

Synthesis of Submicrometer-Sized CdS Hollow Spheres in Aqueous Solutions of a Triblock Copolymer

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Submicrometer-sized hollow CdS spheres with a wall thickness of about 20 nm have been synthesized in aqueous solutions of cadmium acetate ($\text{Cd}(\text{OAc})_2$) and the triblock copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (P123) at room temperature through the slow release of S^{2-} ions from thioacetamide (TAA). X-ray powder diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), thermogravimetric analysis (TGA), UV–vis absorption, and photoluminescence (PL) spectroscopy have been used for the characterization of the obtained hollow CdS spheres. It has been revealed that a minimum concentration of the polymer P123 was required for the formation of hollow CdS spheres and a double sonication condition was essential for the formation of pure hollow spheres. TEM and dynamic light scattering (DLS) studies have suggested that $\text{Cd}(\text{OAc})_2$ could induce P123 to form large complex micelles in the solution but $\text{Cd}(\text{NO}_3)_2$ could not, resulting in the formation of hollow CdS spheres in the acetate system and loose CdS aggregates in the nitrate system. A templating mechanism has been proposed for the production of the hollow CdS spheres; that is, the complex micelles formed by P123 and cadmium acetate acted as soft templates for the precipitation of CdS particles around the surface of the spherical aggregates, leading to the formation of the final hollow spheres.

Introduction

Inorganic hollow spheres having tailored structural, optical, and surface properties represent an important class of materials that may find applications in a wide range of areas such as delivery vehicle systems, photonic crystals, fillers, and catalysts.^{1–5} Recent efforts to prepare inorganic hollow spheres have been focused on inorganic precipitation processes against a variety of sacrificial templates. Generally, the employed templates include “hard templates”, such as silica spheres,^{4,6} polystyrene latex spheres,^{2,7–9} resin spheres,¹⁰ and core–shell gel particles,⁵ and “soft templates”, such as vesicles,¹¹ liquid droplets,^{3,12} emulsion droplets,^{13,14} as well as block copolymer micelles.^{15–18}

Recently, many efforts have been devoted to the synthesis of hollow spheres of chalcogenide semiconductors

because of their useful properties and technological importance. For example, hollow ZnS spheres have been synthesized by using silica⁶ and polystyrene⁹ spheres as hard templates, respectively. On the other hand, hollow CdS spheres have been fabricated through mineralization of cubic lyotropic liquid crystals¹⁹ or through an interface-mineralizing route in CS_2 solutions.^{20,21} In addition, some special synthetic pathways including hydrothermal, sonochemical, and radiation methods have been employed for the synthesis of hollow chalcogenide spheres. For instance, hollow Ag_2S spheres with a novel quasi-network microstructure were produced under hydrothermal conditions²² whereas hollow NiS spheres were synthesized in a PMMA– CS_2 –ethanol–aqueous system using γ -irradiation at room temperature.²³ Notably, Zhu and co-workers²⁴ synthesized hollow CdSe spheres using $\text{Cd}(\text{OH})_2$ as an in-situ template via a sonochemical route. However, it remains a great challenge to develop facile and environmentally benign methods for creating hollow spherical structures of chalcogenide semiconductors.

We have recently demonstrated that micelles formed in mixed solutions of surfactant and double-hydrophilic block copolymer can be used as effective soft templates for the synthesis of hollow spheres of inorganic materials including mineral CaCO_3 ¹⁶ and metal Ag.¹⁷ Furthermore, we have briefly reported a novel synthesis of hollow semiconductor ZnS nanospheres in aqueous solutions of an amphiphilic triblock copolymer at room temperature, which may represent a facile and mild synthetic route to hollow spheres of sulfide semiconductors.¹⁸ However, such an approach remains to be extended to other sulfide

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systems and further investigation is required to elucidate the formation mechanism of hollow sulfide spheres. In this work, submicrometer-sized hollow CdS spheres were produced by a similar synthetic method and the effects of a variety of experimental conditions on the synthesis were examined carefully, which shed new light on the formation mechanism.

