Preparation of Corona-Embedded CdS Nanoparticles

Hanying Zhao and Elliot P. Douglas*

Department of Materials Science and Engineering, University of Florida,
Gainesville, Florida 32611

Received October 29, 2001. Revised Manuscript Received December 21, 2001

In this paper, two novel methods of preparing CdS nanoparticles within the corona of block copolymer micelles are presented. (1) Corona-embedded CdS nanoparticles were prepared by dropping core-embedded CdS nanoparticles into water with a low pH value. The location change of the CdS nanoparticles was accompanied by a structural change of the micelles, from compound micelles to single micelles. The CdS nanoparticles are randomly distributed in the corona of the single micelles. The size of the nanoparticles increases slightly after the transition. (2) Corona-embedded CdS nanoparticles can also be prepared using the "in situ" reaction of S^{2-} with Cd^{2+} ion clusters in the corona of the micelles. The single micelles with Cd^{2+} ion clusters in the corona were prepared by dropping poly(styrene-*block*-2-vinylpyridine)−Cd^{2+} compound micelles into water with a low pH value. The size of the corona-embedded CdS nanoparticles is affected by starting pH value in water, complex concentration, and S^{2-} source.

Introduction

The synthesis of semiconductor nanoparticles or clusters is emerging in the fields of materials science and colloid science because of their wide range of optical and electronic properties.[1−5] In the past decades, many people have prepared nanoparticles in micelles formed by amphiphilic block copolymers consisting of a hydrophobic block and a hydrophilic block.[6−15] Control of the location and distribution of the nanoparticles within the micelles is very important for a variety of applications. In most cases, nanoparticles are prepared in the core of micelles. However, in some cases, the location of the nanoparticles in the corona region (corona-embedded nanoparticles) is desired as well. The location of the nanoparticles in a micelle is determined by the solvent type, the metal precursor type, the reaction conditions, and the interactions between the ions and the polymer.[16] In a typical case, salt ions diffuse into the core of spherical micelles in a nonpolar solvent, and core-embedded nanoparticles can be synthesized with an appropriate reaction.[17] Nanoparticles can also be synthesized around the core of micelles or entirely within the corona region.[16,18] Using poly(styrene-*b*-ethylene oxide) in a polar solvent medium, Mayer et al. prepared small metal colloids surrounding the core of micelles.[19] They called this structure a "strawberry morphology". In this structure, the nanoparticles are located in close vicinity to the micelle core because of the strong interaction between the hydrophobic micelle core and the nanoparticles. They further proposed a possible morphology where the metal colloids locate entirely within the corona region with no preferred closeness or vicinity toward the micelle core.[18] They called this structure a "red currant morphology". They thought it should be possible to obtain this red currant morphology by introducing strong interactions of the corona component with the metal precursor and the metal colloids.

In a previous paper, we described a novel method to prepare CdS nanoparticles with controllable size and stability.[20] Poly(styrene-*block*-2-vinylpyridine) (PS-*b*-P2VP) block copolymer forms compound micelles upon complexation with cadmium ions (Cd^{2+}) in tetrahydrofuran (THF). In a compound micelle, single micelles are bridged by free 2-vinylpyridine (2VP) segments, and a compound micelle can be treated as a cluster of single micelles. CdS nanoparticles grow in the core of single micelles concomitant to introduction of H_2S gas into the

---

* To whom correspondence should be addressed. E-mail: edoug@mail.mse.ufl.edu. Tel: 352-846-2836. Fax: 352-392-3771.

(1) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.

(2) Spanhel, L.; Hoasse, M.; Weller, H. J.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649.

(3) Henglein, A.; Gutierrez, M. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 852.

(4) Wang, Y.; Herron, N. *J. Phys. Chem.* **1991**, 95, 525.

(5) McConnell, W. P.; Novak, J. P.; Brousseau, L. C.; Fuierer, R. R.; Tenent, R. C.; Feldheim, D. L. *J. Phys. Chem. B* **2000**, 104, 8925.

(6) Qi, L.; Colfen, H.; Antonietti, M. *Nano Lett.* **2001**, *1*, 61.

(7) Bronstein, L. M.; Sidorov, S. N.; Valetsky, P. M.; Hartmann, J.; Colfen, H.; Antonietti, M. *Langmuir* **1999**, *15*, 6256.

