Synthesis of CuS Nanoparticles in Water-in-Carbon Dioxide Microemulsions

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The formation of CuS nanoparticles from $Cu(NO_3)_2$ and Na_2S by the mixing of two separate water-in-carbon dioxide (W/C) microemulsions supported by the sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl)-2-sulfosuccinate (di-HCF4) was investigated. At a water-to-surfactant ratio of 10 and a copper concentration of 7.8 mM in the aqueous phase, the size of copper sulfide particles ranged from 4 to 6 nm. The temperature−pressure phase diagrams of W/C microemulsions at various electrolyte concentrations in the aqueous phase were also determined. The presence of the electrolytes was found not to affect the cloud-point pressures significantly, even at high concentrations.

Introduction

A microemulsion is a thermodynamically stable system with at least three components: two immiscible components (generally water and oil) and a surfactant. In water-in-oil (W/O) microemulsions, the aqueous phase is dispersed as nanosize droplets (typically 5−25 nm in diameter) surrounded by a monolayer of surfactant molecules in the continuous hydrocarbon phase. Micellar droplets exhibit a dynamic exchange of their contents that facilitates the reactions between reactants dissolved in different droplets. This micellar exchange has been used to synthesize size-controlled crystallites by carrying out a wide variety of chemical reactions in nanodroplets. Reported examples include nanoparticles of metallic copper,[1] silver,[2] gold,[3] semiconductor cadmium sulfide,[4] copper sulfide,[5] molybdenum sulfide,[6] $BaSO_4$,[7] silver bromide,[8] and rodlike and ellipsoidal $BaCO_3$.[9]

Additional advantages can be realized by using dense carbon dioxide instead of organic solvents. Liquid or supercritical carbon dioxide (l-scCO$_2$) is an attractive substitute for petroleum-based organic solvents as it is nontoxic, environmentally acceptable, nonflammable, inexpensive, and readily available in large quantities. The additional advantages of using l-scCO$_2$ as the continuous phase over organic solvents for synthesis of nanoparticles are as follows: (1) The large compressibility of CO_2 in the vicinity of the critical point compared to organic solvents permits one to use pressure as an additional parameter to influence the phase behavior of such systems. (2) The morphologies of the nanostructured materials prepared in microemulsions depend, to a large extent, on the nature of the surfactant and solvent used.[10] Novel surfactant and CO_2 combinations can lead to novel framework structures and morphologies. (3) Nanoparticles can be obtained in powder form by a reduction in pressure without the need for extraction from reverse micelles as in the case of organic solvents. (4) A wide variety of surfaces can be coated with nanoparticles directly by the rapid expansion of l-scCO$_2$ solutions.

Investigations of water-in-carbon dioxide (W/C) microemulsions started with the pioneering work of Johnston et al., who discovered that an ammonium carboxylate perfluoropolyether [$CF_3O(CF_2CF(CF_3)O)_3$-CF_2−COO$^-$NH$_4^+$, PFPE] surfactant could support microemulsions in scCO$_2$.[11] The water cores within these microemulsions were probed by elegant techniques including X-band electron paramagnetic resonance (EPR),[12] time-resolved fluorescence depolarization, and FTIR spectroscopy.[13] The PFPE-based W/C microemulsions were subsequently used as nanoreactors for reactions of acidified potassium dichromate with sulfur dioxide and sodium nitroprusside with hydrogen sulfide,[12] as well as for the oxidation of cholesterol by chlosterol oxidase,[14] with promising results. Recently, we reported on the ability of fluorinated analogues of the sodium salt of bis(2-ethylhexyl) sulfosuccinate (AOT) to support the formation of W/C microemulsions and investigated the effect of the fluoroalkyl chain length on the phase behavior.[15] We also investigated the effects of the water-to-surfactant ratio (W_0) and surfactant concentration on the phase behavior for W/C microemulsions stabilized by the sodium salt of bis(2,2,3,3,-4,4,5,5-octafluoro-1-pentyl)-2-sulfosuccinate (di-HCF4) and probed the micelle size by small angle X-ray scattering (SAXS).[16]