Experimental Section

The Pluronic amphiphilic triblock copolymer P123, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{\text{av}} = 5800$), was obtained from Aldrich. The synthesis of hollow CdS spheres was similar to the reported synthesis of hollow ZnS spheres¹⁸ except for the ultrasonic mixing conditions. In a typical synthesis, 0.4 g of P123 was dissolved completely in 8 mL of water, and then 0.5 mL of 0.5 mol·L⁻¹ cadmium acetate ($\text{Cd}(\text{OAc})_2$) was added to the solution, followed by 5 min of sonication in a normal ultrasonic bath (50 Hz). Then, 0.5 mL of 0.5 mol·L⁻¹ thioacetamide (TAA) was added to the solution, followed by another 5 min of sonication, which gave a final P123 concentration of 44 g·L⁻¹ and a final $\text{Cd}(\text{OAc})_2$ (or TAA) concentration of 0.028 M. The mixture was then maintained under a static condition at 27 °C for 5 h (unless otherwise stated), and the slow release of S^{2-} ions from TAA led to the formation of CdS particles. The resulting solution was centrifuged at 3000 rpm, and a yellow solid was obtained. After removal of the supernatant, the remaining solid was repeatedly washed with ethanol under sonication and separated by centrifugation. The final product was dried as a powder at 50 °C. In the experiments, the concentration of P123 was varied from 0 to 88 g·L⁻¹, various ultrasonic mixing conditions were examined, and cadmium nitrate was also used to replace cadmium acetate for investigating the effect of the cadmium source.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) investigations were conducted on a JEOL JEM-200CX microscope operated at 160 kV and a Hitachi H-9000HAR microscope operated at 300 kV, respectively. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax-2000 diffractometer with Cu K α radiation. UV-vis absorption spectra were obtained on a Shimadzu UV-250 spectrophotometer, and photoluminescence (PL) spectra were recorded with a Hitachi F-4500 spectrofluorometer. Thermogravimetric analysis (TGA) was measured on a Thermal Analysis SDT 2960 instrument in air. Dynamic light scattering (DLS) experiments were carried out in water at 27 °C with ALV SLS-5022F laser light scattering spectroscopy and a Spectra-Physics 2017 Ar laser (514.5 nm wavelength). The scattering angle was 90°, and the intensity autocorrelation functions were analyzed by using the methods of Contin and Cumulant. For the DLS measurements, P123 and $\text{Cd}(\text{OAc})_2$ (or $\text{Cd}(\text{NO}_3)_2$) solutions were centrifuged at 12000 rpm to remove the dust in advance, respectively. Then, 0.5 mL of 0.5 mol·L⁻¹ $\text{Cd}(\text{OAc})_2$ (or $\text{Cd}(\text{NO}_3)_2$) solution was mixed with 8 mL of 44 g·L⁻¹ P123 solution, followed by 5 min of sonication, and the resultant solution was used for the DLS measurements.

Results and Discussion

Typical TEM images of hollow CdS spheres obtained in 44 g·L⁻¹ P123 solution after aging for 5 h were presented in Figure 1, which showed strong contrast between the dark edge and the pale center of the spherical particles evidencing their hollow nature. As shown in Figure 1a, the diameter of the hollow spheres is about 80–120 nm, with an average diameter about 100 nm, and the wall thickness is about 20 nm. The related electron diffraction (ED) pattern showed principally three rings with d spacings 0.33, 0.195, and 0.164 nm, which corresponded to the (111), (220), and (311) planes of cubic CdS of the zinc blende structure, respectively. The enlarged TEM images shown in Figure 1b suggested that the wall of hollow CdS spheres consisted of primary CdS nanoparticles. The HRTEM image shown in Figure 1c exhibited clear lattice fringes with d spacings of 0.33 and 0.29 nm,

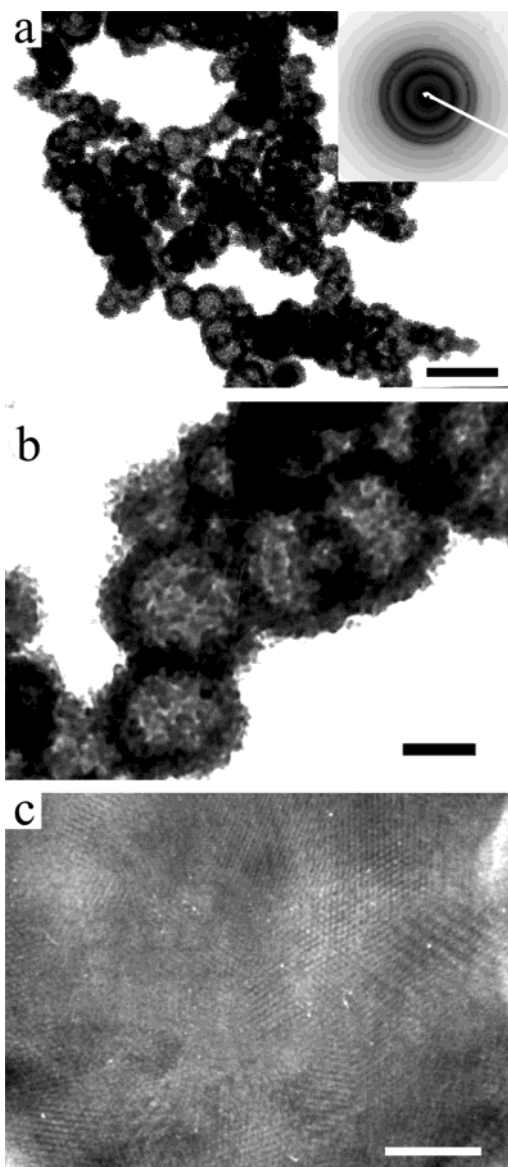


Figure 1. TEM (a and b) and HRTEM (c) images of hollow CdS spheres obtained in an aqueous solution of P123 after aging for 5 h. $[\text{P123}] = 44 \text{ g}\cdot\text{L}^{-1}$. The inset shows the corresponding ED pattern. Scale bars: (a) 200 nm, (b) 50 nm, (c) 5 nm.

