

Effects of a Nonionic Surfactant on the pH-Controlled Hydrothermal Synthesis of CdS Sub-micrometer Particles

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The morphological control of semiconductor nanomaterials has received considerable attention for decades because of their unique properties originating from their shapes and sizes.¹⁻⁴ In particular, many researcher has paid much attention to the synthesis and characterization of cadmium sulfide (CdS) nanostructures owing to their useful properties originating from the electronic structures and applications including photocatalysts,⁵ light-emitting diodes,⁶ and solar cells.⁷ CdS has been synthesized by such various methods as solidstate methods,⁸ solvothermal methods,⁹ hydrothermal methods,¹⁰ and calcinations of Cd-thiolate complexes.¹¹ In the previous paper, we reported that spherical submicrometer-sized CdS could readily be synthesized from cadmium ion (Cd²⁺) and L-cysteine (L-Cys) *via* hydrothermal reaction by pH control.¹⁰ However, one shortcoming is that it requires rather long reaction time, namely 3 d, to achieve narrow size distribution, which hampered the practical use of the synthetic method. Therefore, we have been seeking for more facile methods that can shorten the reaction time of the above-mentioned synthetic method. One of the possible ways to achieve the goal might be the use of surfactants to narrow the size distribution. Among many candidates, Pluronic[®] F127 (F127) is a triblock copolymer composed of ethyleneoxide and propyleneoxide (EO₁₀₆-PO₇₀-EO₁₀₆) as shown in Figure 1 and was chosen because it is water-soluble and has been used for the synthesis of many metals, and metal chalcogenide materials.¹²⁻¹⁴ Moreover, it is reported that PF127 forms micelles offering amphiphilic environments in which CdS grows.^{15,16b} Herein, we report the use of a nonionic surfactant, PF127 to shorten the reaction time in the hydrothermal synthesis of spherical CdS submicrometer structures by controlling the solution pH using NaOH in the aqueous mixture of Cd(II) and L-cysteine (L-Cys).

Experimental Section

All the chemicals were of analytical grade and were used

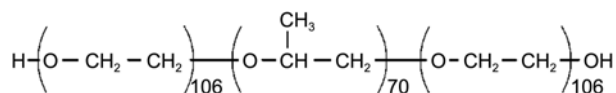


Figure 1. Chemical structure of Pluronic[®] F127.

as-received without further purification. Distilled water was purified by a New P.nix UP 900 water purification system (Human Corporation, South Korea). IR spectra were recorded using a MIDAC M series spectrometer. Powder X-ray diffraction (XRD) spectra were recorded at 40 kV and 30 mA using a Bruker D8 Avance X-ray diffractometer; CuK α radiation was used as the source ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were performed using a HITACHI S-3000N SEM spectrometer. X-ray photoelectron spectra (XPS) were recorded using an ESCALAB 210 X-ray Photoelectron Spectroscopy. ¹H NMR spectra were recorded on a Bruker Avance 400 spectrometer (operating at 400.33 MHz).

Preparation of CdS Samples. Synthetic method is similar to that reported before except for adding PF127 as a surfactant.¹⁰ Specifically, to prepare the reaction solution, aqueous solutions containing PF127 (MW = 12,500 Da) (1 mM, 1.26% (w/v)), Cd(NO₃)₂ (5 mM) and L-Cys (50 mM) were prepared in a vessel (150 mL) and vortexed for 10 min to ensure complete dissolution of the components. Then, NaOH (5 M) solution was added under constant magnetic stirring to adjust the pH of the solution from 3 to 12. The change in the solution pH was monitored by using a pH meter. Subsequently, the solution was transferred to a hydrothermal reactor, heated to 150 °C, and maintained at this temperature for a designated time (6 h (3) or 72 h (4)). The resulting products were washed several times with distilled water with a centrifugation (rpm: 3000) and dried in a vacuum. For comparison, solutions without PF127 was also prepared and synthesized with the same procedures (6 h (1) and 72 h (2)).