There have been three recent communications describing the synthesis of nanoparticles in scCO$_2$. Holmes et al. reported the synthesis of CdS nanoparticles in W/C microemulsions supported by PFPE at 45 °C and 345 bar.[17] The mean particle radius was found to range from 0.9 to 1.8 nm depending on the value of W_0. Ji et al. reported the synthesis of Ag nanoparticles in AOT and perfluoropolyether−phosphate ether (PFPE−PO$_4$) stabilized W/C microemulsions at 400 bar.[18] The size of the particles ranged approximately from 5 to 15 nm, and a relatively high degree of polydispersity was observed. Both of these studies involved the injection of one of the reactants in solution [aqueous solutions of NaBH(OAc)$_3$ or Na_2S] directly into high-pressure W/C microemulsions. An alternative and more effective way of control-

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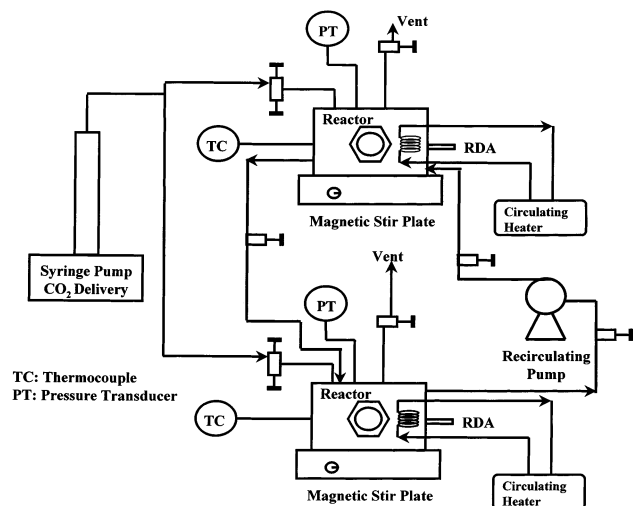[‡] Department of Metallurgy and Materials Engineering.

Figure 1. Experimental setup for the synthesis of nanoparticles in l/scCO2.

Figure 2. Pressure−temperature phase diagram for water-in-carbon dioxide microemulsions with $Cu(NO_3)_2$ at [di-HCF4] = 0.1 M and $W_0 = 10$.

ling the particle size might be by taking advantage of the micellar exchange process by mixing two separate W/C microemulsion systems. Such an approach is frequently employed with organic solvents. Ohde et al.[19] recently utilized this method to synthesize silver halide nanoparticles using AOT and the cosurfactant PFPE−PO_4. In this article, we report the results of our investigations on the formation of CuS nanoparticles from $Cu(NO_3)_2$ and Na_2S in scCO2 upon the mixing of two separate W/C microemulsions supported by di-HCF4. An important consideration in such systems is the stability of the W/C microemulsions in the presence of added electrolytes, and such data in the literature are scarce. Therefore, the temperature−pressure phase diagrams of W/C microemulsions at various electrolyte concentrations in the aqueous phase were also determined.

Experimental Section

The chemicals 2,2,3,3,4,4,5,5-octafluoro-1-pentanol, 1,4-dioxane, *p*-toluenesulfonic acid monohydrate, sodium hydrogen sulfite, maleic anhydride, toluene, acetone-d_6, copper nitrate, sodium sulfide, and isooctane were all obtained from Aldrich; AOT was obtained from Acros; and all of them were used as received. The surfactant di-HCF4 was synthesized by the reaction of sodium hydrogen sulfite with bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl) maleate in a mixture of 1,4-dioxane and water. The details of the synthetic procedure and surfactant characterization data are given elsewhere.[15] The macroscopic phase behavior of the W/C microemulsions was investigated by using a high-pressure vessel equipped with sapphire windows. The details of the experimental procedure are given elsewhere.[15]