which corresponded to (111) and (200) reflections of the cubic CdS structure, respectively, confirming the crystalline nature of the primary CdS particles. The HRTEM image also indicated that the diameter of the individual CdS nanocrystals was about 3–5 nm. The XRD pattern of the hollow CdS spheres was shown in Figure 2, which was consistent with the cubic CdS structure. The diffraction peaks were fairly broad, and an average crystallite size of about 3 nm was roughly estimated according to the line width analysis of the (111) diffraction peak based on the Scherrer formula. Thermogravimetric analysis of the as-dried powder sample in air shows about 4.1% weight loss corresponding to desorption and decomposition of occluded polymer. This result suggests that only a rather small amount of polymer was occluded in the hollow structures, indicating that the CdS shell comprising primary particles was not completely solid and most of the copolymers were washed out through the small holes in the closed shell, leading to the formation of really hollow CdS spheres. It is noted that hollow spheres fabricated by using soft templates in solution usually consisted of a

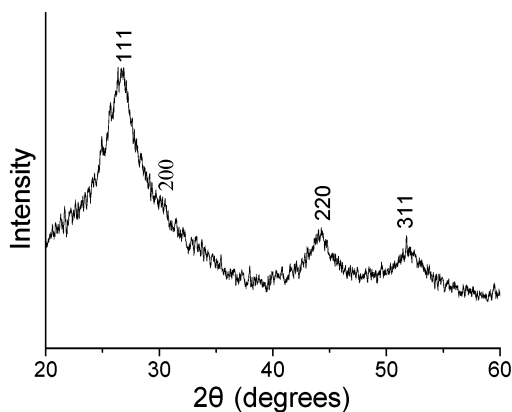


Figure 2. XRD pattern of hollow CdS spheres obtained in an aqueous solution of P123 after aging for 5 h. $[P123] = 44 \text{ g}\cdot\text{L}^{-1}$.

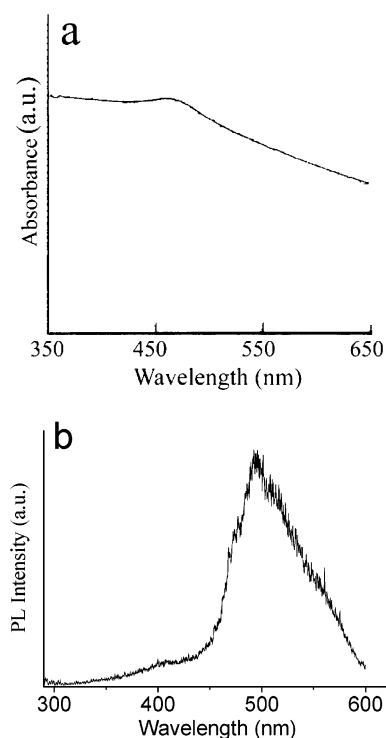


Figure 3. UV-vis absorption (a) and photoluminescence (b) spectra of CdS hollow spheres obtained in an aqueous solution of P123 after aging for 5 h. $[P123] = 44 \text{ g}\cdot\text{L}^{-1}$; $\lambda_{\text{ex}} = 224 \text{ nm}$.

porous rather than a solid shell that allowed for the transport of organic templates out of the shell upon washing.^{16–18}

Figure 3 shows the UV-vis absorption and photoluminescence (PL) spectra of the obtained hollow CdS spheres, which were obtained after the dried product was redispersed in ethanol. As shown in Figure 3a, the absorption spectrum shows a peak at 460 nm, which is blue-shifted considerably relative to the absorption onset of bulk CdS (ca. 515 nm) because of the quantum size effect. The spectrum shows a long absorption tail due to scattering by the particles in the dispersion system, which is similar to the case of hollow ZnS spheres.¹⁸ Basically, the position of the excitonic peak will not be influenced by the long tail in the spectrum. According to the experimental correlation between the absorption onset and the particle diameter for CdS,²⁵ the particle size of

