

Preparation of Zinc Oxide Nanocrystals with High Stability in the Aqueous Phase

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ABSTRACT: ZnO nanocrystals (NCs), potential candidates for photoluminescent applications, have attracted increasing attention recently because of their good biocompatibility, low cost, and convenient synthesis. However, their stability and fluorescent quenching, particularly in the aqueous phase, still hampers their use in biological applications. We report herein the synthesis of ZnO NCs modified by amphiphilic methoxy poly(ethylene glycol)-grafted poly(styrene-*alt*-maleic anhydride) (SMA-*g*-MPEG) copolymer based on the sol-gel method. We demonstrated a simple solution to address those challenges. Compared with unmodified ZnO NCs, SMA-*g*-MPEG modified ZnO NCs exhibited a significantly improvement in the stability and photoluminescent properties in the aqueous phase over current unmodified ones. This simple synthesis provides a novel platform for the preparation of ZnO NCs for biological applications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: copolymers; nanoparticles; nanowires and nanocrystals; optical properties

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INTRODUCTION

In the past, considerable efforts have been concentrated on the use of II–VI semiconductor nanocrystals (NCs) as photoluminescent materials.^{1–4} ZnO NCs, potential candidates for photoluminescent applications, have attracted increasing attention recently because they are nontoxic, inexpensive, and conveniently fabricated and have great potential for biological applications.^{5–7} However, the applications of ZnO NCs are still hampered by their low stability and fluorescent quenching in the aqueous phase.^{8–10} The modification of the NC surface, particularly with organic ligands, is considered an effective method to stabilize NCs.^{11–13} To date, ZnO nanocrystals with high stability and photoluminescent properties have been successfully prepared with various small molecules or polymers as ligands, such as diethanolamine/oleic acid,¹⁴ triethylene glycol/oleic acid,¹⁵ [3-(2,3-epoxypropoxy)propyl]trimethoxysilane,¹⁶ poly(ethylene glycol) methyl ether, and poly(methacrylic acid)/poly(methyl methacrylate).^{17,18} Nonetheless, the use of amphiphilic grafted copolymer as ligands for the preparation of ZnO NCs has not been reported. Compared with small molecules and polymers ligands, amphiphilic copolymer ligands may endow ZnO NCs with not only excellent dispersion and photoluminescent properties in various organic solvents and water solution but also

with a desired self-assembly ability that broadens the application fields of ZnO NCs.

Herein, we describe a novel synthesis method of ZnO NCs based on the sol-gel process. An amphiphilic grafted methoxy poly(ethylene glycol)-grafted poly(styrene-*alt*-maleic anhydride) (SMA-*g*-MPEG) copolymer was synthesized and used as a ligand to stabilize the ZnO NCs. The SMA-*g*-MPEG modified ZnO NCs could be stably dispersed in the aqueous phase with highly photoluminescent quantum yield (QY).

EXPERIMENTAL

Synthesis of SMA-*g*-MPEG

An amount of 11.8 g of methoxy poly(ethylene glycol) (MPEG; number-average molecular weight = 1100, Aldrich, Beijing city, China) was dissolved in 50 mL of tetrahydrofuran (THF; dried by Na and distilled before use), and then, 0.5 g of Na was added to the MPEG solution; this was followed by 12 h of refluxing to obtain a THF solution of MPEG–Na. With strong stirring during the whole process, the THF solution of MPEG–Na was slowly added to 270 mL of the containing 5 g of SMA (number-average molecular weight = 2000, Sigma, Beijing city, China; the molar ratio of maleic anhydride in SMA to MPEG was 2 : 1), and then, the reaction was allowed to proceed at 30°C for 48 h. The