Results and Discussion

We describe the synthesis and characterization of size-monodisperse CdS submicrometer particles in the presence of a nonionic surfactant PF127 (Fig. 1) under a hydrothermal condition. Our previous report revealed that simple reaction between two components, Cd²⁺ and L-Cys, in a hydrothermal condition by adjusting solution pH to 12, can produce the CdS spheres with narrow size distribution.¹⁰ That reaction is quite pH-sensitive and in order to attain narrow size distri-

bution, a rather long time (3 d) is required. Therefore, we have been seeking for routes which can shorten the reaction time with no change in morphology. One of possible ways to attain this goal might be the use of surfactants as shape-directing agents or passivating agents. Of many candidates, PF127 was chosen because it is water-soluble and can dissolve the insoluble reactants in aqueous solution.^{12-15,16b}

First, we synthesized the CdS under such a condition as reported before.¹⁰ We mixed Cd²⁺ and L-Cys (5 mM:50 mM) and adjusted the solution pH to 12 and transferred it to a hydrothermal reactor and heated in an oven (150 °C) for 6 h (1) or 72 h (2). While SEM images reveal that the reaction for 6 h produces irregular-sized CdS particles (1) with a bimodal size distribution, CdS particles synthesized for 72 h (2) exhibit narrow size distribution, which is in good agreement with what we reported before.¹⁰ On the other hand, in order to test the effect of PF127 on the morphology, a reaction for 6 h with PF127 with other conditions unchanged (3) was performed and it produced size monodisperse CdS product which is quite different from that in the absence of PF127 (Figure 1(c)). This is probably due to the passivation of CdS particles by the surfactant. Even though the precise metal-coordination mechanism is unclear, the effect of presence of PF127 on the CdS morphology has been demonstrated by other reports.^{13,16} Size of the particles is measured as 650 ± 50 nm with a standard deviation smaller than 10%. Surprisingly, contrary to our expectation, the reaction for 72 h with PF127 at the same temperature (4) produces irregular-sized CdS particles with the size distribution of 408 ± 104 nm (Figure 1(d)).

We speculated the unexpected difference in morphology between 3 and 4 with various aspects. Firstly, we checked the solution pH after the hydrothermal reaction. Importance of pH in this reaction has been demonstrated by our previous report.¹⁰ We measured the pH of 3 to be 11.7 which was virtually unchanged during the reaction. On the other hand, that of 4 was measured to be about 9.4 which dropped from pH 12 during the reaction. Even one pH unit influences the morphology of CdS.¹⁰ The reason why pH of the solution dropped might be due to degradation of PF127 during the reaction for prolonged reaction time (72 h). In the reaction of 3, gel was formed on the bottom of the reaction vessel when the reaction was cooled to room temperature after the reaction, which shows that PF127 remained intact. To prove the gel is intact PF127, we isolated the gel and performed ¹H NMR experiments. ¹H NMR spectrum of the gel is found to be almost identical to that of intact PF127 because peak position and integration ratio between methyl peaks from PO units and rest proton peaks of PF127 (see Supporting information). Even though precise mechanism is still unclear,¹⁶ a proposed mechanism might be the micelles formation of PF127 isolating the Cd ions inside micelles in aqueous solution and subsequent formation of CdS seeds by reaction of Cd ions with the S²⁻ ions provided by thermo-degradation of L-Cys. Such regular isolation of Cd ions into micelles might guide the regular growth of CdS particles. Detailed study to uncover the mechanism will be needed in the future.

