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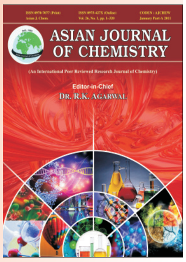

Blue Luminescent ZnO Nanoclusters Stabilized by Esterifiable Polyamidoamine Dendrimers and their UV-Shielding Applications

FAN ZHANG*, BO WANG and YONGQIANG SHEN

College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, P.R. China

*Corresponding author: Tel/Fax: +86 743 8563911; E-mail: chemfzhang@163.com; zhangfan8346@sina.com

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Zinc oxide quantum dots (QDs) were added to the water solutions of esterifiable polyamidoamine (PAMAMs) and the ZnO nanoclusters were prepared. The ZnO nanoclusters are stable in water and show bright blue fluorescence under UV lamp. TEM images showed that the ZnO nanoclusters consisted of numerous ZnO QDs. FTIR spectra of ZnO nanoclusters demonstrated the successful modification of ZnO QDs by the esterifiable polyamidoamine dendrimers. The UV-visible absorption spectra indicated that the ZnO nanoclusters exhibited wider and red-shifted comparing with ZnO QDs. The fluorescent spectra showed that the emission peaks at 404 nm of the ZnO QDs became weaker and a new emission peaks appeared at 330 nm after modifying the ZnO QDs with polyamidoamine dendrimers. The UV-visible transmittance spectra showed that the poly(vinyl alcohol)/ZnO nanoclusters film absorbed nearly 99 % of UV light at wavelengths between 200 and 240 nm while 75 % between 240 and 300 nm.

Keywords: ZnO quantum dots, Nanoclusters, Polyamidoamine dendrimers, UV-shielding, Poly(vinyl alcohol).

INTRODUCTION

As one of a group of II-VI semiconductors, zinc oxide has attracted much attention for its potential applications in blue/UV optoelectronics, transparent electronics, pintronic devices and sensor applications. Zinc oxide has been commonly used in its polycrystalline form for over a hundred years in a wide range of applications *e.g.*, facial powders, ointments, sunscreens, catalysts, lubricant additives, paint pigmentation, piezoelectric transducers, varistors and transparent conducting electrodes[1]. However, the nanoscale crystals tend to aggregate or to undergo Ostwald ripening because of their high surface energy. Therefore, appropriate surface modification is needed to stabilize the ZnO nanocrystals[2-10]. Hagura *et al.*[11] had reported that highly luminescent silica-coated ZnO nanoparticles dispersed in an aqueous medium were synthesized using the sol-gel process. Liu and co-workers[12] described a new approach for preparation of ZnO nanocrystals stabilized by ionic liquid components. The ionic liquid-ZnO nanocrystal composite was formed directly from an ionic liquid salt containing Zn(II) cations. Xia and co-workers[13] recently obtained polymer-stabilized ZnO nanoparticles with remarkable blue fluorescence, however, the origin of the emission was not very clear. An organic dispersion of 9-15 nm size dysprosium oxide incorporated zinc oxide nanocomposites exhibiting luminescence in the visible region had been synthesized by a wet chemical precipitation technique at room temperature[14], and the work showed that stability and functionalization of the same nano-composites in organic medium was achieved by using 1:1 volume ratios of (tetraethoxysilane [$(C_2H_5O)_4Si$], (3-aminopropyl) trimethoxysilane) as the capping agent.

Polyamidoamine dendrimers (PAMAMs) with large amounts of terminal functional groups have been paid more and more attention due to their unique features such as excellent biocompatibility, good solubility and high reactivity[15-21]. In this paper, esterifiable PAMAMs was chosen as modifiers, because esterifiable PAMAMs contained lots of tertiary amine, which could act as organic ligands and stabilize the ZnO quantum dots (QDs). Our goal is to obtain a kind of water soluble ZnO clusters which could be applied at the domain such as UV-shielding, medicine, biomedical material. The reports about water soluble ZnO clusters were little found. Here, we describe the fabrication of ZnO-PVA nanocomposite thin films by casting homogeneous solution of ZnO nanoclusters and poly(vinyl alcohol) (PVA). The ZnO clusters were characterized by FTIR spectra, TEM, UV/visible absorbance spectra and photoluminescence (PL) emission and excitation spectra. The luminescent features of ZnO clusters/PVA film were also investigated.

EXPERIMENTAL

$Zn(CH_3COO)_2{\cdot}2H_2O$, KOH and CH_3OH were obtained from Tianjin Kemiou Chemical Reagent Co Ltd., in Tianjin, China. All chemicals were analytical reagent and used without further purification.

