

# The Photoluminescence Properties of Hyperbranched Poly(ester-amine)/ZnS Particle Self-Assembled Multilayer Films

By Teng QIU, Chunfeng SONG, Jianhui YU, and Xiaoyu LI\*

The interaction between a hyperbranched polymer and ZnS particles dispersed in water was studied and the multilayer films were layer-by-layered fabricated based on the electrostatic attraction of the hyperbranched polymer and ZnS particles. Finally, the photoluminescence properties of the films were detected. With plenty of characteristic alkalescence amine groups on its backbone, the hyperbranched poly(ester-amine) (HPEA) molecules are water-soluble and self-assemble into micelles in water, and this micellization effect were used to increase the dispersion and stabilization of ZnS particles in water. Meantime, HPEA/ZnS particles could be fabricated into multilayer films based on the mutual strong interaction. The multilayer fabrication process was monitored by UV-vis spectrometer and the surface morphology of the multilayer film was characterized by atom force microscope (AFM). The results showed that with ZnS particles as the outmost layer, the film surface was composed by global particles, and most of them with diameters of about 50 to 100 nm. And when the film was excited by UV light at 244 nm, an emission peak at 495 nm was detected.

**KEY WORDS:** Hyperbranched Polymer / ZnS Particles / Self-Assembly / Fluorescence / Multilayer /

Transition-metal sulfides, in particular ZnS particles, have attracted great attention due to their special properties caused by their unique photo-luminescence and catalytic functions.<sup>1,2</sup> As the great potential application in molecular or supramolecular devices in non-linear optical and photocatalysis fields, hybrid films fabricated by semiconductor ZnS particles have been one focus of extensive researches.<sup>3</sup>

During the plenty of polymers which could be complicated with inorganic nanoparticles, hyperbranched polymer was an outstanding one for its low viscosity, good solubility, multi-functionality and easy preparation.<sup>4</sup> Further studies on hyperbranched polymers with amphiphilic structures have shown that they could be assembled into supramolecules in solution.<sup>5,6</sup> Large mount of internal cavities make such global molecules are able to be served as single or multi-molecule micelles to stabilize or transfer inorganic particles, biomolecules or other functional materials.<sup>7,8</sup> Among hyperbranched polymers with various structures, hyperbranched poly(ester-amine) which could be synthesized simply from ordinary chemical products is of amphiphilic structures and soluble in both organic solvents and water. Former studies have shown that such molecules could be served as phase transfer agent and extract methyl orange from aqueous phase into CHCl<sub>3</sub> phase.<sup>9</sup>

Developed by Decher *et al.* the electrostatic adsorption self-assembly has been proved to be a simple but effective technique to fabricate ultrathin functional hybrid films on various surfaces.<sup>10</sup> It has been reported that hyperbranched polyelectrolytes could self-assemble into multilayers with both linear and hyperbranched polymer counter ions.<sup>11,12</sup>

To combine the unique properties of hyperbranched polymers and ZnS, in this work, the molecule behavior of HPEA in

aqueous dispersant was concerned when interacted with inorganic ZnS molecules. Furthermore, hyperbranched poly(ester-amine)/ZnS hybrid multilayers was successfully prepared layer-by-layer by electrostatic adsorption self-assembly method.

## EXPERIMENTAL

### Reagents

All of the chemicals in this paper were of A.R. grade and were used as purchased.

### Instruments

The molecule structure was characterized by <sup>1</sup>H NMR (AV600, BRUKER) and FT-IR (TENSOR 37, BRUKER). The solution surface tension was measured by OCA 20, Data Physics. The particle size, distribution and zeta potential in solution were measured by Zetasizer NanoZS, Malvern. The UV-vis spectra were obtained by UV-3150, Shimadzu. The fluorescence emission spectra of the films were obtained by CARY Eclipse, Varian, excited by UV light at 244 nm in air. The surface morphologies were recorded by a tapping mode Atomic Force Microscope (AFM), Nanoscope IIIa, Digital Instruments.

### Preparation of ZnS Powders

6 g Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O was dissolved in 200 mL water and heated to 80 °C. Then 3 g thioacetamide (TAA) was added in the solution. The solution pH was adjusted to about 1.5 by 1:1 HNO<sub>3</sub> (vol). The mixture was stirred until it looked light-blue. Then the reaction was stopped by cooling in ice water. The

Key Laboratory for Nanomaterials, Ministry of Education, School of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

\*To whom correspondence should be addressed (Tel: 086-010-64423162, Fax: 086-010-64423162, E-mail: lixy@mail.buct.edu.cn).

product was centrifugally isolated. After washed by ethanol twice and once by isopropanol, the final white powder was dried in oven at 60 °C.