A schematic diagram of the experimental setup for the synthesis of nanoparticles is given in Figure 1. Two high-pressure vessels were used to create two separate W/C microemulsions. The vessels (internal volumes of 54 cm^3) were custom manufactured from 316SS and were equipped with two sapphire windows (diameter = 1.25 in., thickness = 0.5 in.). The windows were sealed on both sides with PEEK seals. For a typical experiment, a certain amount of di-HCF4 and an aqueous solution of copper nitrate were placed in one of the vessels, and a certain amount of di-HCF4 and an
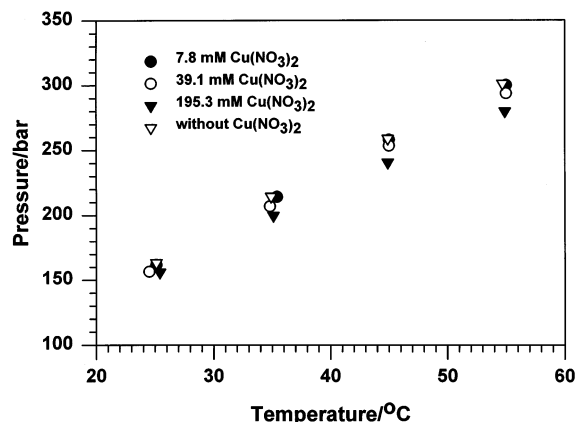
aqueous solution of sodium sulfide were placed in the other vessel. The vessels were sealed, placed on magnetic stir plates, connected to each other, and heated to the desired temperature by a recirculating heater/cooler (Fischer) via machined internal coils. The vessels were charged with CO_2 from a syringe pump (ISCO, 260D) until the desired pressure was reached. When optically transparent solutions were obtained in both vessels, valves between them were opened, and a recirculation pump (Thermo Separation Products, minipump) was started to mix the two solutions. The pump was operated for about 1 h, during which time the solutions in both vessels were transparent and yellowish. The vessels were then depressurized; the materials in the reactor were collected and then dissolved in acetone. The solution was centrifuged, and the particles obtained were collected and dispersed in acetone with a sonicator. The solution containing the particles was processed for characterization by transmission electron microscope (TEM). The pressures in each vessel were measured using pressure transducers (Omega Engineering Inc., PX01K1-5KGV). Characterization was performed with a Philips EM420 analytical electron microscope operated at 100 kV. An EDAX spectrometer and software provided chemical compositions as needed. The use of a beryllium-lined specimen holder minimized interference from the copper peaks from the specimen holder. The particles, suspended in solvent, resided on a carbon film following evaporation of the solvent. The film, in turn, was suspended on a 200-mesh copper grid. Contrast, in addition to the particles and forming the background of the images, results from the carbon film.

Results and Discussion

The pressure−temperature phase diagram for W/C microemulsions at different $Cu(NO_3)_2$ concentrations in the aqueous phase is shown in Figure 2. The microemulsions in all cases were optically transparent and stable for long periods of time in the single-phase region. For example, the microemulsion at a $Cu(NO_3)_2$ concentration of 39.1 mM was stable for 2 days. The microemulsion at a $Cu(NO_3)_2$ concentration of 195.3 mM had a bluish tint. The ability to form stable microemulsions at electrolyte concentrations as high as 0.2 M is very promising for various applications. At concentrations of 7.8 and 39.1 mM, the presence of $Cu(NO_3)_2$ had no significant effect on the cloud point, whereas at 195.3
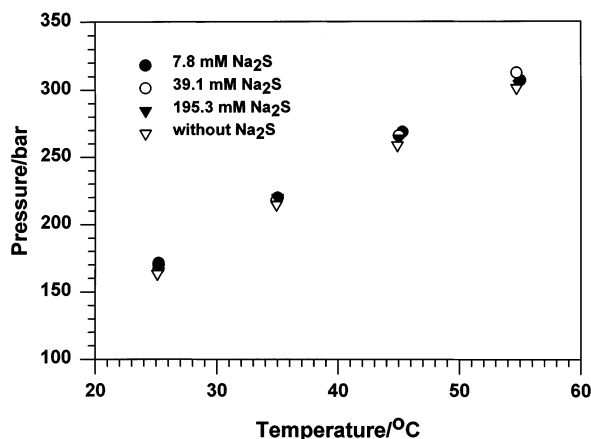
Figure 3. Pressure−temperature phase diagram for water-in-carbon dioxide microemulsions with Na_2S at [di-HCF4] = 0.1 M and $W_0 = 10$.

Figure 4. Pressure−temperature phase diagram for water-in-carbon dioxide microemulsions with CuSat [di-HCF4] = 0.1 M and $W_0 = 10$.

mM, the presence of $Cu(NO_3)_2$ seemed to decrease the cloud-point pressures slightly. For microemulsions supported by PFPE, the presence of $Cd(NO_3)_2$ even at a concentration of 10 mM was found to decrease the cloud point.[17] This was attributed to a change in charge screening between surfactant headgroups, which increased the surfactant membrane rigidity in the micellar interfacial region. The difference in behavior between the two systems might be indicative of the effect of the cation on the phase behavior. The pressure−temperature phase diagram of Na_2S is given in Figure 3. A slight increase in the cloud-point pressures compared with those without Na_2S was observed, but the concentration of Na_2S had no effect on the cloud point. In conclusion, measurements with both of these systems indicate that the electrolyte concentration has no significant effect on the cloud point, which suggests that the micelle size does not change upon the addition of electrolytes.