(8) Sidorov, S. N.; Bronstin, L. M.; Valetsky, P. M.; Hartmann, J.; Colfen, H.; Schnablegger, H.; Antonietti, M. *J. Colloid Interface Sci.* **1999**, *212*, 197.

(9) Antonietti, M.; Forster, S.; Hartmann, J.; Oestreich, S.; *Macromolecules* **1996**, *29*, 3800.

(10) Moffitt, M.; Vali, H.; Eisenberg, A. *Chem. Mater.* **1998**, *10*, 1021.

(11) Moffitt, M.; Vali, H.; Eisenberg, A. *Macromolecules* **1997**, *30*, 4363.

(12) Moffitt, M.; McMahon, L.; Pessel, V.; Eisenberg, A. *Chem. Mater.* **1995**, *7*, 1185.

(13) Mayer, A.; Antonietti, M. *Colloid Polym. Sci.* **1998**, *276*, 769.

(14) Underhill, R. S.; Liu, G. *Chem. Mater.* **2000**, *12*, 3633.

(15) Underhill, R. S.; Liu, G. *Chem. Mater.* **2000**, *12*, 2082.

(16) Mayer, A. B. R. *Polym. Adv. Technol.* **2001**, *12*, 96.

(17) Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater.* **1995**, *7*, 1000.

(18) Mayer, A. B. R. *Mater. Sci. Eng., C* **1998**, *6*, 155.

(19) Mayer, A. B. R.; Mark, J. E.; Morris, R. E. *Polym. J.* **1998**, *30*, 197.

(20) Zhao, H.; Douglas, E. P.; Harrison, B. S.; Schanze, K. S. *Langmuir* **2001**, *17*, 8428.

10.1021/cm011581+ CCC: $22.00

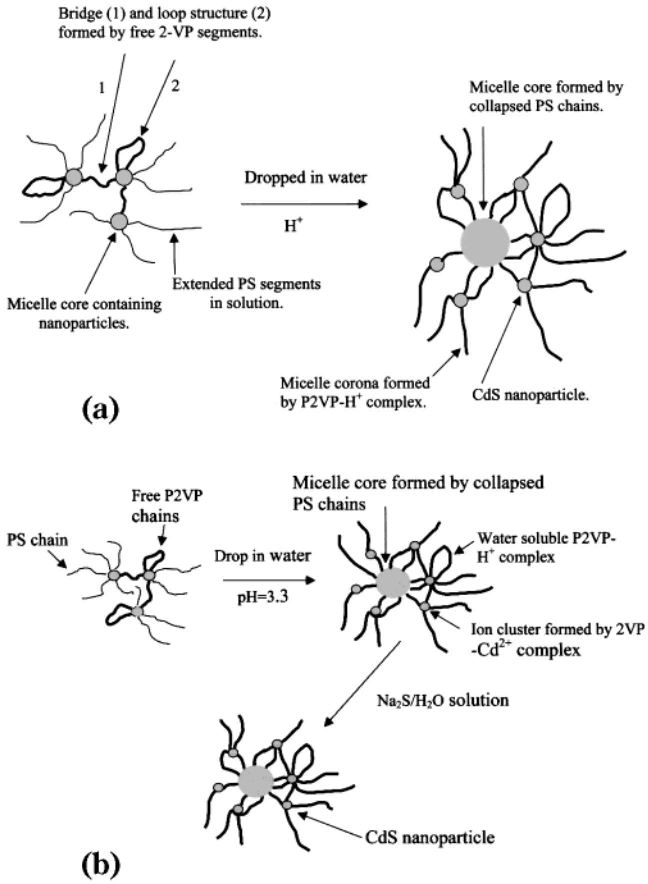

Figure 1. Schematic illustrations for the transition of core-embedded CdS nanoparticles to corona-embedded CdS nanoparticles (a) and in situ preparation of corona-embedded CdS nanoparticles from complex solution (b).

solution. The result of this process is core-embedded nanoparticles. The purpose of this paper is to study the preparation of corona-embedded CdS nanoparticles using (1) transition of core-embedded nanoparticles to corona-embedded nanoparticles and (2) “in situ” reaction of S^{2-} with ion clusters in the corona of micelles.

