

Synthesis of Ag<sub>2</sub>S quantum dots in water-in-CO<sub>2</sub> microemulsionsJuncheng Liu,<sup>a,b</sup> Poovathinthodiyil Raveendran,<sup>a,b</sup> Zameer Shervani<sup>a,b</sup> and Yutaka Ikushima<sup>a,b</sup><sup>a</sup> *Supercritical Fluid Research Center, National Institute of Advanced Industrial Science and Technology, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan. E-mail: y-ikushima@aist.go.jp*<sup>b</sup> *CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi 332-0012, Japan*

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Ag<sub>2</sub>S nanocrystals with a mean diameter of 5.9 nm ( $\sigma = 1.65$  nm) and characteristic surface plasmon resonance absorption at 330 nm have been synthesized in water-in-supercritical CO<sub>2</sub> reverse microemulsion using the commonly used AOT surfactant with 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (F-pentanol) as cosurfactant.

Water-in-CO<sub>2</sub> (w/c) reverse microemulsions (RMs) have attracted much interest in the recent years as nanoscopic aqueous reactors for growing metal and semiconductor nanoparticles using supercritical (sc) CO<sub>2</sub> as a “green” solvent alternative.<sup>1</sup> Not only does the reverse micellar organization provide spatially confined aqueous domains for the synthesis of the nanoparticles from their water-soluble precursor, but also the surfactant interfacial monolayer helps to passivate the surface and quench the growth of the nanoparticles which would otherwise aggregate due to the high surface energy of these systems. The easily tunable solvent properties, low interfacial tension, excellent wetting behavior, and high diffusion coefficients, make scCO<sub>2</sub> a superior solvent medium for the synthesis of nanoscale materials.<sup>2</sup> Also, the stability of the w/c RMs depends on the system density; thus the breakdown of the RMs can be easily achieved by simply varying the temperature and CO<sub>2</sub> pressure, making it possible to directly deposit nanoparticles on desired substrates without any residual solvent. This presents tremendous opportunities and advantages in the bottom-up development of nanotechnological devices.

Previous works on w/c RMs have indicated that conventional hydrocarbon surfactants do not form RMs in scCO<sub>2</sub>;<sup>3</sup> only several fluorinated surfactants, which do stabilize w/c RMs, have been used to synthesize nanoparticles in scCO<sub>2</sub>.<sup>1b,e,4</sup> Nevertheless, most of these surfactants require specialized synthesis, and therefore remain expensive. The commonly used surfactant AOT has been shown to form RMs in organic solvents<sup>5</sup> and supercritical alkane.<sup>6</sup> However, AOT is completely insoluble in CO<sub>2</sub> due to the poor miscibility of the alkyl chains with CO<sub>2</sub>, restricting its utilization in this environmentally benign medium. Hutton and Stevens<sup>7</sup> proposed that AOT could be solubilized in scCO<sub>2</sub> and form w/c RMs in the presence of a cosolvent/cosurfactant such as ethanol (15–17 mol%) or 1-pentanol (10 mol%). In this case, a large amount of cosolvent was required and also, ionic species could not be solubilized in the RMs. Subsequently, Ji *et al.*<sup>1a</sup> reported that AOT, together with perfluoropolyether phosphate ether (PFPE-PO<sub>4</sub>) could form w/c RMs, and this mixed surfactant system has been used as nanoreactor to synthesize various nanoparticles.<sup>1a,c,d,8</sup> PFPE-PO<sub>4</sub> is also an expensive synthetic chemical and difficult to obtain commercially. Also, the synthesis of monodisperse nanocrystals within the quantum-size domain (under 10 nm) has been a large challenge for these w/c RM systems.<sup>1a,d,4c</sup> In this context, it is necessary to explore how to enable commercially available surfactants to form w/c RMs that can grow monodisperse quantum dots in scCO<sub>2</sub>. Recently, we showed that AOT could form w/c RMs in the presence of a small quantity of commercially available F-pentanol (1.2 mol%), and the RMs formed could provide polar aqueous domains for the solubilization of organic dyes, biomacromolecules and ionic species.<sup>9</sup> In this work, we demonstrate that it is possible to grow relatively monodisperse crystalline Ag<sub>2</sub>S quantum dots (which have potential application as

photoelectric and thermoelectric devices) in the aqueous pools of AOT/F-pentanol (AOTF) w/c RMs, suggesting the possibility of the commercial utilization of this environmentally benign approach.

