle.

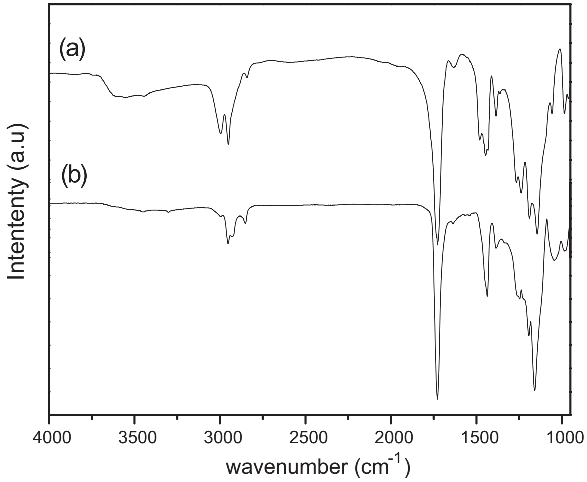

Figure 1.

FTIR spectrum of (a) the poly(MA-co-MMA-co-GMA-IDA) microsphere and ATR-FTIR spectrum of (b) the poly(MA-co-MMA-co- GMA-IDA) membrane.

Characterization of the Hybrid Zn(II)-doped CdS Nanocluster/Copolymer Nanocomposite

The better method of Zn(II) doped into CdS nanocluster is the chemical precipitation method. Therefore, the fix amount of Zn(II) and Cd(II) aqueous solution is mixed first and added into the polymer microsphere solution. Because the strong-field chelating group, iminodiacetic acid, is located on the surface of polymer microsphere, the Zn(II) and Cd(II) could be almost adsorbed on the surface of polymer microsphere. Thus, the Zn(II)-doped CdS nanoclusters could be in-situ formed on the surface of polymer microsphere when the S^{2-} anion is added by H_2S gas, as shown in Figure 2. Figure 2(a) is the TEM photographs of the hybrid Zn(II)-doped CdS nanocluster/copolymer particles and Figure 2(b) is the high magnification photograph of Figure 2(a). The morphology of the Zn(II)-doped CdS nanocluster on the surface of the hybrid nanocomposites approach to spherical and the size of Zn(II)-doped CdS nanocluster is on the nanometer scale (3∼10 nm in diameter) from the Figure 2(b). In addition, the EDX spectrum can prove the Zn(II) is successfully introduced into CdS nanocluster, as shown in Figure 2(c). Unfortunately, the mean diameter of the Zn(II)-doped CdS nanoclusters of all the samples cannot be clearly determined from the TEM photographs or XRD diffraction pattern, because the magnification is limited and the amount