For the synthesis of CuS nanoparticles, two separate microemulsions were prepared in two separate vessels at 25 °C and 300 bar. The surfactant concentration was kept at 0.1 M, and W_0 was 10. For runs in which the $Cu(NO_3)_2$ concentration was 7.8 or 39.1 mM, the color in the reactors changed from colorless to yellow as soon as the recirculation pump was started, indicating the formation of nanoparticles. The recirculation pump was run for a period of 0.5 h at a flowrate of 400 mL/h. During this time, the solutions in both vessels were optically clear and yellow. A similar experiment was also conducted using water-in-isooctane microemulsions supported by AOT at the same electrolyte concentrations as above, and it was found that the color of solutions also turned yellowish as soon as the two separate microemulsions were mixed. This indicates that di-HCF4 behaves in a manner similar to its nonfluorinated analogue, AOT. On the other hand, experiments conducted in carbon dioxide at a $Cu(NO_3)_2$ concentration of 195.3 mM resulted in the immediate formation of a bright orange/red color in the vessels. Immediately thereafter, large particles were observed to precipitate, suggesting that there is a critical CuS concentration limit above which the microemulsion system is not stable.

The pressure−temperature phase diagram for W/C microemulsions of CuS is displayed in Figure 4 and shows that the phase behavior of CuS in W/C microemulsions is very similar to that of pure surfactant.
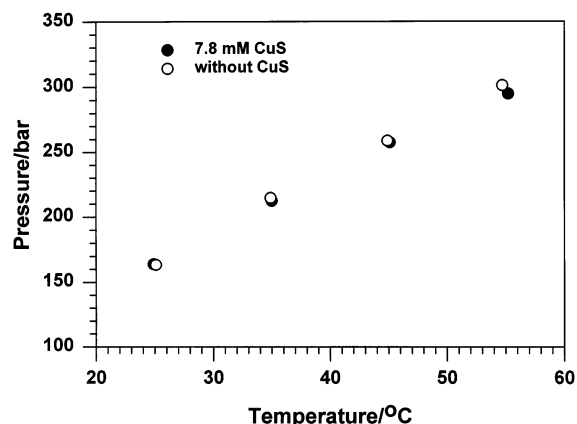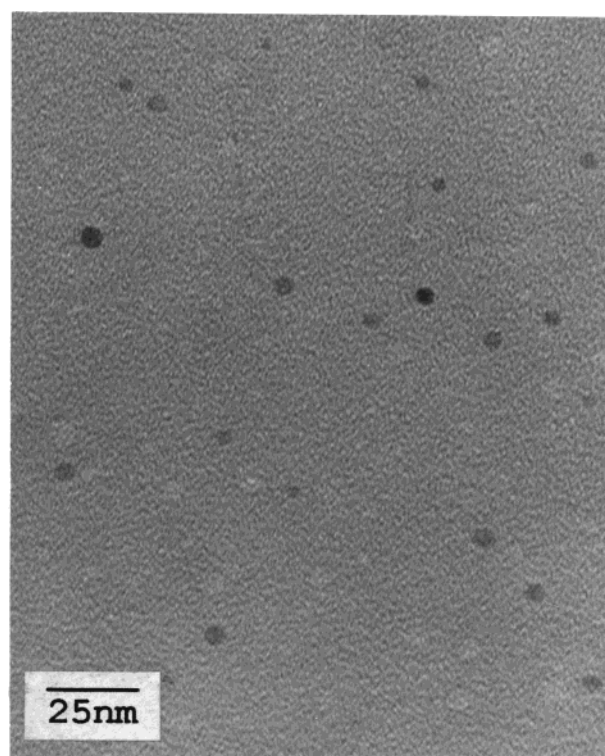

Figure 5. Transmission electron microscope image of CuS nanoparticles.