### Preparation of Hyperbranched Poly(ester-amine) (HPEA)

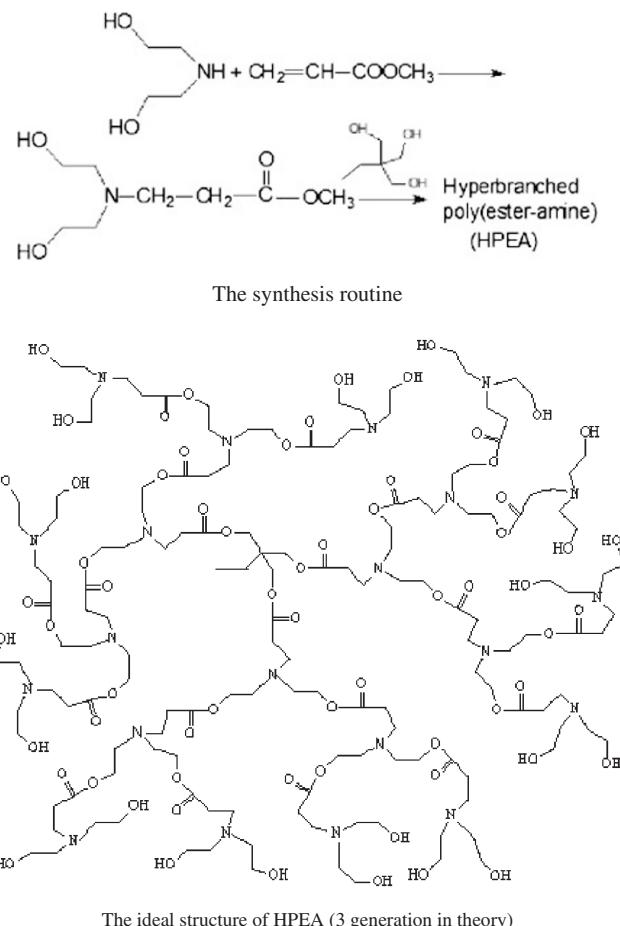
The aliphatic hyperbranched poly(ester-amine) was prepared according to ref 13. 40 mL diethanolamine was added in a four neck flask with a nitrogen inlet and outlet and stirred at room temperature. 38 mL methyl acrylic ester was dissolved in 30 mL methanol and dripped into the flask. After the addition, the mixture was stirred for 6 h at room temperature. The methanol was removed by rotated evaporation and the left oil-like substance was the AB2 monomer.

0.02 mol trimethyl propane (B3 monomer), 0.18 mol above AB2 monomer and 0.2 g *p*-toluenesulfonic acid (catalyst) was added in a four neck flask with a nitrogen inlet and outlet and a mechanical stirring. The flask was moved into oil bath preheated to 120 °C. The reaction proceeded in a weak N<sub>2</sub> current for 1 h. Then the N<sub>2</sub> supply was stopped and vacuum of 2–3 mmHg was applied for 2 h. The reaction proceed as a pseudo one-step procedure and 2 generation (in theory) polymer was prepared. Then the N<sub>2</sub> supply was recovered and 0.24 mol AB2 monomer was added in the system. Vacuum was applied again on the system for 2 h after the new added monomer was dissolved in the polymer melting, and 3 generation (in theory) polymer was prepared. Then the third batch of monomer (0.48 mol) was added in the system in the protection of N<sub>2</sub> current. The reaction proceeded as above and the final product (4 generation in theory) was obtained as yellow syrupy substance. The polymer was characterized by <sup>1</sup>H NMR (in deuterium oxide,  $\delta$  in ppm): 0.8 ppm (CH<sub>3</sub>-CH<sub>2</sub>-), 1.2 ppm (CH<sub>3</sub>-CH<sub>2</sub>-), 2.5–2.8 ppm (-NCH<sub>2</sub>-, -CH<sub>2</sub>CO-), 3.5–3.7 ppm (-CH<sub>2</sub>-O-), 4.5 ppm (-OH). FT-IR: 3300 cm<sup>-1</sup> (-OH), 1600 cm<sup>-1</sup> (-CO-). The molecule weight could be calculated by the integral ratio of the -CH<sub>2</sub>R- at 2.5–2.8 ppm and -CH<sub>3</sub> at 0.8 ppm, which was about 35.2:1. Then it could be deduced that the HPEA molecule weight was about  $5.7 \times 10^3$  (5668). <sup>13</sup>C-NMR (in deuterium oxide,  $\delta$  in ppm): 179.0 ppm (-CO-), 62.1 ppm ( $\text{C}=\text{CH}_2\text{-O-}$ ), 57.6 ppm (-CH<sub>2</sub>-OH), 54.8 ppm (R-O-CH<sub>2</sub>-CH<sub>2</sub>-N-), 51.3 ppm (R-O-CH<sub>2</sub>-CH<sub>2</sub>-N-), 49.0 ppm (-CO-CH<sub>2</sub>-N-), 31.4 (-CO-CH<sub>2</sub>-CH<sub>2</sub>-), 28.6 ppm (-CH<sub>3</sub>), 20.9 ppm (CH<sub>3</sub>-CH<sub>2</sub>-C-), 6.6 ppm ( $\text{C}=\text{CH}_2$ ).