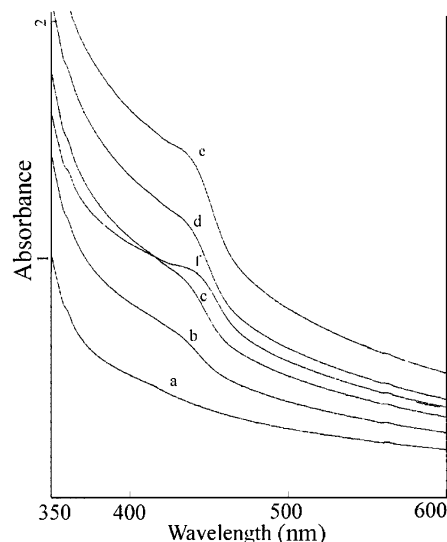


Figure 4. UV-vis spectra of CdS products formed in an aqueous solution of P123 at earlier stages of the formation of hollow CdS spheres. $[P123] = 44 \text{ g}\cdot\text{L}^{-1}$. Aging time: (a) 0, (b) 10, (c) 20, (d) 30, (e) 60, and (f) 80 min.

the CdS nanocrystals was estimated to be about 3 nm. It suggests that the size of the CdS nanocrystals constituting the hollow spheres is about 3 nm, which is in good agreement with the results obtained from both TEM and XRD. The PL spectrum of the hollow CdS spheres was shown in Figure 3b, which exhibited a broad emission peak centered around 440 nm, blue-shifted considerably from the emission of bulk CdS (ca. 520 nm). The observed broad PL peak is commonly attributed to the recombination of charged carriers trapped in the surface states and is related to the size of the CdS nanoparticles; that is, the PL band of the smaller nanoparticles appears at shorter wavelengths.^{26–28} Therefore, the PL emission of the hollow CdS spheres indicated they actually consisted of primary CdS nanocrystals showing a quantum size effect.

The formation process of the hollow CdS spheres was examined by measuring the UV-vis absorption spectra of the reaction solution at various aging times. After 5 min of sonication following the addition of TAA, the mixture was transferred into a 1 cm quartz cell thermostated at 27 °C immediately and UV-vis spectra were recorded at varied time intervals, which were shown in Figure 4. At the right beginning, the solution showed no color and there was no obvious peak in the absorption spectrum (Figure 4a). After being aged for 10 min, the solution became pale yellow and a shoulder peak around 440 nm appeared in the absorption spectrum accompany a considerable increase in the absorbance (Figure 4b), indicating a gradual formation of CdS particles due to the release of S^{2-} ions from TAA. With increasing time up to 1 h, the overall absorbance increased continuously and the position of the shoulder peak remained unchanged essentially, suggesting the formation of more and more CdS particles and the possible presence of large aggregates of the primary CdS particles. After 1 h of aging, some yellow precipitates were observed on the bottom of the quartz cell by naked eyes, indicating a considerable sedimentation occurred. Accordingly, the absorption spectrum obtained at an aging time of 80 min showed a considerable decrease in the overall absorbance and the

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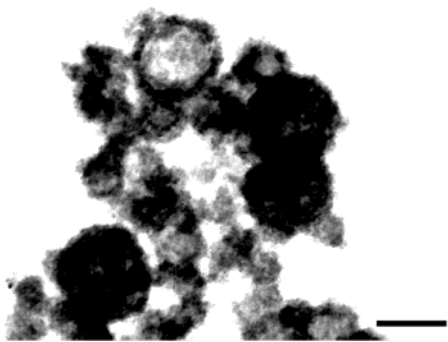


Figure 5. TEM image the CdS product obtained in an aqueous solution of P123 after aging for 30 min. $[P123] = 44 \text{ g}\cdot\text{L}^{-1}$. Scale bar = 100 nm.

absorption peak red-shifted to about 460 nm (Figure 4f), which was very similar to the case of the absorption spectrum of the CdS product obtained after aging for 5 h (Figure 3a). Figure 5 presents a typical TEM image of the CdS product obtained after 30 min of aging, which shows the coexistence of hollow spheres and irregular aggregates. It indicates that at this stage hollow CdS spheres already formed but most of them did not grow well, resulting in an incomplete or unstable shell, which could be easily crippled into irregular aggregates during repeated washing and separation.

For developing a comprehensive understanding of the formation mechanism of the hollow CdS spheres, it is essential to investigate the effects of various synthesis conditions on the formation of the hollow spheres. Hence, a variety of reaction parameters such as the polymer concentration, the ultrasonic mixing conditions, as well as the cadmium precursor were examined in detail.