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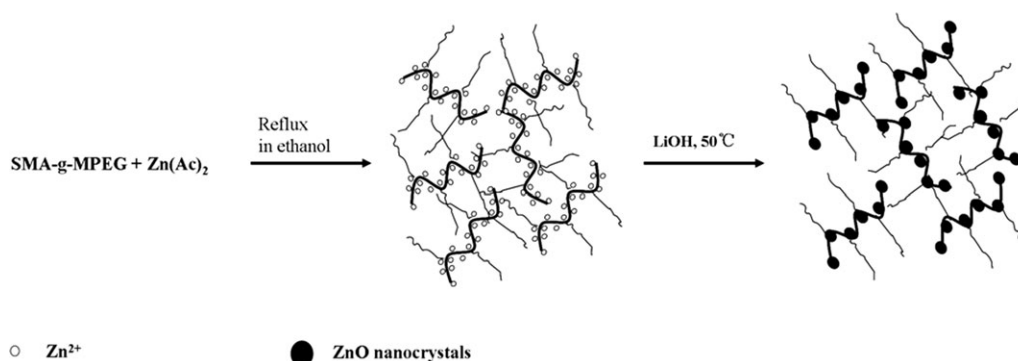


Figure 1. Schematic showing the synthesis of the SMA-g-MPEG modified ZnO NCs.

products were precipitated with anhydrous ether and then dissolved in THF. The process was repeated three times to purify the products. The reaction mechanism and ¹H-NMR results are shown in the Supporting Information (Figures S1 and S2).

Preparation of SMA-g-MPEG Modified ZnO NCs

SMA-g-PEG (0.1, 0.2, and 0.3 g) and 0.33 g (0.0015 mol) of Zn(Ac)₂·2H₂O were added to 15 mL of ethanol, and then, the mixture solution was refluxed for 2 h to obtain a homogeneous and clear ethanol solution of SMA-g-MPEG/Zn²⁺. A volume of 0.088 g (0.0021 mol) of LiOH·H₂O in 15 mL of ethanol solution (LiOH·H₂O was completely dissolved by a sonication process) was added drop by drop to the SMA-g-MPEG/Zn²⁺ ethanol solution at 50°C within 1 h. Then, the mixture was stirred at 50°C for another 2 h, and SMA-g-MPEG modified ZnO NCs were obtained and were well dispersed in the ethanol solvent, which was successively evaporated by a rotary evaporator. The obtained ZnO NCs were redispersed in deionized (DI) water and dialyzed in a dialysis bag (cutoff = 50 kDa) for 2 days.

Characterization

Transmission electron microscopy (TEM) images were obtained by a Hitachi H 8100 electron microscope, Beijing city, China. Fourier transform infrared (FTIR) spectra were obtained with a Bruker FTIR spectrometer, Beijing city, China. Structural

characterization was conducted by X-ray diffraction (XRD; Rigaku wide-angle X-ray diffractometer, D/max γA, with Kα radiation at a wavelength of 1.541 Å). ¹H-NMR spectra were recorded on a Bruker Ultrashield 500 MHz. Thermogravimetric analysis (TGA) were performed on a PerkinElmer thermal analysis, Beijing city, China. Photoluminescent emission spectra were determined on a PerkinElmer LS 55 spectrophotometer. To evaluate of the photoluminescent QY of the ZnO NCs, quinine sulfate in 0.5M sulfuric acid was used as a reference.

RESULTS AND DISCUSSION

The synthesis of amphiphilic grafted copolymer (SMA-g-MPEG) modified ZnO NCs is illustrated in Figure 1. First, the Zn²⁺ ions were attached to the polymer chains by electrostatic interaction between Zn²⁺ and carboxylic groups of SMA-g-MPEG. Subsequently, the introduction of LiOH changed the pH value and induced the formation of ZnO NCs, which were linked to the SMA-g-MPEG ligands through carboxylic groups.¹⁹ Because of the modification of SMA-g-MPEG, the ZnO NCs were able to disperse well in the aqueous phase.

To prove the importance of SMA-g-MPEG ligands to the stability of the ZnO NCs, ZnO NCs were prepared with 0, 0.1, 0.2, and 0.3 g of SMA-g-MPEG, which were named ZnO-A, ZnO-B,