The Ag<sub>2</sub>S nanoparticles were synthesized by the reaction between AgNO<sub>3</sub> and Na<sub>2</sub>S in the aqueous domains of the AOTF w/c RMs with  $W$  value ( $W = [\text{water}]/[\text{surfactant}]$ , where the water dissolved in the scCO<sub>2</sub> continuous phase was subtracted) of 5.6.† Upon the injection of aqueous Na<sub>2</sub>S solution into the w/c RM system, a significant yellow cloudiness was visually observed, indicating the initial formation of Ag<sub>2</sub>S nanoparticles. The nanoparticle dispersion in scCO<sub>2</sub> (protected by the surfactant interfacial monolayer) was stable for prolonged duration and did not show any signs of aggregation or precipitation. The UV-vis spectrum of the samples, showing the surface plasmon resonance absorption of these colloidal Ag<sub>2</sub>S nanoparticles (characteristic of maximum absorption wavelength at 330 nm),<sup>10</sup> is presented in Fig. 1. The absorption spectrum of these Ag<sub>2</sub>S nanoparticles indicates that these are quantum confined, and may find potential application as photoelectric materials (the band gap for bulk Ag<sub>2</sub>S is  $\sim 1$  eV (1240 nm)).<sup>11</sup>

A typical TEM image of the Ag<sub>2</sub>S nanoparticles formed is presented in Fig. 2. As expected, characteristic spherical Ag<sub>2</sub>S nanoparticles with a narrow polydispersity were observed. Fig. 3 presents a histogram of the Ag<sub>2</sub>S particle size distribution with an average diameter of 5.9 nm ( $\sigma = 1.65$  nm). The Ag<sub>2</sub>S nanoparticles are in the size range from 3 to 9 nm, with over 70% of the particles in the 5–7 nm range. The corresponding electron diffraction (ED) pattern of the Ag<sub>2</sub>S nanoparticles is also presented in Fig. 2 (inset), in which many diffraction circles existed but were too diffuse (primarily owing to the small size of these nanoparticles) to study the detailed structure. However, the observed ED pattern suggests a monoclinic structure rather than a cubic one when correlated to the standard diffraction patterns of Ag<sub>2</sub>S. The high-resolution TEM (HRTEM) image in Fig. 4(A) shows that the Ag<sub>2</sub>S nanocrystals (lattice fringes could be observed) seem to be uniformly coated with a surfactant interfacial monolayer in a core-shell like arrangement, with interlinking between individual nanocrystals plausibly through the interdigitation of the surfactant tails of

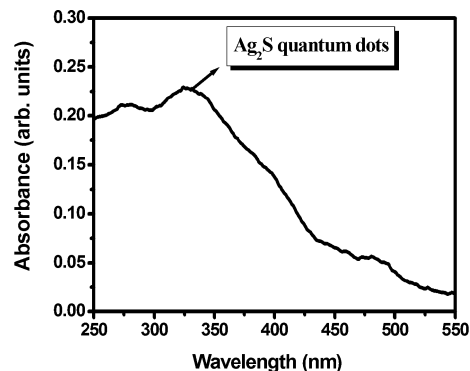
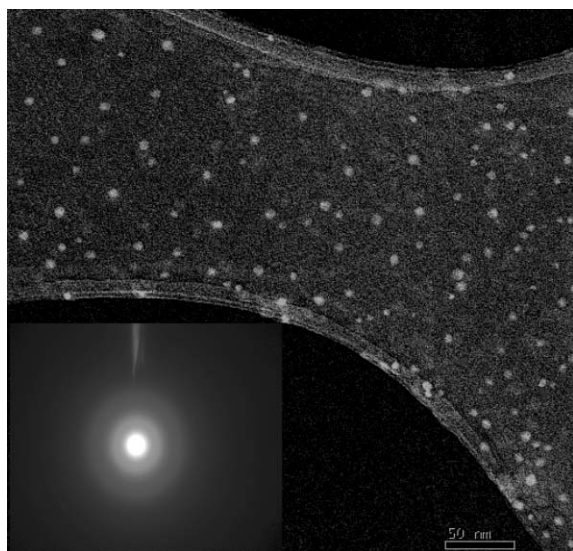
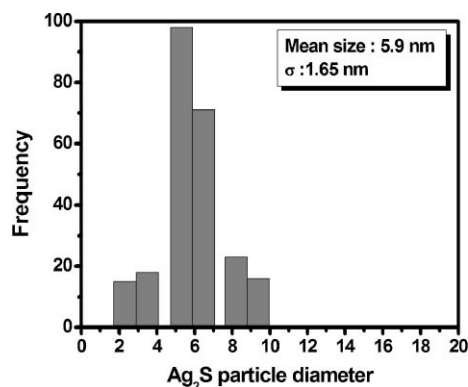


Fig. 1 UV-vis spectrum of the Ag<sub>2</sub>S quantum dots synthesized in AOTF w/c RMs with  $W = 5.6$  at 38.0 °C and 34.50 MPa (the background of the AOTF w/c RM system has been subtracted).