Preparation of ZnO QDs: The preparation of ZnO QDs was based on literature[12,22]. Typically, 0.98 g $Zn(CH_3COO)_2 \cdot 2H_2O$ and 50 μL of deionized water were added into a flask containing 40 mL of methanol. The solution was heated to 64 °C with vigorous magnetic stirring. 0.496 g KOH was dissolved into 20 mL of methanol as the stock solution that was then added into the flask within 10-20 min. At a constant temperature of 64 °C, it took 3 h to obtain ZnO QDs. When the reaction was finished, the upper fraction of the reaction solution was discarded after 120 min. 50 mL of methanol was added to the solution and stirred for 2 min. Again, the upper fraction of the solution was discarded after 120 min. The methanol washing process was repeated and the upper fraction of the solution was taken away after overnight staying. The isolated ZnO QDs were dissolved in chloroform.

Preparation of esterifiable polyamidoamine dendrimers: Generation 2.5, 3.5, 4.5 (G2.5, G3.5, G4.5) PAMAMs were prepared according to the procedures described in thce literature[23,24], then the water solutions of PAMAMs of different half generation were prepared.

Preparation of the ZnO nanoclusters: A desired amount of ZnO QDs was added to the water solutions of PAMAMs of different half generation respectively and the ZnO QDs were fully dissolved in the solution very slowly about two months later, and then the ZnO nanoclusters were prepared. The molar ratios of ZnO QDs and 2.5G PAMAMs, 3.5G PAMAMs, 4.5G PAMAMs are 4:1, 8:1 and 16:1, respectively. The typical preparation of the ZnO clusters is depicted in Fig. 1.

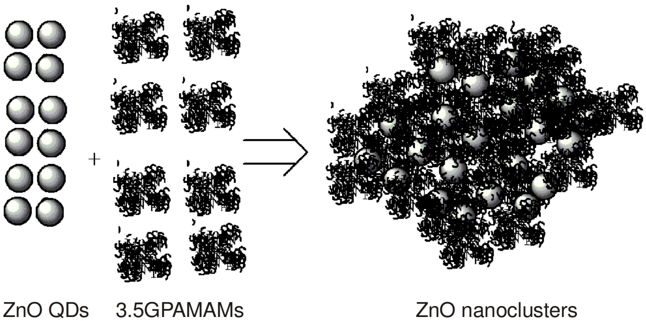

Fig. 1. Schematic illustration of the preparation of the ZnO nanoclusters

Preparation of PVA/ ZnO nanoclusters film: The fabrication process of the PVA/ZnO nanoclusters film was depicted as follows: a desired amount of water solution of ZnO nanoclusters (0.04 g ZnO) was mixed with a water solution of PVA (2 g PVA, 50 mL of deionized water), Then the intermixed solution of ZnO nanoclusters and PVA was casted into a petridish, followed by solvent evaporation at 30 °C under vacuum to obtain PVA/ZnO nanoclusters composite film (200 μm in thickness). The pure PVA film and PVA/ ZnO QDs composite film were obtained under the same condition as PVA/ZnO nanoclusters film, the concentrations of ZnO in PVA/ZnO nanoclusters film and PVA/ZnO QDs composite film were 2 wt. %.

Characterization: FTIR spectra were recorded on a IRAffinisy-1 spectrometer (Shimadzu) by using potassium bromide discs prepared from powdered samples mixed with dry KBr. The microstructures of ZnO QDs and ZnO nanoclusters were observed by transmission electron microscopy (TEM) (HR-TEM, JEOL Model 3010F). Drops of the diluted suspension were placed onto Cu TEM grids. As the CH_3Cl and water solvents were evaporated, ZnO nanoclusters and ZnO QDs were left on the Cu support.

UV/Visible absorbance spectra of ZnO QDs and ZnO nanoclusters were recorded with a Perkin Elmer Lambda-6 UV-visible spectrophotometer. Photoluminescence (PL) emission and excitation spectra of ZnO QDs and ZnO nanoclusters were recorded at room temperature by using Shimadzu-RF-5000 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

Fig. 2 shows the digital photographs of a chloroform solution of ZnO QDs and a typical water solution of ZnO nanoclusters. It was found that the chloroform solution of ZnO QDs displayed in colorless under daylight and in yellow fluorescence under UV lamp (λ = 365 nm). However, the ZnO nanoclusters, which modified by PAMAMs of different half generation emitted bright blue fluorescence under the excitation of UV light (λ = 365 nm). For preparing ZnO nanoclusters, the ZnO QDs were dissolved in the water solutions of PAMAMs of different half generation very slowly. The resulted water solution of ZnO nanoclusters could be stable even under sunlight over a year.