### The Fabrication of Hyperbranched Polymer/ZnS Multilayers

0.03637 g HPEA was dissolved in 50 mL Milli-Q water. 0.002435 g ZnS powder was sonicated in Milli-Q water. The pH of both solutions was adjusted to 3 by diluted hydrochloric acid.

The HPEA/ZnS multilayers were fabricated by sequentially dipping quartz substrate (pre-treated by H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>-NH<sub>3</sub>·H<sub>2</sub>O solution) into the two solutions. The immersion time in solution was controlled to 10 min. After each dipping, the film was carefully washed by Milli-Q water. The final film was dried at room temperature for further characterization.



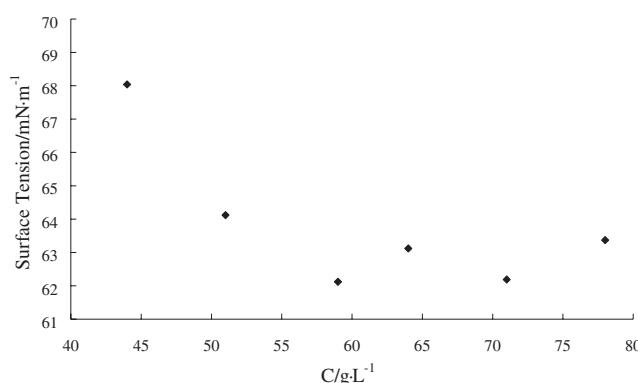
Scheme 1. Hyperbranched aliphatic poly(ester-amine).

## RESULTS AND DISCUSSION

### The HPEA Solution Analysis

The ideal structure of HPEA was shown in Scheme 1. The polymer was synthesized by pseudo one-step procedure similar to that reported in the literature.<sup>13</sup> With the hydrophilic ternary amine structure introduced into the globe molecule backbone, the HPEA molecule was amphiphilic and would form micelles in aqueous solution.

Figure 1 was the relationship between the polymer concentration and the surface tension of HPEA solution. It was clear that with the increase of polymer concentration, surface tension of the solution was decreased until the concentration reached a certain point (cmc). After that, although the solution concentration was kept increasing, the surface tension of the solution was stable to a certain value. Characterized by the dynamic laser scattering (DLS), a steady colloidal solution was formed at the concentration near the cmc. The Z-average diameter of such colloids was 322 nm and the polydispersity of 0.365. Figure 2 showed the number average results of DLS. From the DLS results, 90 nm micelles were formed in water dispersant. The particles with diameters of about 280 nm should be the high-order aggregates of the micelles. The number of 90 nm



**Figure 1.** The relationship between the HPEA concentration and the surface tension.

colloids occupied about 90% in the total number of particles in solution. But as the large particles have much stronger intensities than small ones, the large aggregates contribute more on the Z-average diameter than small colloids.

When the polymer concentration is much above the cmc, aggregates with large polydispersity were counted, which might be caused by the random aggregation of the colloids.

The zeta-potential of HPEA colloids was changed with the pH value in aqueous phase. The results were shown in Table I. In general, the HPEA aqueous solution was alkaline with the pH value of ~8, and the zeta potential of the solution was negative. With the addition of HCl which adjusted the solution to the acidic, the large amount of protonized tertiary amine groups made the zeta-potential positive.