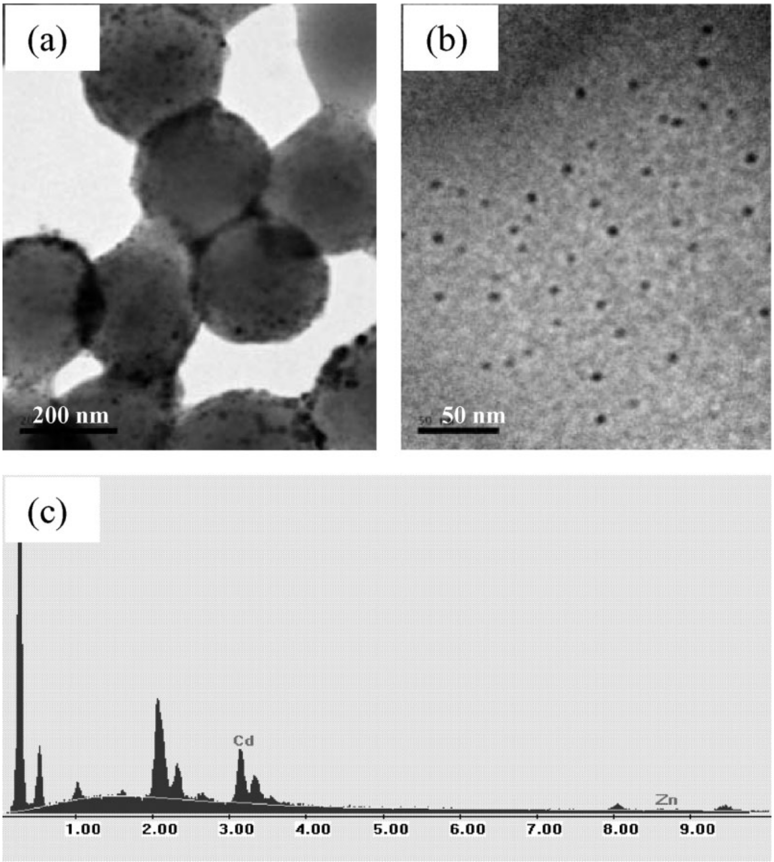

Figure 2.

TEM photographs of (a) the Zn(II)-doped CdS nancluster coated on the surface of the poly(MA-co-MMA-co-GMA-IDA) particle, (b) High magnification photograph of sample (a), and (c) the EDX spectrum of sample (a).

of nanocluster is too low. Thus, it is difficult to measure whether the size of the Zn(II)-doped CdS nanocluster is a single crystalline or an agglomeration nanocluster. In fact, no any photoluminescence can be detected if the size of CdS nanocluster is larger than 5 nm according to our previous study.[6] Hence, if the Zn(II)-doped CdS nanocluster can display the high photoluminescence property, it reveals that the size of the Zn(II)-doped CdS nanocluster should be no more than 5 nm. Consequently, we can estimate that major part of the Zn(II)-doped CdS nanocluster diameter in copolymer particle should be lower than 5 nm. The photoluminescence of Zn(II)-doped CdS nanocomposites were further studied as shown below.

Photoluminescence Property of the Zn(II)-doped CdS Nanocomposite

Figure 3 shows the photoluminescence (PL) spectrum obtained at an excitation wavelength of 366 nm for the CdS nanocluster/copolymer latex (Figure 3(a)) and the Zn(II)-doped CdS nanocluster/copolymer (Figure 3(b)) latex, respectively. The photoluminescence spectra in Figure 3 exhibit a red-shift from 515 nm to 522 nm with an accompanying broad band when Zn(II) was doped into CdS nanocluster. In addition, the photoluminescent intensity of the Zn(II)-doped CdS nanocluster/copolymer latex is obviously higher than that of the CdS nanocluster/copolymer latex. This result is attributed from the new active site of Zn(II) formation in CdS nanocrystal. Restated, the Zn(II)-doped CdS nanocluster can improve the active site and thus enhance their photoluminescence property.

On the other hand, the hybrid Zn(II)-doped CdS nanocluster/copolymer membrane also presents the similar result, as shown in Figure 4(a)(b). Preparation the Zn(II)-doped CdS nanocluster by using in-situ chemical precipitation can obtain the better photoluminescence property than that of the CdS nanocluster/copolymer membrane, the Zn(II)-doped CdS nanocluster/copolymer membrane passivated by Zn(II) and the Zn(II)-doped CdS nanocluster/copolymer membrane passivated by Zn(II), as shown in Figure 4(c)(d). While, the CdS nanocluster passivated by Zn(II) is a popular method[14] to prepare the high photoluminescent of CdS nanoparticle recently. However, this Zn(II) surface passivation method seems not suitable on this system.