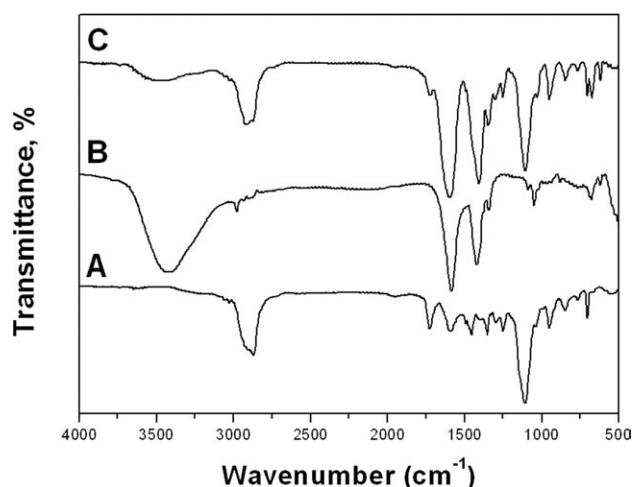


Figure 2. FTIR spectra (KBr pellets) of the (A) SMA-g-MPEG copolymer (curve A), (B) ZnO-A, and (C) ZnO-C NCs.

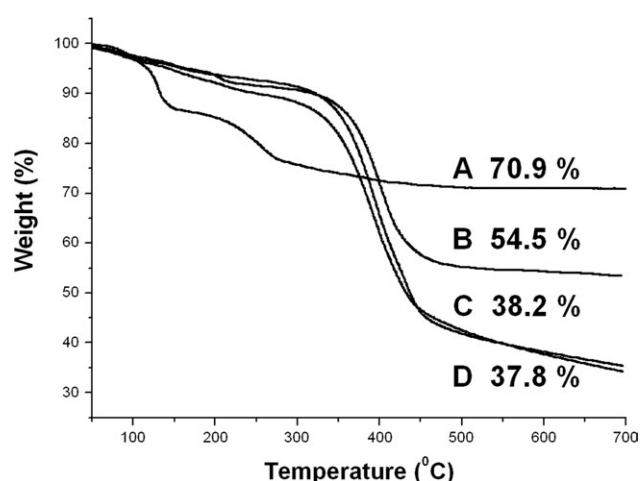


Figure 3. TGA curves of (A) ZnO-A, (B) ZnO-B, (C) ZnO-C, and (D) ZnO-D NCs.

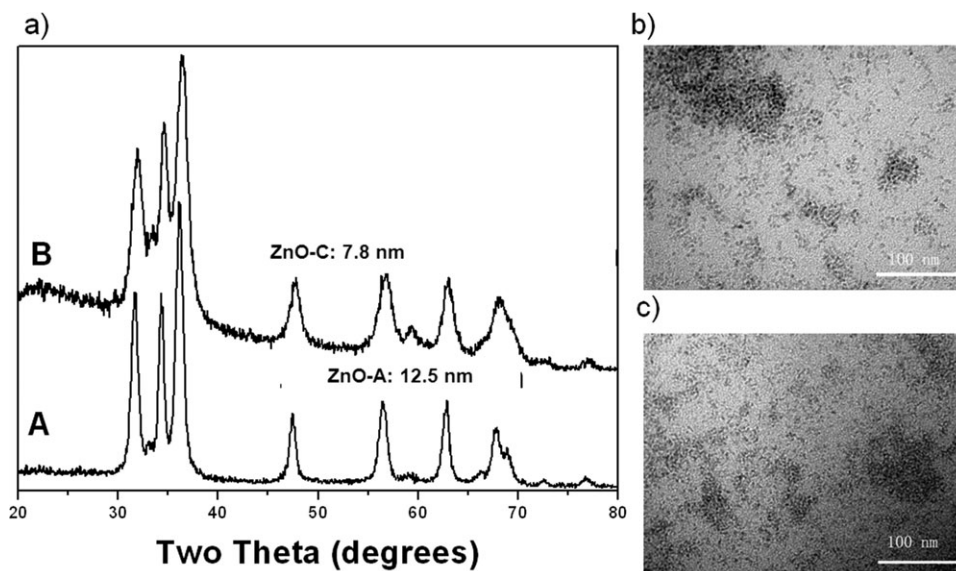


Figure 4. (a) XRD pattern of the (A) ZnO-A and (B) ZnO-C NCs, (b) TEM image of the ZnO-A NCs, and (c) TEM image of the ZnO-C NCs.