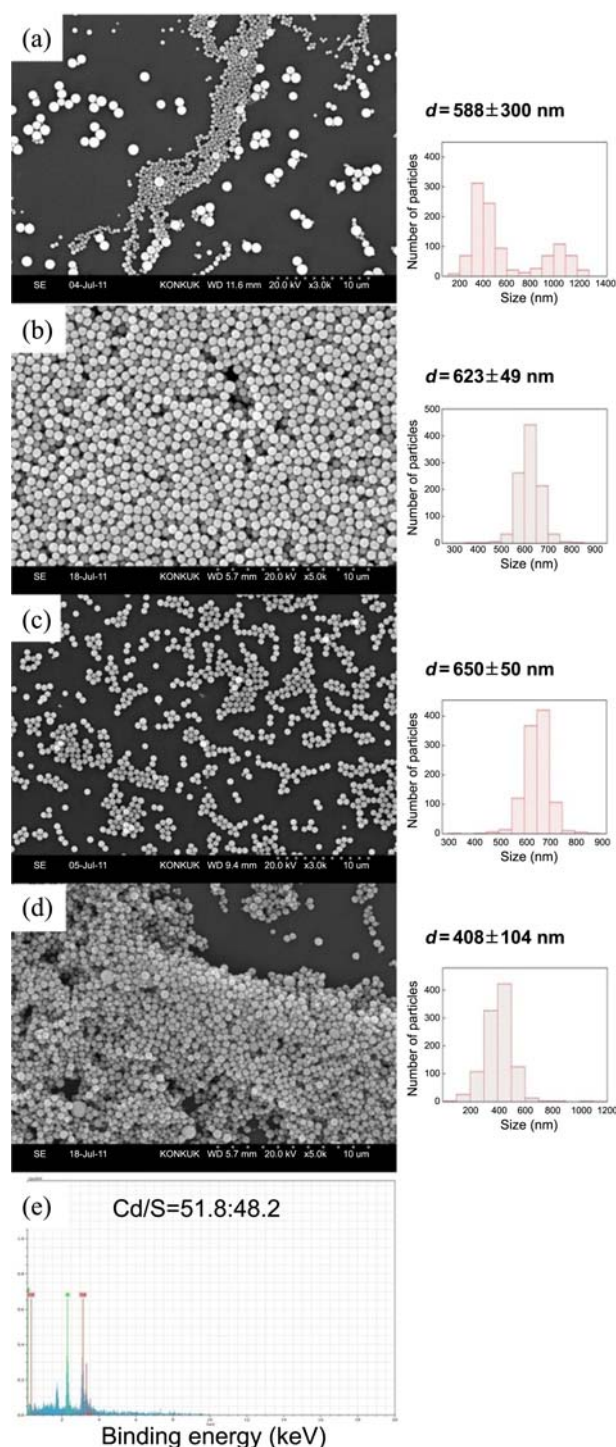


Figure 2. SEM images and size distribution of CdS samples for (a) 1, (b) 2, (c) 3, and (d) 4. (e) EDS spectrum of 3.

For 4, no gel was formed on the bottom of the reaction vessel and the solution pH decreased by more than 2 pH units, which is indicative of the degradation of PF127 during the reaction. Degradation of PF127 for the sample 4 can be ascribed to the prolonged heating at high temperature. An hydrolytic degradation of PF127 in acidic solution^{17a} and pH change of a hydrothermal reaction by 2 pH unit in the presence of PF127 in basic solution (pH = 11.13) at 180 °C

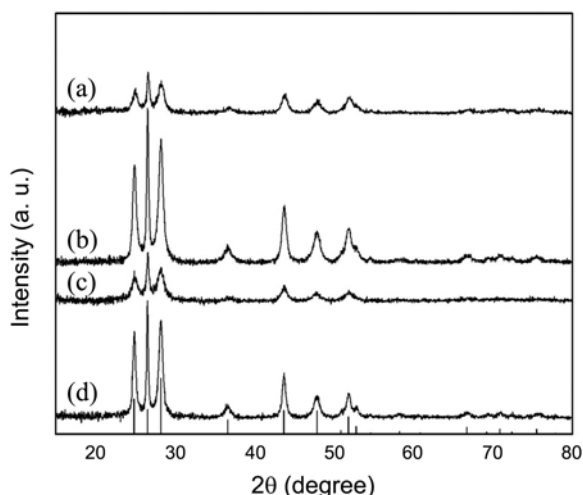


Figure 3. Powder X-ray diffraction (XRD) pattern of (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

for **4 d**, which are presumably the results of hydrolysis of the surfactant, was already observed and reported by other researchers.¹⁷ It is usually accepted that a nonionic block copolymer PF127 which has ether linkage could be susceptible to degradation depending on reaction conditions such as high concentration of acids or bases, a high temperature, and long synthesis time.^{17a} Taken together, the prolonged heating for 72 h might induced degradation of PF127, at the same time it lowered the solution pH, which lead to irregular sized CdS in case of **4**. On the hand, CdS synthesized for 6 h in the presence of PF127 (**3**) exhibits narrow size distribution without degradation of the surfactant.