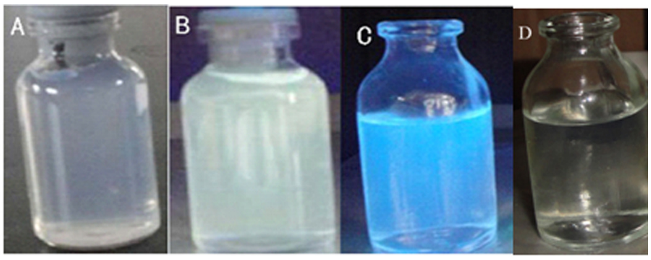

Fig. 2. Digital photographs of ZnO QDs in chloroform under daylight (A) and under UV lamp (λ = 365 nm) (B), and the typical digital photographs of aqueous solution of ZnO nanoclusters modified by 3.5 G PAMAMs under UV lamp (λ = 365 nm) (C) and under daylight (D)

Fig. 3 shows the FTIR spectra of ZnO QDs and ZnO nanoclusters modified by 3.5G PAMAMs. The typical absorption bands of strong ester C=O bond at 1738 cm^{-1}, C-N bond at 1090, 1055 and 1028 cm^{-1}, N-H bond at 2962 cm^{-1}, C-H stretch vibration at 2846 cm^{-1}, Zn-N bond at 990 cm^{-1} and Zn-O bond at 586 cm^{-1} were detected[10,25]. The above characteristic bands indicated that the surface of ZnO QDs was successfully modified by the PAMAMs.

The typical TEM images of ZnO nanoclusters modified by 3.5G PAMAMs and ligand-free ZnO QDs were displayed in Fig. 4. The ZnO nanoclusters were composed of numerous ZnO QDs and the size of the corresponding ZnO QD measured from the TEM image (B) was approximately 10 nm for all samples. Nevertheless, ZnO nanoclusters presented different sizes, and the size of ZnO cluster varied from 10 nm to 60 nm. The HRTEM image of ZnO QDs indicated that the ZnO QDs showed excellent crystallinity, however, ZnO nanoclusters demonstrated a typical amorphous structure.

Fig. 5 presented the UV-visible absorption spectra of ZnO nanoclusters in water and ZnO QDs in $CHCl_3$. The ZnO nanoclusters exhibited wider and red-shifted optical absorption