#### The Interaction of HPEA and ZnS in Aqueous Solution

ZnS was prepared in our lab and deposited as white powder. The powder could re-disperse in water with a Z-average diameter of 448 nm and the polydispersity of 0.500. The solution zeta potential was -8.29 mV. The zeta potential value

**Table I.** The HPEA solution zeta-potential (ZP) and the pH value

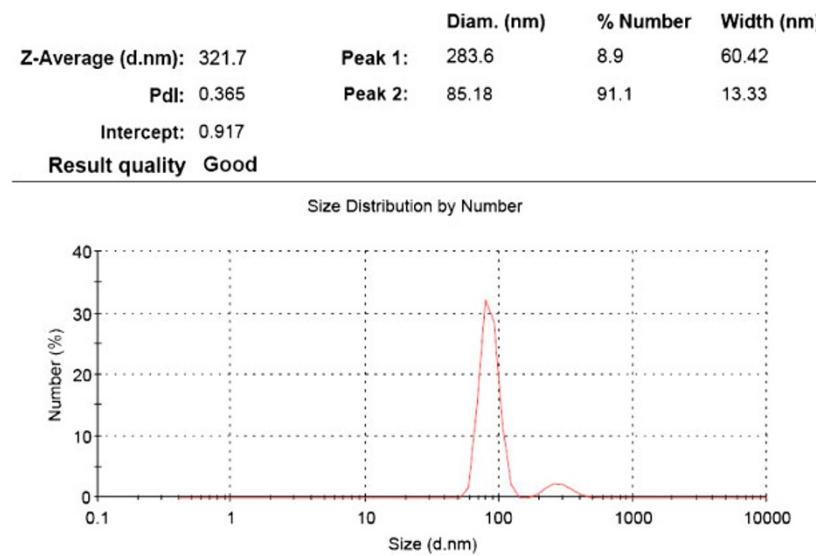
pH	13	9	8	6	4	3	2	1
ZP/mV	-12.6	-18.7	-10.7	0.420	4.06	4.17	5.80	15.1

also changed with the solution pH. When the solution pH was adjusted to 3 by diluted HCl solution, the ZnS zeta potential was changed to -24.9 mV.

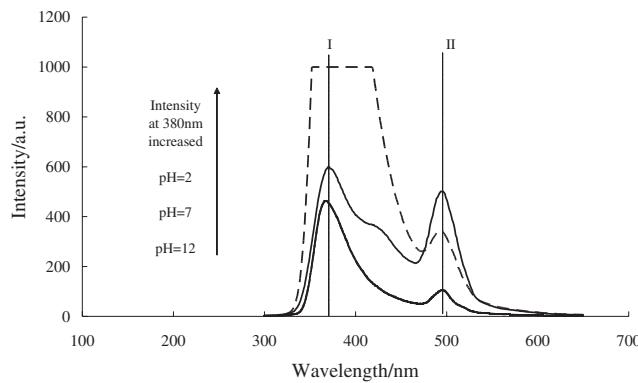
As a typical II-IV semiconductor with a direct band gap of about 3.58 eV, the dispersed ZnS showed photo-luminescence upon light excitation at UV band. Figure 3 was the fluorescence spectrum of ZnS in water excited at 244 nm. It could be discerned that there were two main peaks in the emission spectra: one maximum at 380 nm (I) and the other (II) at 495 nm. A shoulder peak at about 430 nm could also be observed. Based on the characterization on bulk ZnS, the peak at 380 nm should be attributed to the band edge emission,<sup>14</sup> and peaks at 430 and 495 nm should be attributed to the surface energy defects, which would capture the excited electron.<sup>15</sup> The shoulder peak at 430 nm should be attributed to the existence of TAA. The N atom would coordinate with the surface Zn atom, and new energy state would be introduced.

When the solution pH value was adjusted to 1 by the addition of HCl, the absolute zeta potential value of ZnS increased to -24.9 mV. ZnS would acid hydrolyze and the emission intensity was correspondingly decreased. However when the solution pH value was adjusted to 12 by the addition of NaOH, the hydrolysis was depressed and the adsorption of NaOH onto ZnS surfaces made the peak at 495 nm decrease but peak at 370 nm much increase.