Typical TEM images of CdS particles obtained at varied polymer concentrations are shown in Figure 6. It can be seen from Figure 6a that only solid CdS particles about 20–30 nm were synthesized in the absence of P123. In the presence of a low concentration of P123 ($11 \text{ g}\cdot\text{L}^{-1}$), loose CdS spheres were obtained (Figure 6b), similar to the loose ZnS spheres obtained in the P123 solution.¹⁸ As the P123 concentration was increased to $22 \text{ g}\cdot\text{L}^{-1}$, hollow CdS spheres with a diameter about 50–90 nm and a shell thickness of about 20 nm were produced (Figure 6c). Increasing the polymer concentration to $44 \text{ g}\cdot\text{L}^{-1}$ resulted in the formation of the hollow CdS spheres shown in Figure 1, which had a relatively larger diameter (80–120 nm) and a similar shell thickness ($\sim 20 \text{ nm}$). If the polymer concentration was further increased to $88 \text{ g}\cdot\text{L}^{-1}$, hollow spheres of about 60–140 nm were produced, which showed a much wider size distribution (Figure 6d). This result indicated that a minimum concentration of the polymer P123 was required for the formation of hollow CdS spheres and the hollow spheres could be produced at P123 concentrations between 22 and $88 \text{ g}\cdot\text{L}^{-1}$. With increasing P123 concentration, the diameter of the hollow spheres increased at first and then the polydispersity of the diameter increased considerably. The overall variation trend upon increasing polymer concentration is reminiscent of the synthesis of hollow ZnS spheres in P123 solutions where the formation of the hollow ZnS spheres could result from templating against Zn(OAc)₂ induced large P123 aggregates.¹⁸ Similarly, the formation of the present hollow CdS spheres could result from templating against complex micelles formed by P123 and Cd(OAc)₂, that is, Cd(OAc)₂ induced large P123 aggregates. The complex micelles could become larger with increasing P123 concentration from 22 to $44 \text{ g}\cdot\text{L}^{-1}$, leading to formation of the larger hollow CdS spheres.

For the synthesis of hollow CdS spheres, a standard ultrasonic mixing condition was adopted, that is, sonication for 5 min after adding Cd(OAc)₂ and sonication for another 5 min after adding TAA. However, CdS particles were also produced under different ultrasonic mixing conditions to explore the effect of ultrasonic mixing (Figure 7). As shown in Figure 7a, only solid CdS particles of about 30 nm were produced without sonication during the whole mixing process. If the sonication was carried out only after the addition of Cd(OAc)₂, irregular aggregates of about several hundred nanometers were obtained (Figure 7b). When the sonication was carried out only after the addition of both Cd(OAc)₂ and TAA, a mixture of hollow spheres and solid spheres was obtained (Figure 7c). These results indicated that the double sonication was essential for the formation of pure hollow CdS spheres. It was reasonably supposed that the role of the first sonication was to mix the Cd(OAc)₂ and P123 completely to form complex micelles in the solution. The role of the second sonication was supposed to be to accelerate the release of S²⁻ ions from TAA, leading to the nucleation of CdS particles around the complex micelles, which is essential for the subsequent growth of complete hollow spheres during the aging stage. It is noted that pure hollow ZnS spheres have been produced by one-step sonication of 10 min after the addition of both Zn(OAc)₂ and TAA,¹⁸ which is in contrast to the present case. It can be rationalized by considering that the reaction between Cd(OAc)₂ and TAA takes place much faster than the reaction between Zn(OAc)₂ and TAA, especially during the ultrasonic mixing stage. For the ZnS synthesis, the reaction between Zn(OAc)₂ and TAA might take place after the mixing between Zn(OAc)₂ and P123 was complete, resulting in the formation of hollow ZnS spheres, whereas the reaction between Cd(OAc)₂ and TAA might take place accompanying the mixing between Zn(OAc)₂ and P123, resulting in the formation of a mixture of hollow and solid CdS spheres. It is noteworthy that hollow CdSe spheres have been sonochemically synthesized by using Cd(OH)₂ as an in-situ template where high-intensity ultrasonic irradiation was employed to accelerate the conversion of Cd(OH)₂ into CdSe.¹⁴ Obviously, the sonication here played a quite different role compared with the sonication used in the present synthesis of hollow CdS spheres.

Investigation on the effect of the cadmium source on the formation of hollow CdS spheres provided useful information about the formation mechanism. Figure 8 shows a typical TEM image of the CdS product obtained by using Cd(NO₃)₂ instead of Cd(OAc)₂ as the cadmium source under otherwise similar conditions. Interestingly, loose CdS aggregates of about 50–80 nm instead of hollow CdS spheres were obtained. This result is reminiscent of the synthesis of hollow CdS spheres through mineralization of cubic liquid crystals formed by amphiphilic block copolymers where Cd(OAc)₂ was in favor of the formation of hollow spheres but Cd(NO₃)₂ was unfavorable although the exact reason was unclear.¹⁹ In a latter report,²⁹ the authors further studied the counterion effects in liquid crystal templating of nanostructured CdS and explained the differences in product morphologies between the acetate and nitrate systems in terms of Ostwald ripening; that is, in the nitrate system the byproduct HNO₃ could dissolve CdS, thus allowing Ostwald ripening, whereas in the acetate system the byproduct HAc could not dissolve CdS and thus Ostwald ripening was not expected. However, this explanation seems not applicable for the