ZnO-C, and ZnO-D, respectively. The modification of SMA-g-MPEG on the ZnO NCs was confirmed by FTIR spectroscopy, TGA, XRD, and TEM characterizations. Compared with unmodified ZnO-A NCs, the FTIR spectrum (Figure 2) of the SMA-g-MPEG modified ZnO-C NCs exhibited the characteristic absorption peaks of SMA-g-MPEG at 2940 cm^{-1} (C—H stretching of methyl and methylene groups), 1730 cm^{-1} (the carbonyl group), and 1106 cm^{-1} (the ether group); this confirmed the modification of SMA-g-MPEG on the ZnO NCs.²⁰ TGA results (Figure 3) further demonstrated that the modified amount of SMA-g-MPEG on the ZnO NCs. Gravimetric losses of 29.1, 45.5, 61.8, and 62.2% were observed for the ZnO-A, ZnO-B, ZnO-C, and ZnO-D, respectively; this indicated that the amount of SMA-g-MPEG binding on the ZnO NCs increased with increasing content of SMA-g-MPEG. Furthermore, the XRD results [Figure 4(a)] show that both the unmodified ZnO-A NCs and SMA-g-MPEG modified ZnO-C NCs presented wurtzite structures, and the average diameters were 12.5 and 7.8 nm, respectively, as estimated with Scherrer's equation [$D = 0.89\lambda/(\beta \cos \theta)$], where λ is the X-ray wavelength (1.5418 \AA), β is the halfwidth of the diffraction peak, and θ is the Prague diffraction angle;²¹ this suggested that the modification of the SMA-g-MPEG on the ZnO NCs significantly controlled particle growth, and ZnO NCs with smaller size could be obtained with this method. TEM images of the unmodified ZnO-A and SMA-g-MPEG modified ZnO-C NCs exhibited that the particle sizes were around 10 and 5 nm [Figure 4(b,c)], respectively; this further demonstrated that the particle size of the NCs showed a decreasing trend with the modification of the SMA-g-MPEG ligands.

The photoluminescent properties of the ZnO NCs with and without SMA-g-MPEG modification are compared in Figure 5. In contrast, with increasing content of SMA-g-MPEG, the maximum emission peak exhibited a continual blueshift from 571 nm (for ZnO-A) to 536 nm (for ZnO-D). Moreover, photoluminescent QYs of 5, 15, 18, and 19% were obtained for ZnO-A, ZnO-B, ZnO-C, and ZnO-D, respectively. Because of the

modification of the SMA-g-MPEG ligands, the growth and aggregation of ZnO NCs were limited during the reaction process; this resulted in SMA-g-MPEG modified ZnO NCs with lower emission wavelengths and higher photoluminescent QYs compared with the unmodified ZnO NCs.

Moreover, the modification of SMA-g-MPEG amphiphilic ligands endowed the ZnO NCs with excellent dispersion in various solvents, such as toluene, dichloromethane, and methanol, particularly in DI water [Figure 6(a)]. Furthermore, ZnO-C formed a thin layer along the interface of water and toluene; this clearly suggested their obvious amphiphilic properties due to the modification of amphiphilic ligands [Figure 6(b)]. The photoluminescent stability of ZnO-A and ZnO-C NCs in DI water was compared under both the freshly prepared condition [Figure 6(c)] and after 1 week of incubation [Figure 6(d)]. With UV irradiation ($\lambda = 365\text{ nm}$), ZnO-A NCs without SMA-g-MPEG ligands were unstable in the aqueous phase and were precipitated

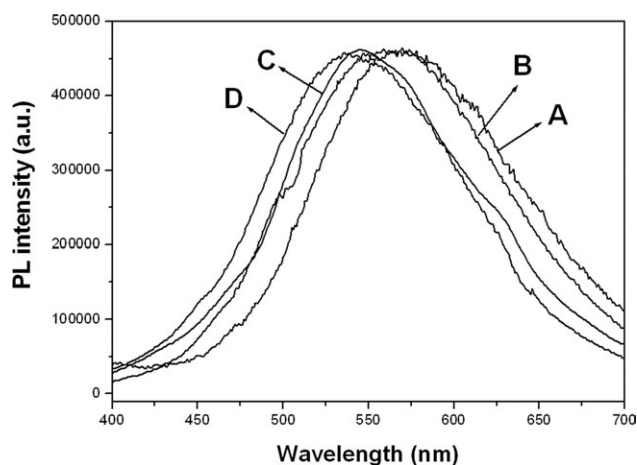


Figure 5. Normalized photoluminescence emission spectra of the (A) ZnO-A, (B) ZnO-B, (C) ZnO-C, and (D) ZnO-D NCs in the ethanol.