The first method to prepare corona-embedded nanoparticles was realized through the transition of core-embedded nanoparticles to corona-embedded nanoparticles. In a compound micelle with core-embedded CdS nanoparticles, both PS blocks and uncomplexed 2VP segments are soluble in THF, and CdS nanoparticles are protected by P2VP chains. When a core-embedded CdS nanoparticle solution is dropped into water with a low pH value, the polystyrene chains collapse and the 2VP segments form water-soluble complexes with acid. Thus, a kind of new micelle with a collapsed PS core and a $P2VP-H^+$ complex corona is formed. After the transition, reaction with a source of sulfide ion (S^{2-}) results in the formation of CdS nanoparticles within the corona of the micelles. Because of the strong interaction between 2VP units and CdS nanoparticles, the CdS nanoparticles can be stabilized in the corona. The location change of the nanoparticles is caused by the structural change of micelles, a change from compound micelles to single micelles. A schematic diagram of this process is shown in Figure 1a.

The other method to prepare corona-embedded CdS nanoparticles was realized through the reaction of S^{2-} with ion clusters in the corona of micelles. We call this method the in situ preparation of corona-embedded CdS nanoparticles. Single micelles are formed when a compound micelle solution in THF is added into water with a low pH value. The collapsed PS chains form the core and complexed P2VP chains form the corona. Cd^{2+} ion clusters exist in the corona of these single micelles. Corona-embedded CdS nanoparticles are prepared by introduction of Na_2S solution or H_2S gas. A schematic is shown in Figure 1b.

For both of these procedures, the CdS nanoparticles distribute randomly in the corona region. The resulting colloidal solutions are similar to the red currant morphology proposed by Mayer et al.[16,18] In addition to providing some details regarding the preparation of the morphology, we also describe the factors that affect the size of the corona-embedded nanoparticles.

Experimental Section

Materials. The block copolymer (PS-*b*-P2VP) was synthesized using sequential anionic polymerization. The polymerization of the PS block was carried out in THF at −75 °C with *sec*-butyllithium as the initiator. 2-Vinylpyridine monomer was added dropwise after the PS block was capped with 1,1-diphenylethylene. The molecular weight of the block copolymer is 25.5×10^3 g/mol (M_n) with a polydispersity of 1.30, measured by GPC relative to PS standards. The molar content of 2VP units in the block copolymer is about 35 mol % as measured by ^1H NMR.

Cadmium acetate dihydrate ($Cd(Ac)_2 \cdot 2H_2O$) and hydrogen sulfide (H_2S) gas were purchased from Aldrich company. They were used without further purification.

UV−Visible Absorption Spectroscopy. UV−vis absorption spectra were recorded on a Shimadzu UV−vis spectrophotometer (UV-2401PC) by scanning the CdS-containing solution in a 1 cm quartz cell. The scanning range was from 190 to 700 nm. Absorption from the solvent was subtracted from each spectrum.

Fluorescence Spectroscopy. Steady-state fluorescence spectra were obtained on a SPEX Fluorolog Spectrophotometer equipped with a 450W Xe arc-lamp and a PMT detector. The excitation wavelength was 350 nm, and the bandwidths were 10 nm for excitation and emission. Fluorescence measurements were obtained on the colloidal suspensions contained in quartz cuvettes.

Transmission Electron Microscopy (TEM). Electron microscopy was performed on a Zeiss EM 10A transmission electron microscope operated at 100 kV. TEM samples were prepared by depositing a droplet of CdS-containing colloidal solution (<0.1 mg/ml) onto a TEM grid which had been coated with Formvar/silicon monoxide film.

Preparation of Corona-Embedded CdS Nanoparticles. *Transition of Core-Embedded Nanoparticles to Corona-Embedded CdS Nanoparticles.* PS-*b*-P2VP block copolymer was dissolved in THF at different concentrations under vigorous stirring for 1 h. $Cd(Ac)_2 \cdot 2H_2O$, dissolved in a mixture of methanol and THF (1:2 v/v), was added to the polymer solution dropwise such that the molar ratio of 2VP to Cd^{2+} was 1:0.5. A light yellow solution of core-embedded CdS nanoparticles was prepared by introducing H_2S gas into the complex solution. Corona-embedded CdS nanoparticles were prepared by dropping varying amounts of the core-embedded CdS nanoparticle solution into water with a low pH value and then removing the THF from the solution under vacuum.