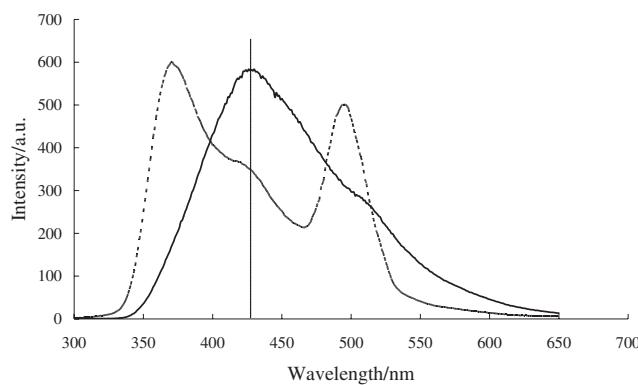
When ZnS powder was dispersed in 50 g/L HPEA colloidal solution instead of pure water, the Z-average diameter of particles was decreased to 218 nm, with the zeta-potential of -28.7 mV. As the absolute value of zeta potential increased and the Z-average size decreased, it could be suggested that the



**Figure 2.** The DLS characterization of HPEA colloidal solution (concentration = 50 g/L).



**Figure 3.** The fluorescence spectra of the ZnS in water excited at 244 nm.



**Figure 4.** The fluorescence spectrum of the ZnS dispersed in HPEA colloidal solution. The dash line was attributed to the pure ZnS dispersed solution.

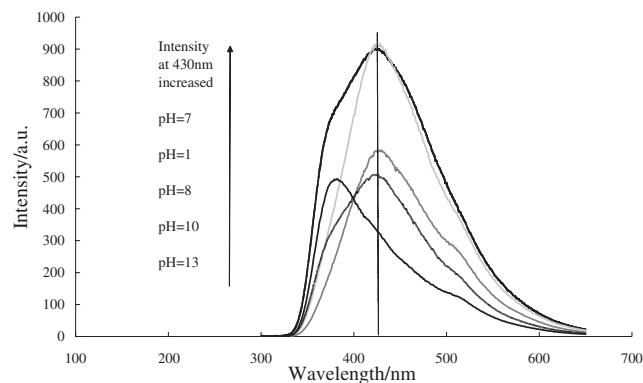
inorganic particles in solution were stabilized by the addition of the hyperbranched polymer.<sup>12</sup>

Figure 4 was the fluorescence spectra of ZnS dispersed in HPEA solution. Only one peak at 430 nm was shown in the luminescent spectrum. The changes in the spectrum indicated the changes happened on the surface of ZnS particles, *i.e.*, ZnS particles were not surrounded by H<sub>2</sub>O but by HPEA molecules. Considering the special structure of HPEA, ZnS should coordinate with the tertiary groups on the backbone of the hyperbranched polymers.

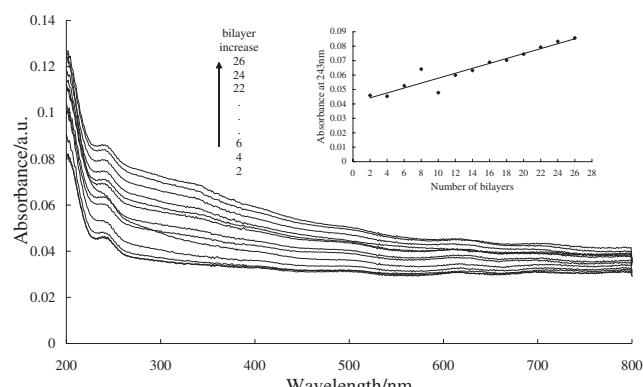
Compared with ZnS in water, ZnS in HPEA colloid solution was less sensitive to the pH value of dispersant. Figure 5 showed the fluorescence spectra at different pH. In Figure 5, it could be shown that the peak at 430 nm was strong in neutral and acid medium. But when the medium was adjusted to basic, the intensity for this peak was much decreased, partially for the adsorption of NaOH onto surfaces. When the solution pH value was reached to 13, the main-peak was blue-shifted to 380 nm.<sup>16</sup>

#### The Fabrication of HPEA/ZnS Multilayers

Using the acidification HPEA as the polycation, while the ZnS nanoparticles as the polyanion, HPEA/ZnS multilayers were successfully fabricated by electrostatic adsorption self-assembly technique. The fabrication process was monitored by UV-vis spectrometer. The UV-vis spectra of the multilayer film



**Figure 5.** The fluorescence spectrum of the ZnS dispersed in HPEA colloidal solution with different pH value.

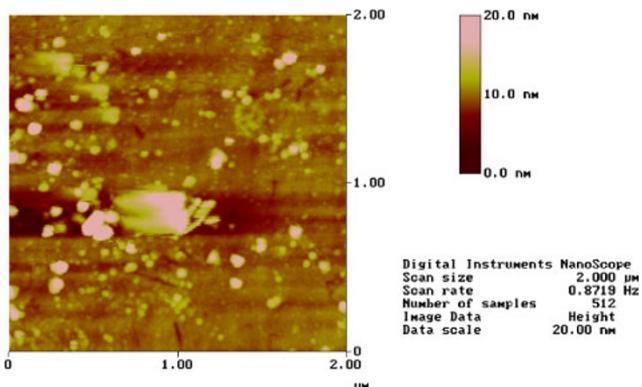


**Figure 6.** The UV-vis spectra of the multilayer of 26 bilayers and the UV absorbance at 228 nm increased with the bilayer numbers (inset).