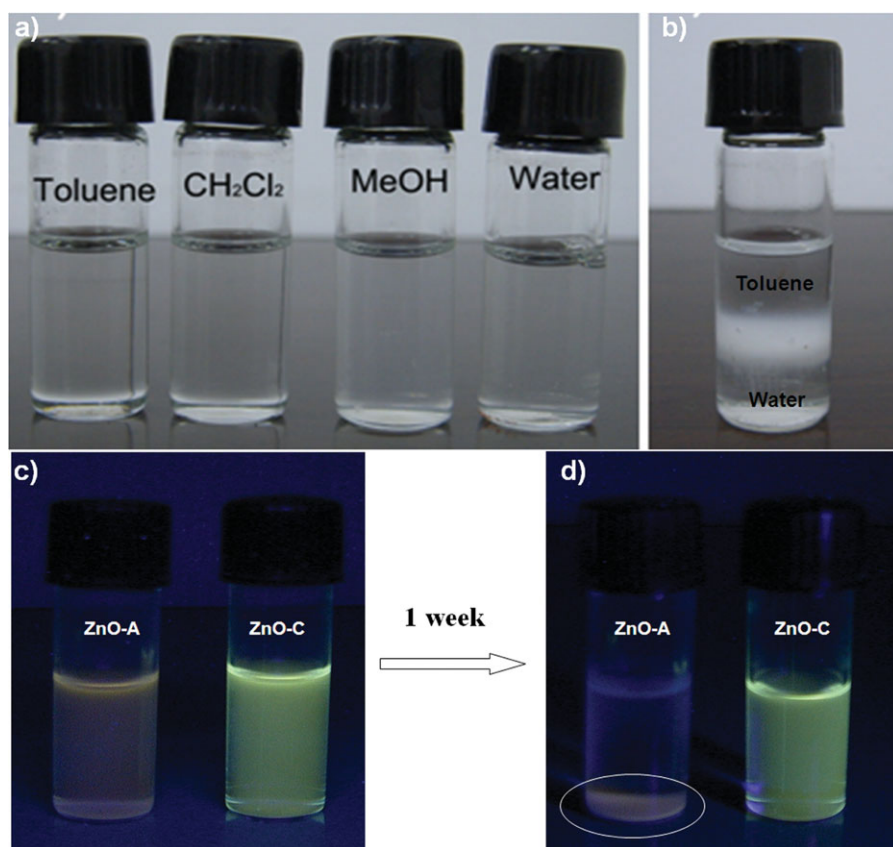


Figure 6. Effect of the SMA-g-MPEG modification on the dispersion and stability of the ZnO NCs: (a) ZnO-C NCs dispersed in toluene, dichloromethane, methanol, and water; (b) the formation of thin films of the ZnO-C NCs at water/toluene interface; (c) ZnO-A; and (d) ZnO-C NCs dispersed in water with UV irradiation. An amount of 0.5 mL of a ZnO NC ethanol solution was dispersed in 5 mL of different solvents for all tests. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at the bottom of the vial with a few photoluminescence after incubation for 1 week. In contrast, ZnO-C, the ZnO with SMA-g-MPEG modification, was still well dispersed in an aqueous phase after it stood for 1 week and kept the photoluminescent properties with a QY of 16% (see Supporting Information, Figure S3). These polymer ligands effectively improved the dispersion properties of ZnO NCs in the aqueous phase; this led to a significantly higher QY than that of the unmodified ZnO NCs.

CONCLUSIONS

In summary, the SMA-g-MPEG modified ZnO NCs that were prepared by the sol-gel method with amphiphilic grafted copolymer as ligands could be dispersed in the aqueous phase with outstanding stability and highly photoluminescent QY. The photoluminescent properties of the SMA-g-MPEG modified ZnO NCs in the aqueous phase will surely make them become a promising material in biological fields. Further investigation of the self-assembly behaviors on the SMA-g-MPEG modified ZnO NCs is under way.

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