In Situ Preparation of Corona-Embedded CdS Nanoparticles. P2VP block copolymer was dissolved in THF at different concentrations under vigorous stirring for 1 h. $Cd(Ac)_2 \cdot 2H_2O$, dissolved in a mixture of methanol and THF (1:2 v/v), was added to the polymer solution such that the molar ratio of 2VP to Cd^{2+} was 1:0.5. A micelle solution was achieved by adding varying amounts of this complex solution into water with a low pH value. A stable yellow corona-embedded CdS nano-

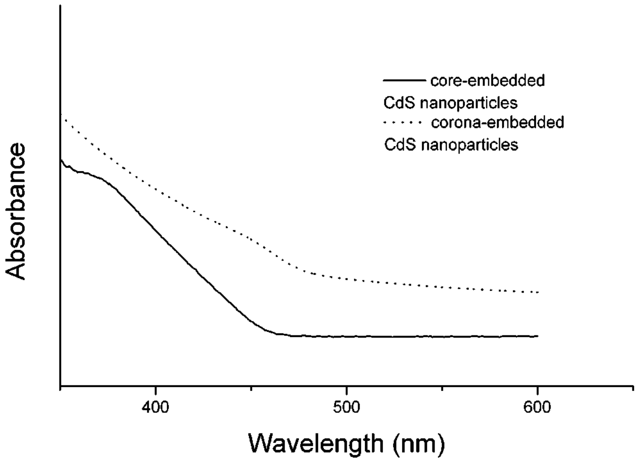

Figure 2. UV-vis absorption spectra of core-embedded CdS nanoparticles and corona-embedded CdS nanoparticles. The concentration of the block copolymer in THF is 2.5 g/L and the molar ratio of 2VP units to Cd^{2+} is 1:0.5.

particle solution was prepared by adding 1-fold excess Na_2S/water solution into the micelle solution.

Results and Discussion

Transition of Core-Embedded Nanoparticles to Corona-Embedded Nanoparticles. Figure 2 shows UV−vis spectra of core-embedded and corona-embedded CdS nanoparticles in THF. For the core-embedded CdS nanoparticle solution with a polymer concentration of 2.5 mg/mL, the absorption edge is at about 457 nm; however, the absorption edge red-shifts to 474 nm when the core-embedded CdS nanoparticle solution is dropped into water with a pH value of 3.3. The absorption edge of CdS nanoparticles is related to the size of the nanoparticles by Henglein's empirical curve,[1,2] allowing us to calculate the change of diameter of the nanoparticles after the transition. The average diameter of the core-embedded CdS particles is about 3.7 nm, and after the transition, it increases to about 4.4 nm, indicating that some nanoparticles aggregated during the transition from core-embedded nanoparticles to corona-embedded nanoparticles.

In the micelles with corona-embedded CdS nanoparticles, collapsed PS chains form the core and P2VP−H^+ complexes form the corona. The stability of CdS nanoparticles is realized through the interaction of P2VP chains and CdS nanoparticles at the surface. The P2VP chains exhibit two tendencies when they are dropped into water with a pH value of 3.3. One is to form complexes with H^+ in water, and another is to stay attached to the CdS nanoparticles surface because of the interaction. When the core-embedded CdS nanoparticles in THF solution are dropped into water, some of the 2VP units attached to the surface of the nanoparticles are desorbed from the particles' surface, and thus the nanoparticles in water become less stable and aggregate together.

Figure 3a is a TEM image of core-embedded CdS nanoparticles prepared by introduction of H_2S gas into the PS-*b*-P2VP−Cd^{2+} complex solution in THF. The polymer concentration of the solution is 2.5 g/L. In this image, nanoparticles in the compound micelles can be observed. A compound micelle is composed of single micelles, and the growth of a CdS nanoparticle is confined to the core of a single micelle.[20] The diameters of the compound micelles range from 20 nm to more than 100 nm, and the diameters of the CdS nanoparticles range from 2.4 to 3.5 nm. Figure 3b is a TEM image of corona-embedded CdS nanoparticles prepared by dropping 1 mL of the core-embedded CdS nanopar-