The results of EDX analysis reveal that the Cd/S ratio in **3** is 51.8:48.2, indicating that Cd and S are nearly in 1:1 molar ratio (Figure 1(e)). Similar EDX results are obtained for all other products. Figure 3 shows the XRD patterns of the synthesized CdS particles. XRD patterns reveal that all the CdS particles have a hexagonal wurtzite structure (JPCDS No. 41-1049). We could not observe any impurity peaks in the XRD patterns. Overall, the patterns show that prolonged reaction time enhances the crystallinities of the samples. Sample **1** and **3** exhibit smaller peak intensities than **2** and **4** do owing to short reaction times. Crystallite sizes calculated by Debye-Scherrer equation are not greatly affected by using PF127.¹⁸ Crystallite sizes are all over 10 nm. TGA pattern and IR spectrum show that no surfactant remained after the wash and drying even though the surfactant was used (Figures 4(a) and 4(b)). This bareness offers many opportunities in decorating and functionalizing the surface of the samples.

Figure 4(c) shows the diffuse-reflectance UV-vis spectrum of **3**. The spectrum reveals that band gap (E_g) of the CdS corresponds to 2.4 eV, which is close to bulk CdS band gap. The results are well justified by the crystallite sizes (> 10 nm) calculated from XRD patterns. Figure 5 shows the XPS spectra of **3**. The peaks of O in the Figure 4(a) is known to originate from OH and CO absorbed on the surface of CdS particles in the air. Figures 4(b) and 4(c) show narrow-scanned photoelectron spectrum of Cd 3d and S 2p. The

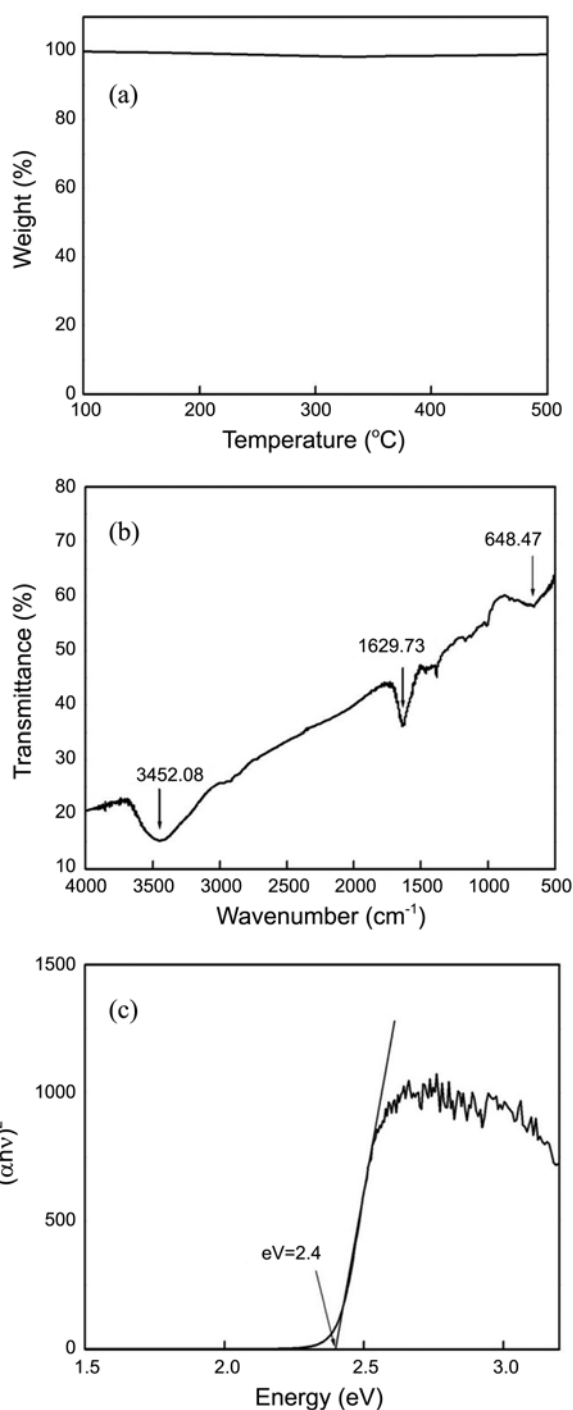


Figure 4. (a) TGA pattern, (b) IR spectrum, and (c) Diffuse-reflectance UV-vis spectrum of **3**.