Figure 5 shows, respectively, the pristine copolymer membrane (Figure 5(a)), the hybrid CdS nanocluster/copolymer membrane (Figure 5(b)), the hybrid Zn(II)-doped CdS nanocluster/copolymer membrane

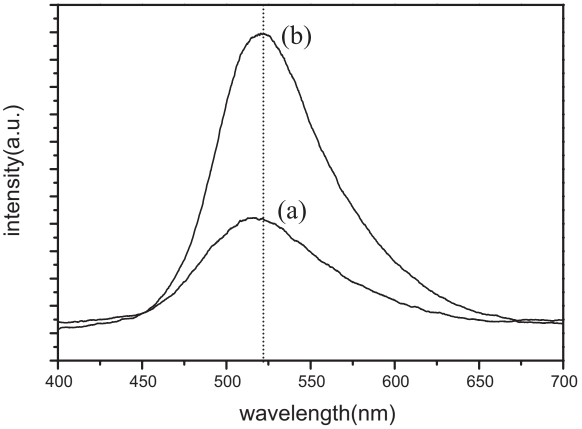

Figure 3.
The photoluminescence (PL) spectra of (a) the CdS nanocluster/copolymer latex and (b) the Zn(II)-doped CdS nanocluster/copolymer latex.

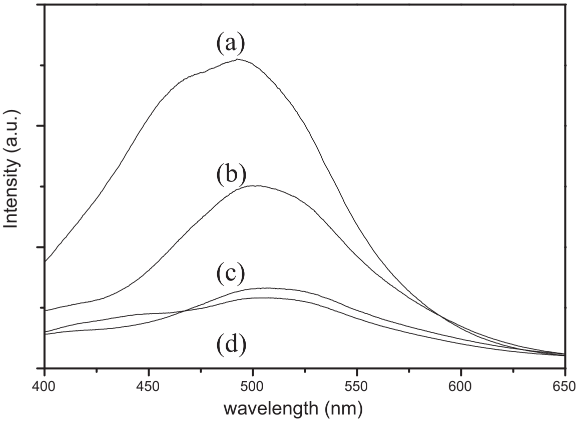

Figure 4.
The photoluminescence (PL) spectra of (a) the Zn(II)-doped CdS nanocluster/copolymer membrane, (b) the CdS nanocluster/copolymer membrane, (c) the Zn(II)-doped CdS nanocluster/copolymer membrane passivated by Zn(II), and (d) the CdS nanocluster/copolymer membrane passivated by Zn(II).

(Figure 5(c)), the hybrid Zn(II)-doped CdS nanocluster/copolymer membrane passivated by Zn(II) (Figure 5(d)), and the hybrid CdS nanocluster/copolymer membrane passivated by Zn(II) (Figure 5(e)) before and after 366 nm UV excitation. Notably, the hybrid Zn(II)-doped CdS nanocluster/copolymer membrane not only shows the highly transparent property but also retains the highest photoluminescence among all the samples. This result is consistent with the above result of photoluminescence spectra, the Zn(II)-doped on CdS nanocluster prepared by using chemical precipitation

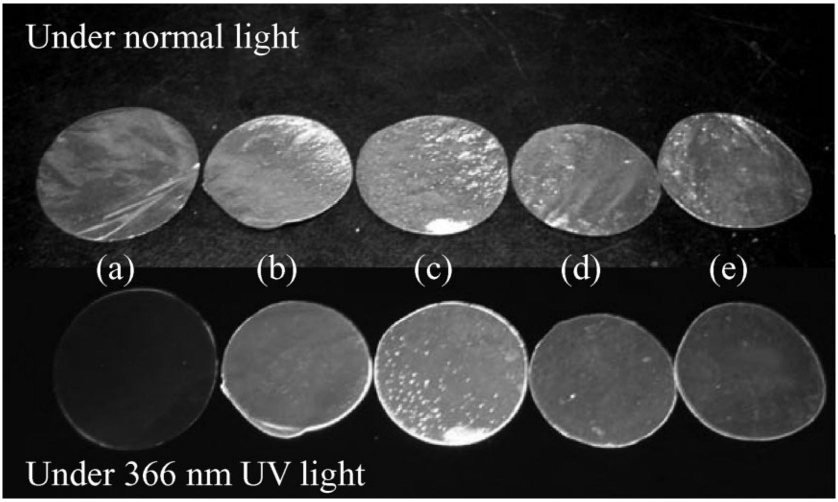

Figure 5.
The photographs of (a) the pristine copolymer membrane, (b) the hybrid CdS nanocluster/copolymer membrane, (c) the hybrid Zn(II)-doped CdS nanocluster/copolymer membrane, (d) the hybrid Zn(II)-doped CdS nanocluster/copolymer membrane passivated by Zn(II), and (e) the hybrid CdS nanocluster/copolymer membrane passivated by Zn(II) before (upper photos) and after (bottom photos) 366 nm UV excitation.