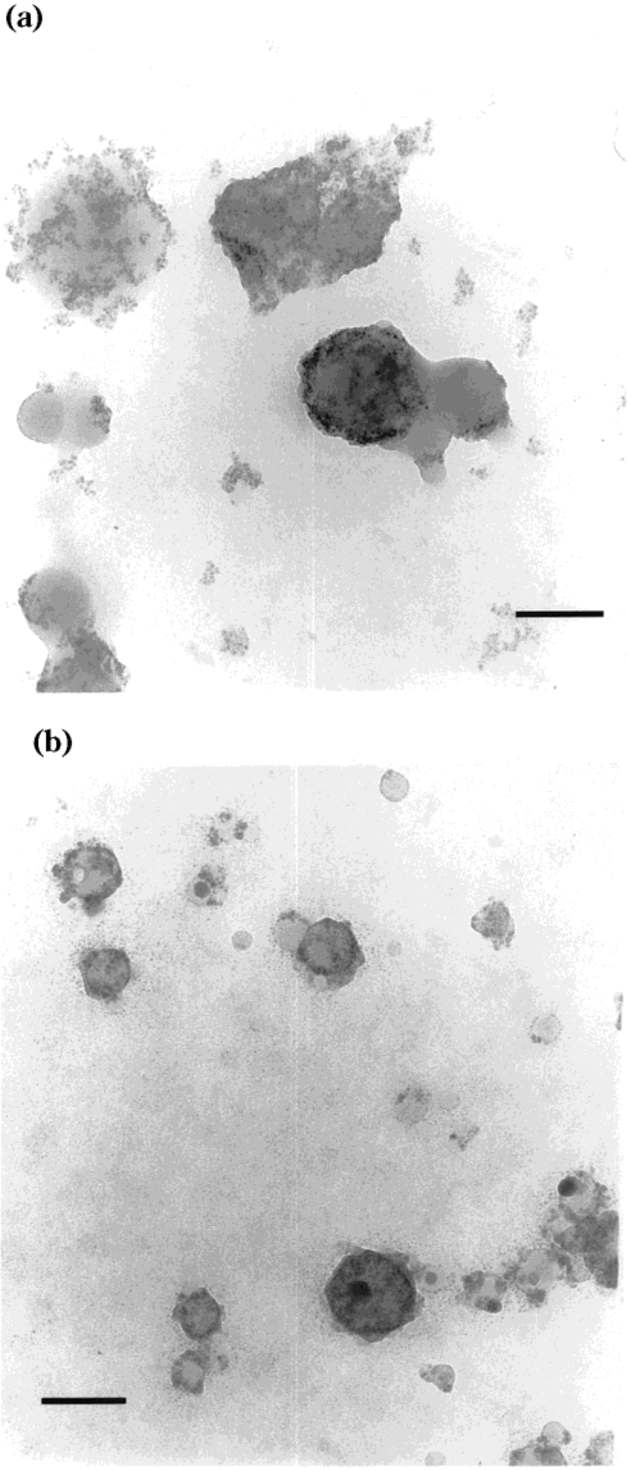

Figure 3. (a) TEM image of core-embedded CdS nanoparticles. The CdS nanoparticles were prepared by introducing H_2S gas into PS-*b*-P2VP−Cd^{2+} complex solution in THF. The concentration of block copolymer in THF is 2.5 g/L and (b) TEM image of corona-embedded CdS nanoparticles prepared by dropping 1 mL of the core-embedded CdS nanoparticle solution into 20 mL of water with a pH value of 3.3. Scale bars on the TEM images represent 100 nm.

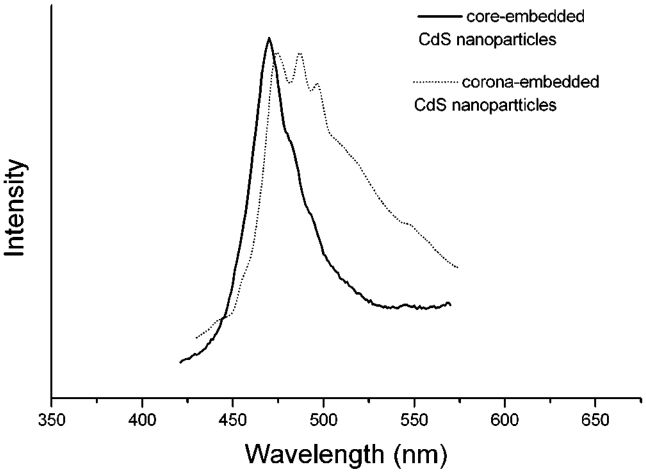

Figure 4. Photoluminescence spectra of core-embedded and corona-embedded CdS nanoparticles. The preparation of core-embedded and corona-embedded CdS nanoparticles and the concentration of block copolymer in THF are the same as described in Figure 3.