peak at 404.8 eV corresponds to the binding energy of Cd 3d_{5/2}. The corresponding binding energy of S 2p is 161.9 eV. Those peaks are originated from the CdS materials.¹⁹ Overall, the observed spectra correspond to CdS submicrometer particles with pure CdS wurtzite hexagonal structure.

Conclusions

We synthesized size-monodisperse CdS submicrometer

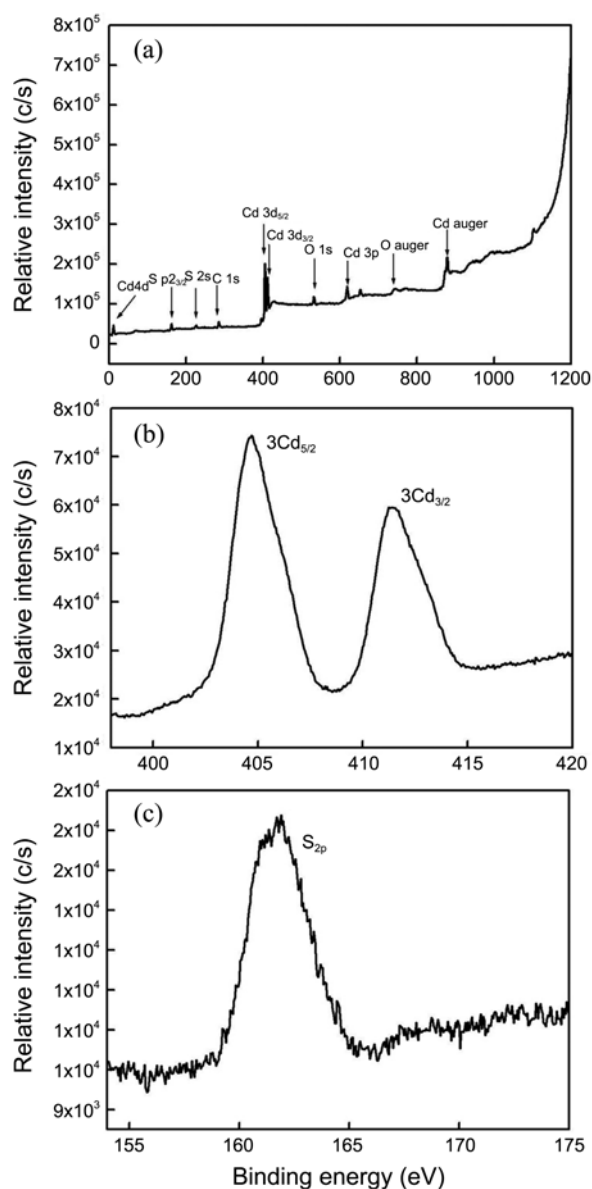


Figure 5. XPS spectra of CdS sample 3, (a) survey spectrum, (b) Cd 3 d, and (c) S 2p cores.

particles in a short time (6 h) from a solution containing Cd(II), L-Cys and PF127 by simply controlling solution pH using NaOH under a hydrothermal condition. While CdS synthesized without PF127 for 6 h (**1**) exhibits a bimodal size distribution and a large standard deviation, that synthesized with Pluronic® F127 (**3**) shows the size-monodisperse distribution with a standard deviation smaller than 10%.

Interestingly, prolonged reaction time in the case of CdS sample synthesized with PF127 for 72 h (**4**) induced the degradation of the surfactant, thus lowered the pH, which caused the irregular size distribution. Taken together, the results of present study will offer an opportunity in producing CdS submicroparticles in a convenient and environment-friendly way in a short time (6 h), and can be used in various applications in the future.

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