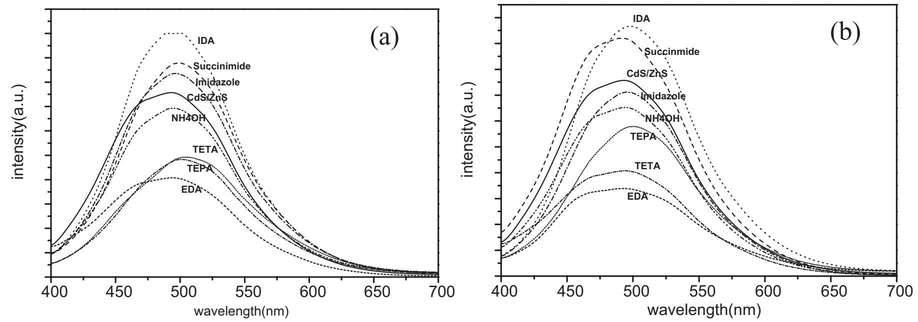

Figure 6.
The photoluminescence (PL) spectra of the Zn(II)-doped CdS nanocluster/copolymer membrane passivated by different kinds of amino solution at (a) 10 mins and (b) 30 mins, respectively.

method can obtain better photoluminescent intensity than that of the sample prepared by using passivation method.

Furthermore, different kinds of amino compounds, including iminodiacetic acid (IDA), ethylene diamine (EDA), tetraethylene tetraamine (TETA), tetraethylene pentaamine (TEPA), succinimide, imidazole and ammonia (NH_4OH), were used as the surface passivation solution for the Zn(II)-doped CdS nanocluster/copolymer membrane, respectively. Figure 6(a) and (b) display that the photoluminescent intensity of the Zn(II)-doped CdS nanocluster/copolymer membrane which were immersed on the amino compounds solution on 10 mins and 30 mins, respectively. One can observe that the photoluminescent intensity of the Zn(II)-doped CdS nanocluster/copolymer membrane was magnificently influenced by the passivation materials. Interestingly, the primary amino compounds, such as EDA, TETA and TEPA, have negative effect and the secondary amino compounds, such as IDA, succinimide and imidazole, have positive effect on the photoluminescent intensity of the Zn(II)-doped CdS nanocluster/copolymer membrane. This result may be attributed to the high metal chelating stability of the primary amino compounds. The high strong-field ligand can compete to the sulfur for the coordinated of cadmium ion and influence on band gap of the Zn(II)-doped CdS nanoparticle. The other possible negative effect may be attributed that the Zn(II) is extracted from the Zn(II)-doped CdS nanocluster by primary amino compound. Thus, the photoluminescent intensity of the Zn(II)-doped CdS nanoparticle will be thus decreased by primary amino compounds.

Conclusion

The high photoluminescence of the hybrid Zn(II)-doped CdS nanocluster/copolymer, including latex and membranes, were successfully prepared by using chemical precipitation method in this study. The size of the Zn(II)-doped CdS nanocluster is lower than 5 nm from the PL and TEM measurement. The Zn(II)-doped CdS nanocluster/copolymer can obtain higher photoluminescent intensity than that of the samples prepared by using the surface passivation method. In addition, when the secondary amine compounds were used as the surface passivation materials, the luminescent intensity of the hybrid Zn(II)-doped CdS nanocluster/copolymer nanocomposite membrane would be enhanced. On the contrary, the hybrid nanocomposite membranes would descend their photoluminescent intensity as the primary amine compounds were used as surface passivation materials. The Zn(II)-doped CdS nanocluster/copolymer membrane is a transparent membrane which has a potential industry application.

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