ticle solution into 20 mL of water with a pH value of 3.3. The diameters of the micelles are in the range of 20−80 nm, which is smaller than the compound micelles. The formation of compound micelles is based on complex formation between 2VP units and Cd^{2+}. In a compound micelle, there exist soluble PS blocks and free P2VP segments because of the equilibrium in the complex formation (Figure 1).[20] However, in the micelles prepared in water, collapsed PS chains exist in the core and P2VP chains exist in the corona along with the nanoparticles. This kind of micelle can be treated as a single micelle. Compared to the single micelles, a compound micelle has a looser structure and a larger size. By careful examination of the TEM image, it can be seen that the nanoparticles are mostly localized in the corona region in Figure 3b. This morphology is just like a colloidal core−shell structure. This TEM image strongly proves that nanoparticles are located around the corona of the micelles and form the red currant morphology.[16,18] The diameters of the corona-embedded nanoparticles are from 2 to 5 nm.

Figure 4 shows photoluminescence (PL) spectra of core-embedded CdS nanoparticles and corona-embedded nanoparticles. It is noted that after the location change of the nanoparticles from core-embedded nanoparticles to corona-embedded nanoparticles the PL maximum red-shifts and becomes broader. The shape of the band also changes; one narrow peak is split into three peaks. For CdS nanoparticles, the position and width of PL peaks are dependent on the size and the size distribution of nanoparticles.[6,21,22] In this experiment, the red-shift and the broadening of the PL peak are related to the increase in the nanoparticle size and the widening of the size distribution. The splitting of the peak may be due to the change of the surface of the nanoparticles and change of the solvent from THF to water.

In Situ Preparation of Corona-Embedded CdS Nanoparticles. Figure 5a shows a TEM image of micelles with corona-embedded CdS nanoparticles prepared by dropping 1 mL of PS-*b*-P2VP−Cd^{2+} complex THF solution into 10 mL of water with a pH value of 3.3, followed by addition of 1-fold excess Na_2S/methanol solution. The polymer concentration is 1.25 g/L. On the image, CdS nanoparticles can be observed in the corona of the micelles. The diameters of the micelles and CdS nanoparticles range from 40 to 100 nm and 2 to 7 nm, respectively. Figure 5 b is a magnified TEM image of an individual micelle with corona-embedded CdS nanoparticles. This image clearly shows that CdS nanoparticles are located in the corona of the micelle, which is similar to a colloidal core−shell structure.

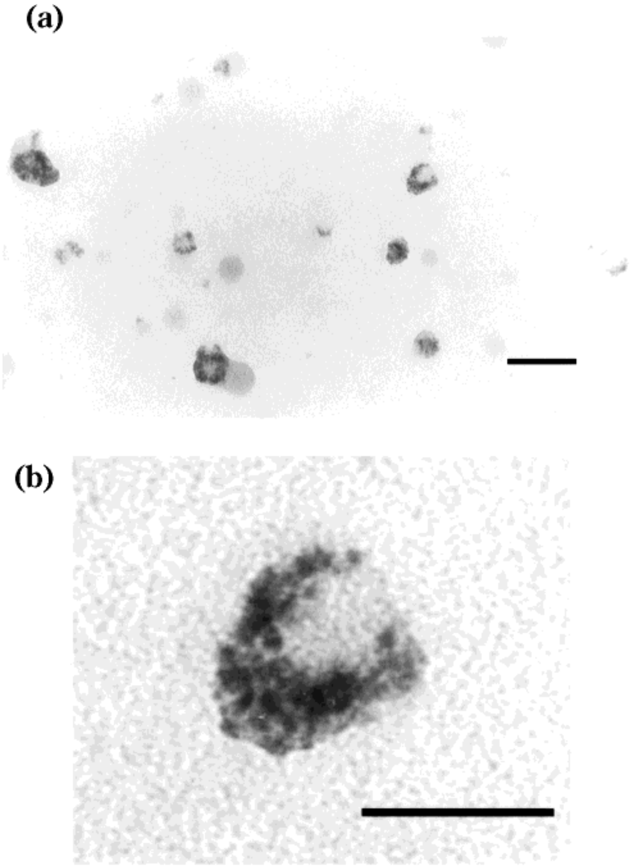

Figure 5. (a) TEM image of corona-embedded CdS nanoparticles prepared by dropping 1 mL of PS-*b*-P2VP−Cd^{2+} complex solution (1.4 g/L) into 10 mL of water with a pH value of 3.3, followed by addition of 1-fold excess Na_2S/H_2O solution and (b) a magnified micelle with CdS nanoparticles. Scale bars on Figure 5a and Figure 5b represent 100 and 50 nm, respectively.