A TEM image of the particles formed at a surfactant concentration of 0.1 M, $W_0 = 10$, and a substrate concentration of 7.8 mM is presented in Figure 5. It shows that the particles are nearly spherical, with sizes ranging from 4 to 6 nm. The particles in the TEM image were confirmed to be CuS by energy-dispersive X-ray analysis, as shown in Figure 6. The ratio between the copper and sulfur peaks should be about 1, but the copper contained in the TEM copper grid leads to a somewhat more intense copper peak. Our previous paper shows that the diameter of the water core in this W/C microemulsion system is around 5 nm,[16] as determined by small-angle X-ray scattering. The size of the nanoscale water droplets greatly influences the size of the nanoparticles. Because particle formation by nucleation and growth occurs very rapidly, as particles approach the water core diameter, coagulation becomes
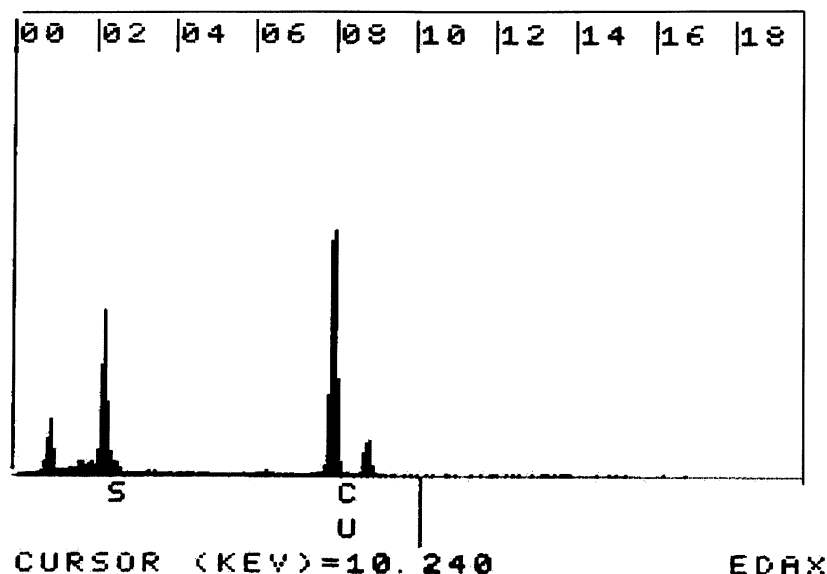
Figure 6. X-ray spectrum from CuS nanoparticles. The x axis (at the top) is the X-ray photon energies given in kiloelectronvolts. The y axis is the X-ray intensity in counts/second. The full scale is 2000 counts/second.

restricted by the micellar diameter because surfactants surrounding water droplets act as protective agents.[20] Accordingly, the particles formed in our system should be less than 5 nm, indicating that such systems might be effective for templating.

Conclusions and Future Work

The formation of CuS nanoparticles from $Cu(NO_3)_2$ and Na_2S upon the mixing of two separate W/C microemulsions supported by di-HCF4 was investigated. At a water-to-surfactant ratio of 10 and a copper concentration of 7.8 mM in the aqueous phase, the size of the copper sulfide particles prepared ranged from 4 to 6 nm. The temperature–pressure phase diagrams of W/C microemulsions at various $Cu(NO_3)_2$ and Na_2S concentrations in the aqueous phase were also determined. The presence of the electrolytes was found not to affect the cloud-point pressures significantly, even at high concentrations. In the future, we intend to study in detail the effects of surfactant concentration, W_0, temperature, and pressure on the size and shape of the CuS nanoparticles.

Acknowledgment

Literature Cited

(1) Pileni, M. P.; Lisiecki, I. Nanometer metallic copper particle synthesis in reverse micelles. *Colloids Surf. A* **1993**, *80* (1), 63.

(2) Taleb, A.; Petit, C.; Pileni, M. P. Synthesis of Highly Monodisperse Silver Nanoparticles from AOT Reverse Micelles: A Way to 2D and 3D Self-Organization. *Chem. Mater.* **1997**, *9* (4), 950.

(3) Wilcoxon, J. P.; Williamson, R. L.; Baughman, R. Optical properties of gold colloids formed in inverse micelles. *J. Chem. Phys.* **1993**, *98* (12), 9933.

(4) Petit, C.; Lixon, P.; Pileni, M. P. Synthesis of Cadmium Sulfide in Situ in Reverse Micelles. 2. Influence of the Interface on the Growth of the Particles. *J. Phys. Chem.* **1990**, *94* (4), 1598.