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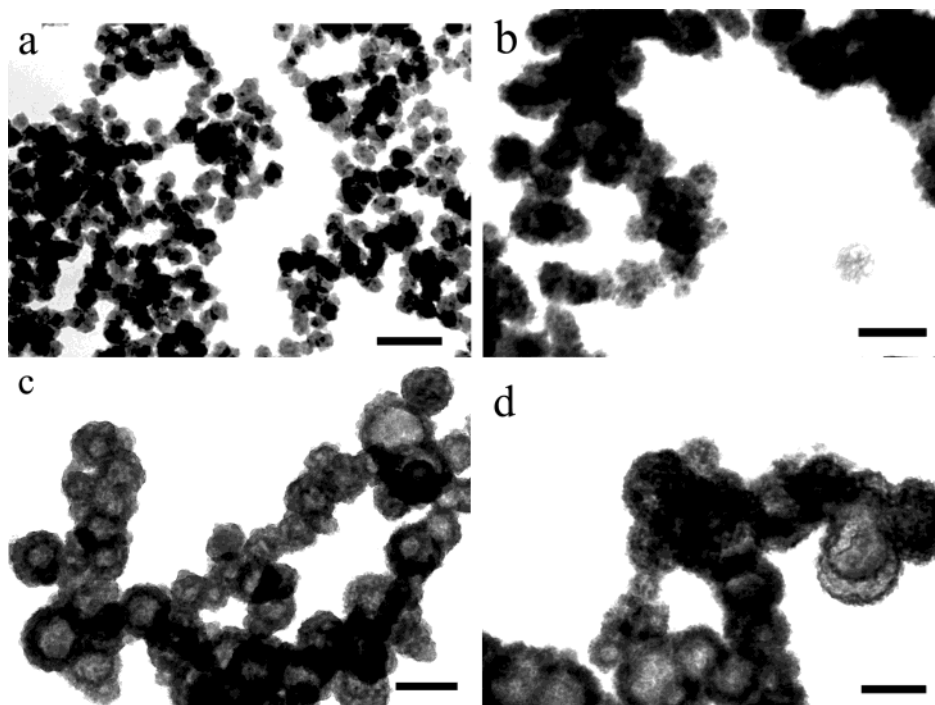


Figure 6. TEM images of CdS products obtained in an aqueous solution of P123 after aging for 5 h. [P123]: (a) 0, (b) 11, (c) 22, and (d) $88 \text{ g}\cdot\text{L}^{-1}$. Scale bars = 100 nm.

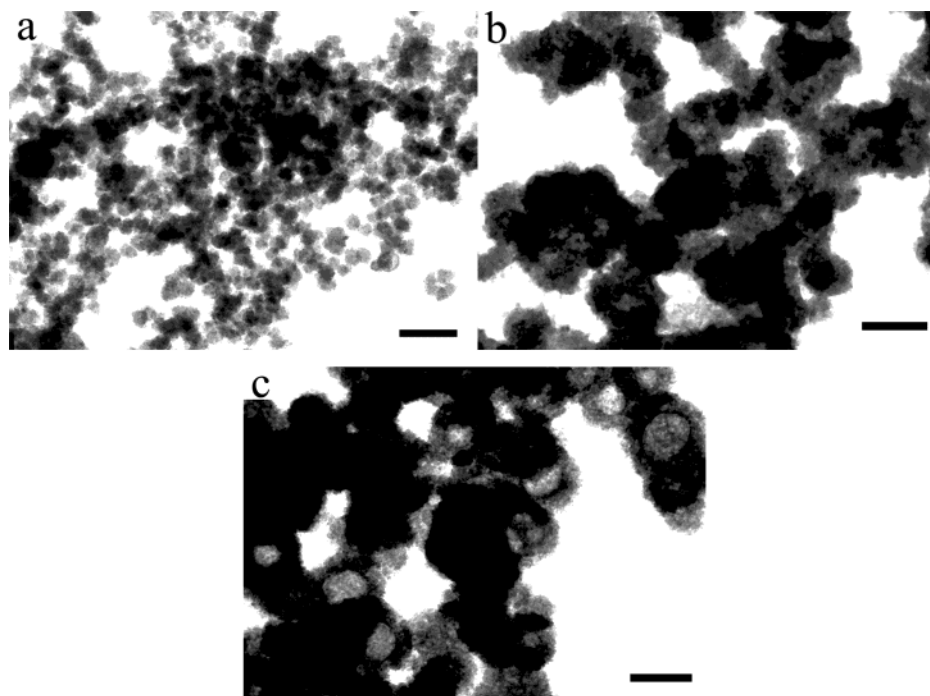


Figure 7. TEM images of CdS products obtained in an aqueous solution of P123 after aging for 5 h but under different ultrasonic mixing conditions: (a) without sonication; (b) with sonication for 5 min after adding $\text{Cd}(\text{OAc})_2$ but without sonication after adding TAA; (c) without sonication after adding $\text{Cd}(\text{OAc})_2$ but with sonication for 5 min after adding TAA. Scale bars = 100 nm.