Since the solubility of the P2VP block in water is dependent on the pH value,[23] it is interesting to investigate the effect of starting pH value on the prepared CdS nanoparticles. Figure 6 shows UV−vis absorption spectra of CdS nanoparticles prepared in water with pH values of 2.5 and 3.3. Their absorption edges are at about 480 and 475 nm, respectively, which means the nanoparticles prepared at a lower starting pH value are larger. This influence can be explained by the fact that in water with a lower pH value, P2VP blocks are more extended and their stabilizing ability is less, causing a greater tendency for smaller CdS

---

(21) Sooklal, K.; Hanus, L. H.; Ploehn, H. J.; Murphy, C. *J. Adv. Mater.* **1998**, *10*, 1083.

(22) Yang, C. S.; Awschalm, D. D.; Stucky, G. D. *Chem. Mater.* **2001**, *13*, 594.

(23) Martin, T. J.; Prochazka, K.; Munk, P.; Webber, S. E. *Macromolecules* **1996**, *29*, 6071.

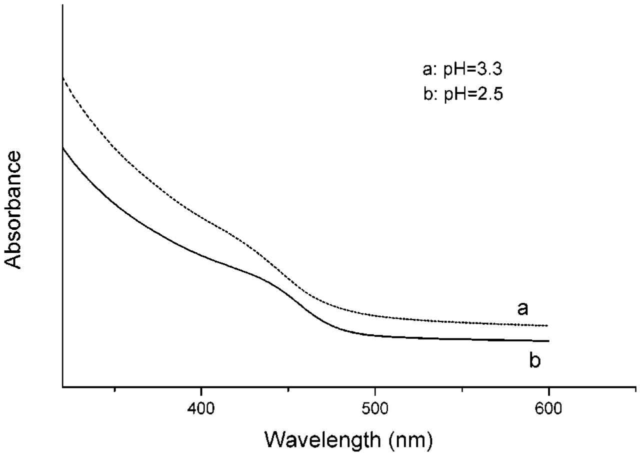

Figure 6. UV-vis absorption spectra of corona-embedded CdS nanoparticles prepared by dropping 1 mL of PS-*b*-P2VP−Cd^{2+} complex solution (20 g/L) into 10 mL of water with pH values of 2.5 and 3.3, respectively, followed by addition of 1-fold excess Na_2S/H_2O solution.

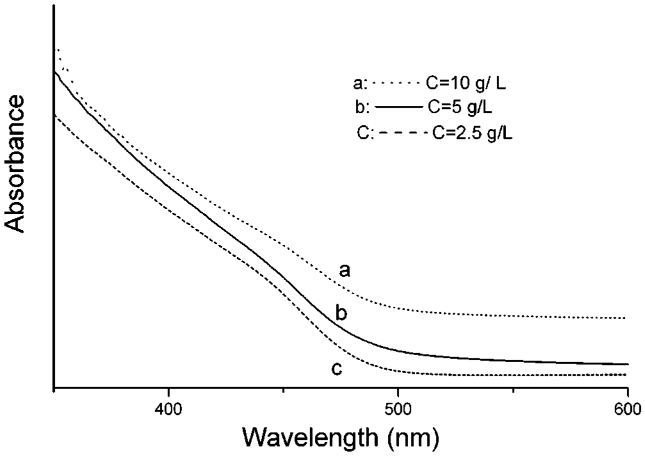

Figure 7. UV-vis absorption spectra of corona-embedded CdS nanoparticles prepared by dropping 1 mL of complex solution with various concentrations into 10 mL of water with a pH value of 3.3, followed by addition of 1-fold excess Na_2S/H_2O solution.

nanoparticles to aggregate into larger particles as they form. When the pH value reached 5.0, polymer precipitation appeared. At this pH value, water is no longer a solvent for the P2VP block.

In the preparation of CdS core-embedded nanoparticles in salt-induced block copolymer micelles, it is found that with a decrease of block copolymer concentration in THF, the size of the CdS nanoparticles decreases.[20] Initial polymer concentration is also an important factor in controlling the size of the nanoparticles in corona-embedded nanoparticles. Figure 7 shows UV−vis absorption spectra of corona-embedded CdS nanoparticles prepared by dropping 1 mL of PS-*b*-P2VP−Cd^{2+} complex THF solution with different concentrations into 10 mL of water (pH = 3.3), followed by addition of 1-fold Na_2S solution. It is noted that as the complex concentration decreases from 10 g/L through 5 g/L to 2.5 g/L, the absorption edge blue-shifts from 492 nm through 487 nm to 482 nm, which means smaller corona-embedded nanoparticles are formed at a lower complex concentration. At a higher complex concentration, there will be more chances for micelles to interact with each other and thus more chances for CdS nanoparticles located in the corona of the micelles to aggregate into larger particles.