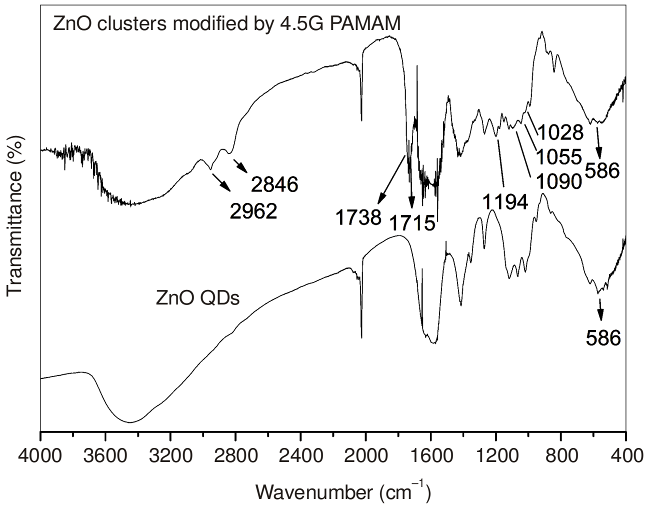

Fig. 3. FTIR spectra of ZnO nanoclusters modified by 3.5G PAMAMs and ZnO QDs

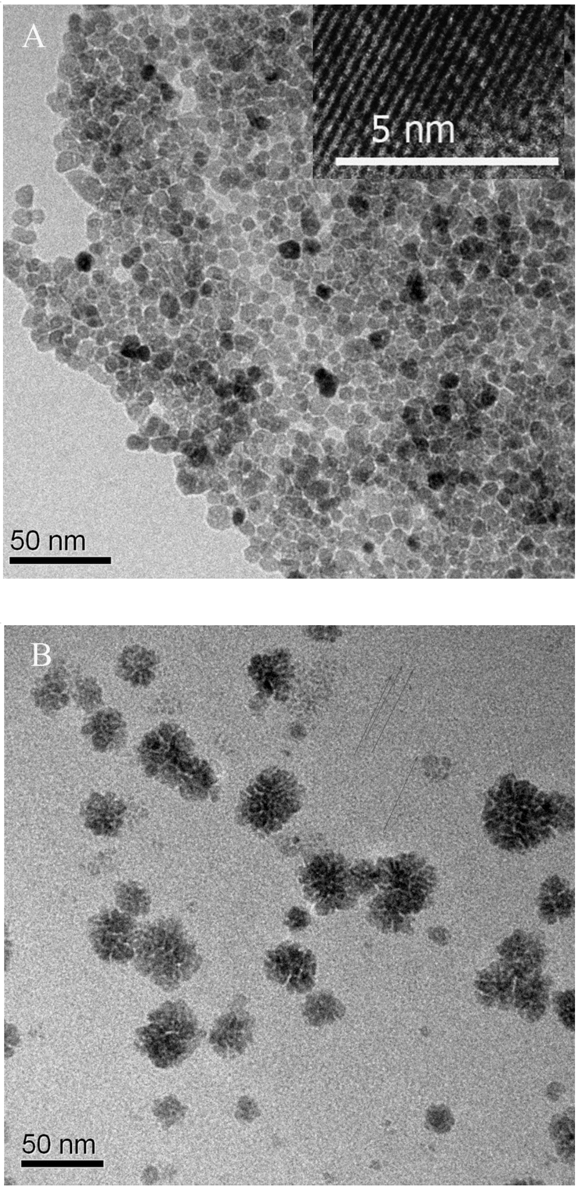

Fig. 4. TEM images of ligand-free ZnO QDs (A, HRTEM (inset)) and ZnO nanoclusters modified by 3.5G PAMAMs (B)

spectra comparing with ZnO QDs (from 284 to 292 nm). All absorption curves of ZnO nanoclusters displayed intensive absorptions in the range 270 to 410 nm, however, ZnO QDs showed sharper absorptions in the range 270 to 320 nm. This may be attributed to the quantum-size effect of nanoparticles[26].

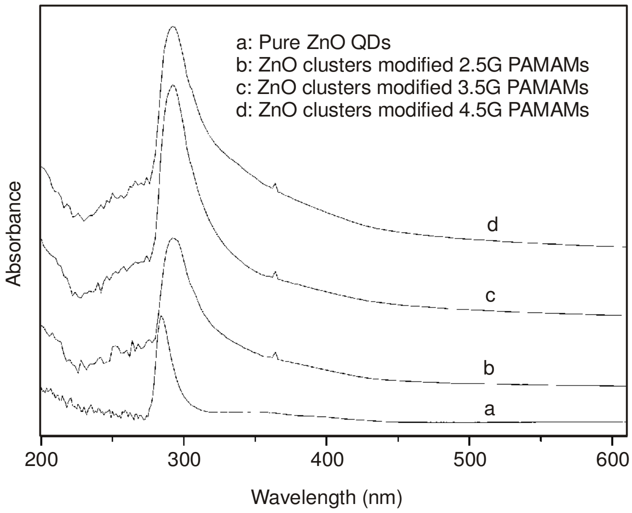

Fig. 5. UV-visible absorption spectra of ZnO nanoclusters modified by 2.5 G PAMAMs, 3.5G PAMAMs, 4.5G PAMAMs (in water) and ZnO QDs (in CHCl$_3$)

Fig. 6 displayed the fluorescent spectra of ZnO QDs and ZnO nanoclusters. It was obvious that the emission peaks of the ZnO nanoclusters were quite different from those of ZnO QDs. The emission peak at 404 nm of the ZnO nanoclusters became weaker comparing with ZnO QDs, and a new emission peak appeared at 330 nm, which may be the characteristic emission peak of the ZnO nanoclusters[27,28].

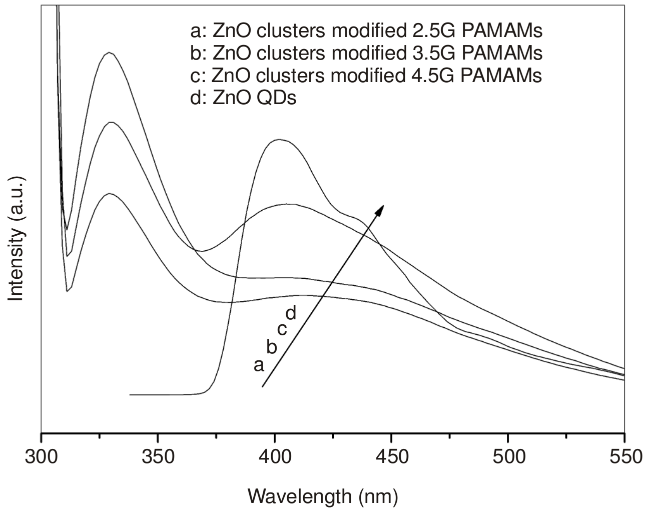

Fig. 6. Fluorescent spectra of ZnO nanoclusters modified by2.5 G PAMAMs, 3.5G PAMAMs, 4.5G PAMAM s(in water) and ZnO QDs (in CHCl$_3$) (λex = 300 nm)