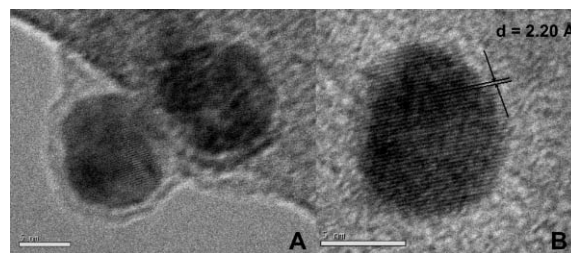
**Fig. 2** TEM image of Ag<sub>2</sub>S quantum dots synthesized in the AOTF w/c RMs with  $W = 5.6$  at 38.0 °C and 34.50 MPa (scale bar is 50 nm); the inset is the electron diffraction pattern of the Ag<sub>2</sub>S quantum dots.



**Fig. 3** Histogram showing the size distribution of the Ag<sub>2</sub>S quantum dots.

adjacent micelles. Additionally, the multiple lattice fringes with an interplanar spacing of 2.20 Å can be observed clearly in the HRTEM image of Fig. 4(B), further confirming the crystalline nature of the Ag<sub>2</sub>S quantum dots.

Molecular dynamics simulations on w/c RMs using hydrocarbon and fluorocarbon based surfactants have shown that there is enhanced CO<sub>2</sub> penetration in the fluorocarbon tail region of the micelles when compared to the hydrocarbon tails.<sup>12</sup> A similar view can be put forward for the F-pentanol tail which will interdigitate between the hydrocarbon tails of AOT molecules. This results in an increase in the solute–solvent interaction cross section between the surfactant tails and CO<sub>2</sub>, and thereby provides greater stabilization of the RM in scCO<sub>2</sub>. The hydroxyl groups of F-pentanol interact with loading water in the polar aqueous regions through hydrogen bonds and CO<sub>2</sub> molecules that penetrated from bulk phase to the surfactant tail region interact with fluorinated tail of the F-pentanol. Both these interactions are beneficial for the F-pentanol to insert itself between surfactant tail domains and reduce the electrostatic repulsion between the ionic head groups of AOT, thereby enhancing the stability of the w/c RM system. The dynamic organization of the surfactant tails allows the diffusion of the reactants into micellar cores, enabling the reaction to occur within the nanosized polar aqueous pools of the AOTF w/c RMs. After the nucleation is initiated, particle growth occurs by collision



**Fig. 4** High-resolution TEM images of Ag<sub>2</sub>S nanocrystals (the scale bars equal 5 nm).

among micelles, which may then exchange water pool contents, leading to further particle growth.<sup>13</sup> This process of exchange and growth continues until the particles reach a terminal size determined by the RM system and where the surfactant aids in stabilization of the particles.<sup>1c</sup>

This commercially viable approach can be used for the industrial-scale synthesis of various nanocrystals of quantum size domain and catalytic reactions (using *in situ* prepared nanocatalysts) in scCO<sub>2</sub> without any environmental hazards.

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## Notes and references

† The AOTF w/c RMs used as nanoreactor to grow Ag<sub>2</sub>S quantum dots were created by mixing the 0.016 M AOT–0.24 M F-pentanol–water–scCO<sub>2</sub> system at 38.0 °C and 34.50 MPa. In a typical sample, the AOTF w/c RMs with  $W$  value of 2.8 (0.1 M aqueous AgNO<sub>3</sub> solution) was prepared at 31.00 MPa which is a little higher than the cloud point pressure (30.30 MPa) for the mixed system of 0.016 M AOT–0.24 M F-pentanol–water ( $W = 5.6$ )–scCO<sub>2</sub>,<sup>9b</sup> and then 0.05 M aqueous Na<sub>2</sub>S solution was injected through a sample loop into the cell using a high-pressure pump attached to a six-port valve, until a final Ag<sup>+</sup>:S<sup>2-</sup> stoichiometry of 2:1 and system pressure of 34.50 MPa were reached. After a reaction of 30 min, the Ag<sub>2</sub>S nanoparticles were collected by slowly decreasing the system pressure.

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