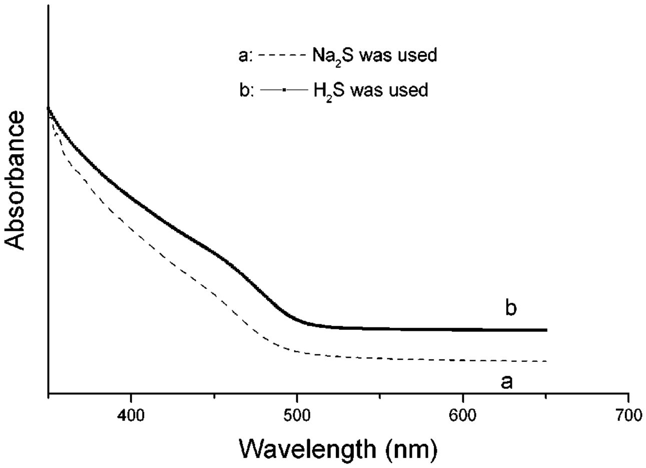

Figure 8. UV-vis absorption spectra of corona-embedded CdS nanoparticles prepared by adding 1-fold excess Na_2S/H_2O solution or introduction of H_2S gas into complex solutions.

H_2S gas also can be used to prepare CdS nanoparticles. Figure 8 shows two UV−vis absorption spectra of corona-embedded CdS nanoparticles, which were prepared by adding Na_2S/H_2O solution or introducing H_2S gas into two micelle solutions with the same polymer concentrations and starting pH values. The absorption edge of the corona-embedded CdS nanoparticles prepared using Na_2S solution is at about 488 nm; however, when H_2S gas is used it is at 502 nm. This difference can be explained by the change of pH values in the solution. After H_2S gas is introduced into the complex solution, the pH value of the solution decreases; after Na_2S solution is added into the complex solution, the pH value of the solution increases. As described above, a lower pH results in the formation of larger particles, and thus H_2S results in larger particles than Na_2S.

Conclusion

Core-embedded CdS nanoparticles were converted to corona-embedded CdS nanoparticles by dropping a THF solution of CdS/block copolymer compound micelle solution into water with a low pH value. This transition is accompanied by a structural change from compound micelles to single micelles. The core of a single micelle is composed of the collapsed PS chains, and the corona is composed of water-soluble P2VP−H^+ complex. CdS nanoparticles exist in the corona of these micelles. P2VP chains interact with the nanoparticles at their surface and stabilize the nanoparticles. CdS nanoparticles distribute randomly in the corona of a single micelle, forming a red currant structure. Compared with core-embedded nanoparticles, the size of the corona-embedded CdS nanoparticles increased slightly after the transition due to the desorption of a part of the 2VP chains from the nanoparticle surface.

When a compound micelle solution formed by PS-*b*-P2VP−Cd^{2+} complex was dropped into water with a low pH value, the compound micelle was transformed to a single micelle. In a single micelle, collapsed PS chains form the core and P2VP−H^+ complex form the corona, with Cd^{2+} clusters in the corona of the micelle. Upon addition of Na_2S/water solution (or introduction of H_2S gas) into the single micelle solution, corona-embedded CdS nanoparticles can be prepared. Again, the CdS nanoparticles distribute randomly in the corona of micelles, forming a red currant structure. The starting pH value of water, the complex concentration, and the S^{2-} source affect the size of the CdS nanoparticles.

Acknowledgment. We would like to thank Dr. Jill Verlander Reed and Ms. Melissa Ann Lewis, College of Medicine, Electron Microscopy Core Facility, University of Florida, for help in performing the transmission electron microscopy and Prof. Kirk S. Schanze and Mr. Benjamin S. Harrison, Department of Chemistry, University of Florida, for help with the fluorescence measurements and analysis. Financial support of the Center for Materials in Sensors and Actuators (MINSA, Grant No. DAAD19-00-1-0002) is gratefully acknowledged.

CM011581+