(5) Haram, S. K.; Mahadeshwar, A. R.; Dixit, S. G. Synthesis and Characterization of Copper Sulfide Nanoparticles in Triton-X 100 Water-in-Oil Microemulsions. *J. Phys. Chem.* **1996**, *100* (14), 5868.

(6) Boakye, E.; Radovic, L. R.; Osseo-Asare, K. Microemulsion-mediated synthesis of nanosize molybdenum sulfide particles. *J. Colloid Interface Sci.* **1994**, *163* (1), 120.

(7) Hopwood, J. D.; Mann, S. Synthesis of Barium Sulfate Nanoparticles and Nanofilaments in Reverse Micelles and Microemulsions. *Chem. Mater.* **1997**, *9* (8), 1819.

(8) Monnoyer, Ph.; Fonseca, A.; Nagy, J. B. Preparation of colloidal AgBr particles from microemulsions. *Colloids Surf. A* **1995**, *100*, 233.

(9) Qi, L.; Ma, J.; Cheng, H.; Zhao, Z. Reverse Micelle Based Formation of BaCO$_3$ Nanowires. *J. Phys. Chem. B* **1997**, *101* (18), 3460.

(10) Nagy, J. B.; Claerbout, A. Preparation of Monodisperse Colloidal Metal/Metal Oxide Particles From Microemulsions: New Developments. *Surfactants Solution* **1991**, *11*, 363.

(11) Johnston, K. P.; Harrison, K. L.; Clarke, M. J.; Howdle, S. M.; Heitz, M. P.; Bright, F. V.; Carlier, C.; Randolph. T. W. Water-in-carbon dioxide microemulsions: An environment for hydrophiles including proteins. *Science* **1996**, *271*, 624.

(12) Heitz, M. P.; Carlier, C.; deGrazia, J.; Harrison, K. L.; Johnston, K. P.; Randolph, T. W.; Bright, F. V. Water Core within Perfluoropolyether-Based Microemulsions Formed in Supercritical Carbon Dioxide. *J. Phys. Chem. B* **1997**, *101* (34), 6707.

(13) Clarke, M. J.; Harrison, K. L.; Johnston, K. P.; Howdle, S. M. Water in Supercritical Carbon Dioxide Microemulsions: Spectroscopic Investigation of a New Environment for Aqueous Inorganic Chemistry. *J. Am. Chem. Soc.* **1997**, *119* (27), 6399.

(14) Kane, M. A.; Baker, G. A.; Pandey, S.; Bright, F. V. Performance of Cholesterol Oxidase Sequestered within Reverse Micelles Formed in Supercritical Carbon Dioxide. *Langmuir* **2000**, *16* (11), 4901.

(15) Liu, Z.; Erkey, C. Water in Carbon Dioxide Microemulsions with Fluorinated Analogues of AOT. *Langmuir* **2001**, *17*, 274.

(16) Dong, X.; Erkey, C.; Dai, H.-J.; Li, H.-C.; Cochran, H. D.; Lin, J. S. Phase Behavior and Micelle Size of an Aqueous Microdispersion in Supercritical CO$_2$ with a Novel Surfactant. *Ind. Eng. Chem. Res.* **2002**, *41*, 1038−1042.

(17) Holmes, J. D.; Bhargava, P. A.; Korgel, B. A.; Johnston, K. P. Synthesis of Cadmium Sulfide Q Particles in Water-in-CO$_2$ Microemulsions. *Langmuir* **1999**, *15* (20), 6613.

(18) Ji, M.; Chen, X.; Wai, C. M.; Fulton, J. L. Synthesizing and dispersing silver nanoparticles in a water-in-supercritical carbon dioxide microemulsion. *J. Am. Chem. Soc.* **1999**, *121* (11), 2631.

(19) Ohde, H.; Ye, X.-R.; Wai, C. M.; Rodriguez, J. M. Synthesizing silver halide nanoparticles in supercritical carbon dioxide utilizing a water-in-CO_2 microemulsion. *Chem. Commun.* **2000**, 2353.

(20) Hirai, T.; Sato, H.; Komasawa, I. Mechanism of Formation of CdS and ZnS Ultrafine Particles in Reverse Micelles. *Ind. Eng. Chem. Res.* **1994**, *33*, 3262.