In order to investigate the application of ZnO nanoclusters in plastics, we prepared three films of poly(vinyl alcohol) (PVA), PVA/ZnO QDs and PVA/ZnO nanoclusters and all the contents of ZnO are 2 wt. % in the composite films. Fig. 7 (A) showed the digital photographs of three films of PVA (a), PVA/

ZnO QDs (b) and PVA/ZnO nanoclusters (c) under UV lamp (λ = 365 nm). It is obvious that the poly(vinyl alcohol) film did not emit fluorescence, PVA/ZnO QDs film emitted weak yellow fluorescence and PVA/ZnO nanoclusters film emitted blue fluorescence. Fig. 7 (B) presented the UV-visible transmittance spectra of pure PVA film and the composite films of PVA/ZnO QDs and PVA/ZnO clusters. It is evident that the PVA/ZnO nanoclusters film absorbs nearly 99 % of UV light at wavelengths between 200 and 240 nm while 75 % between 240 and 300 nm. However, the PVA/ZnO QDs film, absorbs only 80 % of UV light at wavelengths between 200 and 240 nm while 70 % between 240 and 300 nm.

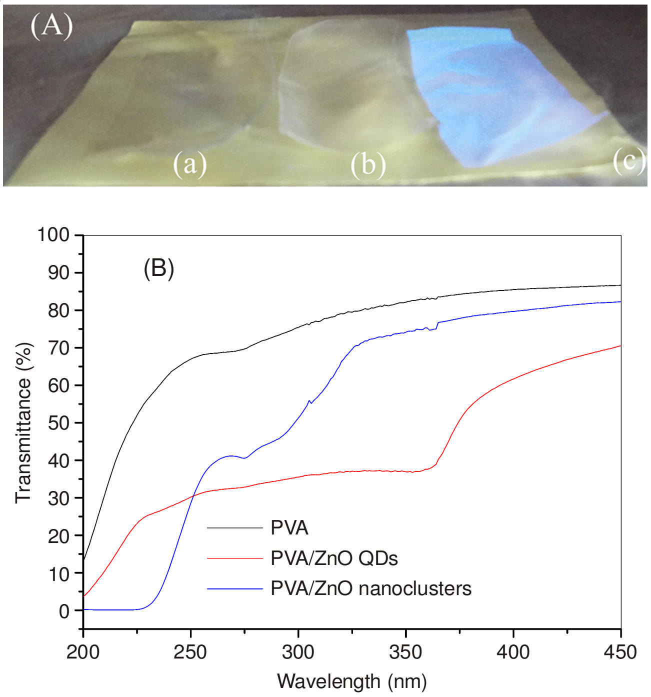

Fig. 7. (A) Digital photographs of films of PVA (a), PVA/ZnO QDs (b) and PVA/ZnO nanoclusters (c) (the background colour: yellow). (B) UV-Visible transmittance spectra of pure poly(vinyl alcohol) film and the composite films of PVA/ZnO QDs and PVA/ZnO clusters)

Conclusion

Zinc oxide nanoclusters prepared by dissolving of ZnO QDs in the water solutions of esterifiable PAMAMs are stable under sunlight and show bright blue under UV lamp. TEM measurements showed that the typical ZnO nanoclusters were made up of ZnO QDs. FTIR spectra of ZnO nanoclusters showed the successful modification of ZnO QDs by the esterifiable PAMAMs. The UV-visible absorption spectra indicated that the ZnO nanoclusters exhibited wider and red-shift optical absorption spectra comparing with ZnO QDs. The fluorescent spectra showed that the emission peaks at 404 nm of the ZnO nanoclusters became weaker and the new emission peaks were found at 330 nm comparing with ZnO QDs. The UV-visible transmittance spectra showed that the PVA/ZnO nanoclusters film absorbed nearly 99 % of UV light at wavelengths between 200 and 240 nm, 75 % between 240 and 300 nm. While the PVA/ZnO QDs film, absorbs only 80 % of UV light at wavelengths between 200 and 240 nm while 70 % between 240 and 300 nm.

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