present case because Ostwald ripening should not be essential for the formation of hollow CdS spheres in the polymer solution. Therefore, further investigation on the interaction of the two Cd^{2+} ion salts with P123 in the solution is required to shed light on the formation mechanism of the hollow CdS spheres.

Both TEM and dynamic light scattering (DLS) studies were carried out for the aqueous $\text{Cd}(\text{OAc})_2$ -P123 and $\text{Cd}(\text{NO}_3)_2$ -P123 systems. Before the TEM sample preparation and the DLS measurements, a solution containing $44 \text{ g}\cdot\text{L}^{-1}$ P123 and 0.028 M cadmium acetate (or nitrate)

was ultrasonified for 5 min as in the preparation of hollow CdS spheres. A drop of the solution was directly dropped on a TEM copper grid, which was dried in air and then used for the TEM observation. Spherical, compact aggregates up to larger than 100 nm were evident in the acetate system (Figure 9a) whereas irregular, loose aggregates were observed in the nitrate system (Figure 9b). It is speculated that large spherical aggregates or complex micelles, which were induced by $\text{Cd}(\text{OAc})_2$, existed in the acetate system and only primary P123 micelles existed in the nitrate system, which aggregated into

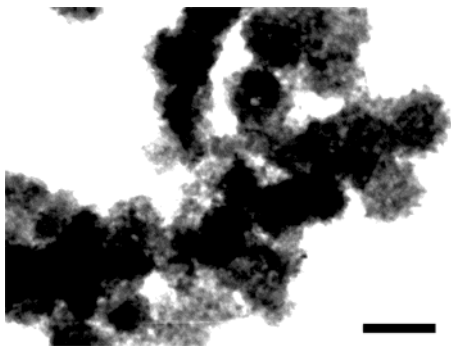


Figure 8. Loose CdS aggregates obtained in an aqueous solution of P123 after aging for 5 h by using $\text{Cd}(\text{NO}_3)_2$ instead of $\text{Cd}(\text{OAc})_2$ as the cadmium source. $[\text{P123}] = 44 \text{ g}\cdot\text{L}^{-1}$. Scale bar = 100 nm.

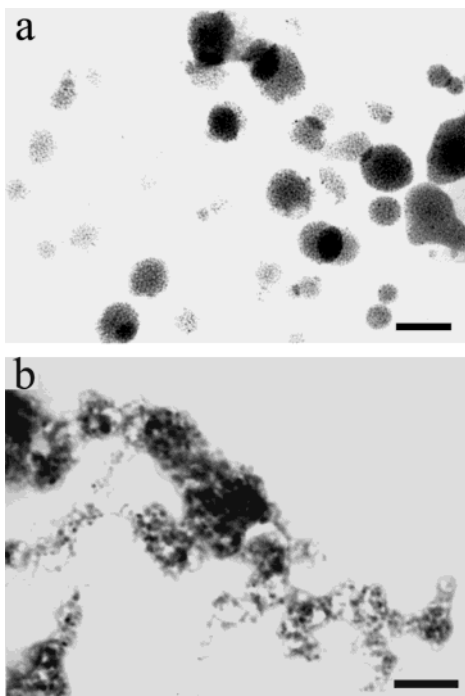


Figure 9. TEM images of P123 micelles containing $\text{Cd}(\text{OAc})_2$ (a) and $\text{Cd}(\text{NO}_3)_2$ (b). $[\text{P123}] = 44 \text{ g}\cdot\text{L}^{-1}$; $[\text{Cd}(\text{OAc})_2]$ and $[\text{Cd}(\text{NO}_3)_2] = 0.028 \text{ M}$. Scale bars = 100 nm.

irregular aggregates upon drying on the copper grid. The related DLS result (Figure 10) provided support for this speculation. It was shown that large aggregates (larger than 100 nm) coexisted with primary polymer micelles (average hydrodynamic radius $R_h \sim 9.3 \text{ nm}$) in the $\text{Cd}(\text{OAc})_2$ -P123 system whereas only primary polymer micelles ($R_h \sim 8.9 \text{ nm}$) existed in the $\text{Cd}(\text{NO}_3)_2$ -P123 system. Similar spherical aggregates have also been observed in the solution of $\text{Cd}(\text{OAc})_2$ and polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) in THF where the spherical aggregates formed due to the complexation of Cd^{2+} ions with the 2-vinylpyridine units.²⁷ In the current situation, the large spherical aggregates could result from the complexation of Cd^{2+} with the EO units, as it has been revealed that the EO units of nonionic surfactants can form hydrogen bonds with Cd^{2+} in the aqueous solution.³⁰ It has been documented that anions significantly influence the self-assembly and phase behavior of amphiphilic triblock copolymers in water.^{31,32} According to the Hofmeis-