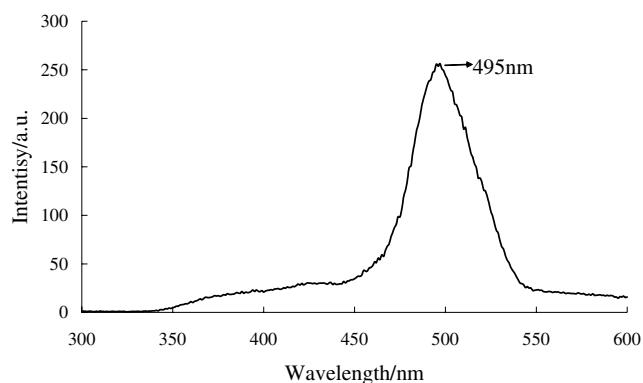
with 26 bilayers were shown in Figure 6. The layer-by-layered increase of the UV absorption demonstrated the electrostatic self-assembly of ZnS and HPEA. The inset of Figure 6 showed the linear relationship between the UV absorbance at 228 nm increased with the bilayer numbers, which indicated an equal deposition of each bilayer.

Figure 7 was the AFM height image of HPEA/ZnS multilayer surface with ZnS as the outmost layer. In the scan scale, the surface was composed by global particles. Although relatively large particles with the diameters of about 250 nm were observed, the diameters of most of the particles were distributed between 50 to 100 nm. Compared with the DLS data of ZnS particles dispersed directly in water, it seems that the small ZnS particles have stronger tendency to be assembled on the multilayers than large ones.

Figure 8 showed the fluorescence spectrum of the multilayer film. Compare with the spectra obtained in colloidal solution, the peak at 430 nm was much depressed and the maximum peak was shown at 495 nm, which is attributed to the surface defects of the bulk ZnS. The changes on the photo-luminescent spectra could be explained by the different interaction between ZnS particles and polymer in the electrostatic adsorption process,<sup>17</sup> where the HPEA served mostly like polycations but not coordinate molecules.



**Figure 7.** The AFM height image of HPEA/ZnS multilayer surface (ZnS as the outmost layer).



**Figure 8.** The fluorescence emission spectrum of the multilayer film fabricated by hyperbranched polymer and ZnS particles.

Although obvious coordinate would happen between HPEA and ZnS when dispersed directed in aqueous phase, the coordinate did not contribute much to the self-assembly of the HPEA/ZnS multilayer film. The driven force for the assembly was still the coulomb force between opposite charges distributing on the polymer chains and the particles, respectively. In HPEA molecules, the positive charges were provided by the protonized tertiary amine groups. So the polymer monolayer was formed by part of the protonized amine groups fixed on the substrate by electrostatic adsorption, which restricted the molecule conformation compared with the case in solution. When the polymer monolayer interacted with the negative charged hard particles, part of the remaining unfixed amine groups, especially the groups located adjacent the ZnS surfaces were provided for the ZnS particles adsorption. It is possible that the amine groups located far from the ZnS surfaces could not reached the ZnS at all. As a result, ZnS could not be sufficiently surrounded by HPEA and the coordinate between amine groups and the ZnS was in correspondingly much suppressed. This is consistent with the

AFM results. The smaller the particles was, the larger surface area it could provide for adsorption, the more stable it stay on the multilayer film. As many small particles with plenty of surface defects have much more contribution on the spectrum than the few of large ones, the peak at 495 nm was found to be the main peak in the photo-luminescent spectrum of the multilayer film layer-by-layered self-assembled by HPEA and ZnS particles.

## CONCLUSION

With the plenty of cavity structures and alkalescence amine groups, the water soluble hyperbranched poly(ester-amine) hyperbranched polymer was found to interact with ZnS particles in water, which induced the changes on the fluorescence spectra of ZnS. Furthermore, HPEA/ZnS hybrid-multilayer film was layer-by-layered fabricated. Excited by UV light at 244 nm, emission peak at 495 nm was observed in fluorescence emission spectrum.

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