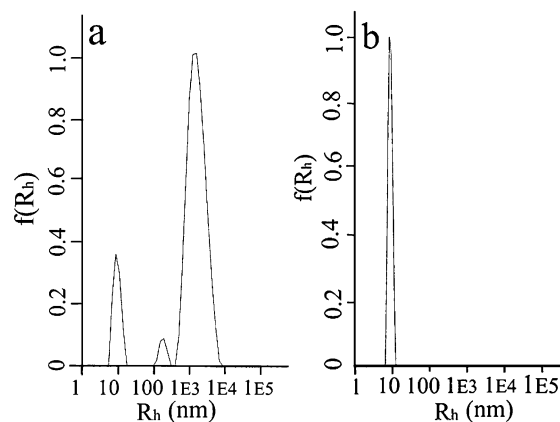


Figure 10. Hydrodynamic radius (R_h) distribution of P123 micelles containing $\text{Cd}(\text{OAc})_2$ (a) and $\text{Cd}(\text{NO}_3)_2$ (b). $[\text{P123}] = 44 \text{ g}\cdot\text{L}^{-1}$; $[\text{Cd}(\text{OAc})_2]$ and $[\text{Cd}(\text{NO}_3)_2] = 0.028 \text{ M}$.

ter series of anions,³³ acetate ions are salting-out ions that are able to decrease the solubility of the PPO block whereas nitrate ions are salting-in ions that are able to increase the solubility of the PPO block. Accordingly, $\text{Cd}(\text{OAc})_2$ could induce P123 to form large complex micelles in the solution but $\text{Cd}(\text{NO}_3)_2$ could not, which would result in the formation of the hollow CdS spheres templated by the complex micelles in the acetate system and the production of the loose CdS aggregates in the nitrate system.

Therefore, the formation mechanism of the hollow CdS spheres was proposed as follows. At first, $\text{Cd}(\text{OAc})_2$ and P123 formed large complex micelles in aqueous solution upon the first sonication. Then, the S^{2-} ions released from TAA reacted with the Cd^{2+} ions near the surface of complex micelles to form CdS nuclei surrounding the spherical aggregates, which was considerably accelerated by the second sonication. With aging, the Cd^{2+} ions in the inner part of the complex micelles gradually diffused outward and reacted with the S^{2-} ions released from TAA, resulting in the formation of the final hollow CdS spheres. In short, the complex micelles formed by P123 and cadmium acetate acted as soft templates for the formation of the hollow CdS spheres.

Conclusion

Submicrometer-sized hollow CdS spheres have been facilely synthesized in aqueous solutions of $\text{Cd}(\text{OAc})_2$ and the triblock copolymer P123 at room temperature through the slow release of S^{2-} ions from thioacetamide. The hollow CdS spheres have a wall thickness about 20 nm, which consisted of CdS nanocrystals ($\sim 3 \text{ nm}$) with the cubic zinc blende structure. It has been revealed that a minimum concentration of the polymer P123 was required for the formation of hollow CdS spheres and that, with increasing P123 concentration from 22 to 88 $\text{g}\cdot\text{L}^{-1}$, the diameter of the obtained hollow spheres increased at first and then the polydispersity of the diameter increased considerably. A double sonication condition was found to be essential for the formation of pure hollow CdS spheres. It was supposed that the role of the first sonication was to mix the $\text{Cd}(\text{OAc})_2$ and P123 completely to form complex micelles in the solution whereas the role of the second sonication was to accelerate the release of S^{2-} ions from TAA leading to the nucleation of CdS particles around the complex micelles. It has been shown that $\text{Cd}(\text{OAc})_2$

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could induce P123 to form large complex micelles in the solution but $\text{Cd}(\text{NO}_3)_2$ could not, resulting in the formation of hollow CdS spheres templated by the complex micelles in the acetate system and the production of loose CdS aggregates in the nitrate system. Finally, a templating mechanism has been proposed for the production of the hollow CdS spheres; that is, the complex micelles formed by P123 and cadmium acetate acted as soft templates for the precipitation of CdS particles around the surface of the spherical aggregates, leading to the formation of the final hollow spheres. It is expected that this convenient

synthetic route to hollow CdS spheres may be readily extended to the fabrication of hollow spheres of other technologically important metal chalcogenide semiconductors.

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