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Synthesizing and Dispersing Silver Nanoparticles in a Water-in-Supercritical Carbon Dioxide Microemulsion

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Reverse micelles and microemulsions formed in liquid and supercritical carbon dioxide (CO₂) allow highly polar or polarizable compounds to be dispersed in this nonpolar fluid.¹ However, since the polarizability per unit volume of dense CO₂ is quite low, it is difficult to overcome the strong van der Waals attractive interactions between particles in order to stably suspend macro-molecular species. Conventional surfactants by themselves do not form reverse micelles or microemulsions in CO₂ because the van der Waals interdroplet attractions are too high. The use of surfactants or cosurfactants with fluorinated tails provides a layer of a weakly attractive compound covering the highly attractive droplet cores, thus preventing their short-range interactions that would destabilize the system. Using this strategy, we describe a method to synthesize and stabilize metallic silver nanoparticles having diameters from 5 to 15 nm in supercritical CO₂ using an optically transparent, water-in-CO₂ microemulsion.

In this work, the size of the particles in the microemulsion was estimated from the height and width of the surface plasmon resonance band in the UV–visible absorption spectra.² TEM micrographs of offline samples confirmed the in situ measurements of Ag particle size. Microemulsions containing Ag particles had relatively long stability (>1 h) in supercritical CO₂ at 35 °C, 400 bar ($T_c = 31.2$ °C). This is the first report of the stable suspension of nanometer-sized metallic particles in CO₂ and represents a significant advance for the future application of CO₂ solvent-based systems for a wide range of particle synthesis and catalytic reactions in this environmentally friendly solvent.

There are numerous studies of reverse micelles or microemulsions in supercritical fluids starting from the late 1980s.³ Early studies showed that nanometer-sized water droplets could be thermodynamically stabilized in supercritical alkanes, hydrochloro-fluorocarbons, and more exotic fluids such as xenon. Over the past decade, there have been significant advances toward the formation of microemulsions in CO₂ by using a variety of different fluorinated surfactants.¹ In a related area, fluorinated chelates have been used to “dissolve” a number of different metal ions in CO₂.⁴ Another process that was used to produce nanomaterials involved dissolving a compound (on a molecular level) in a supercritical fluid

and then rapidly expanding this supercritical solution (RESS) through a nozzle whereby the nucleation processes produce nanometer-sized powders.⁵ A variation of this process has recently been reported⁶ for the production of Ag particles, in which the precursor AgNO_3 is dissolved in supercritical ammonia and then sprayed into a liquid ethanol solution containing a reducing agent.

There are only a few reported studies of reactions in supercritical fluid microemulsions. Nanometer- and micrometer-sized metal oxide and metal sulfide particles have been synthesized in reverse micelles and microemulsions in the supercritical alkanes⁷ where the colloidal attractive forces are much weaker. Micrometer-sized titanium dioxide particles were produced using a CO_2 /surfactant technique.⁸ Clarke et al. reported an investigation of simple aqueous inorganic reactions in the cores of supercritical CO_2 microemulsions.⁹ More recently, Roberts et al. reported formation of colloidal silver in supercritical alkanes.¹⁰ The results reported here of colloidal silver stabilization in a supercritical CO_2 microemulsions offer significant advantages over conventional liquid-phase systems including (i) being one of the most environmentally benign solvents available, (ii) providing high diffusivities and thus accelerated reactions rates, (iii) the ability to recover reaction products and the catalyst particles through the manipulation of fluid density, and (iv) the potential to synthesize the particles in the fluid and to subsequently conduct catalytic reactions using these particles.

The Ag(0) particles were synthesized directly in a high-pressure UV-vis absorption cell so that the reaction rates could be monitored in situ.¹¹ The surfactant system¹¹ consisted of a mixture of sodium bis(2-ethylhexyl)sulfosuccinate ($[\text{AOT}] = 12.8 \text{ mM}$) with a fluorinated cosurfactant, a perfluoropolyether-phosphate ether ($[\text{PFPE-PO}_4] = 25.3 \text{ mM}$) at a water-to-surfactant ratio of $W = [\text{H}_2\text{O}]/[\text{AOT}] = 12$. The W value has been corrected for the water that dissolves in the CO_2 continuous phase at a level of approximately 0.2 mol %. The PFPE-PO_4 is very soluble in CO_2 but, by itself, is unable to form a microemulsion phase with large water cores. Thus, its role in this system is probably more like that of a cosurfactant for the AOT micelles.¹¹ The cosurfactant in this case partitions into the interface region with the AOT, and the fluorinated tails reduce the interdroplet attractive interactions to the point where the AOT microemulsion droplets can be stably dispersed. One supercritical condition (35 °C and 367 bar) and a liquid condition (25 °C and 300 bar) were explored. The two common reducing agents used in alkane-microemulsion systems are hydrazine (N_2H_4) and sodium borohydride (NaBH_4).¹² However, both of these compounds readily react with the aqueous carbonic acid (pH 2.9) in the micelle core that is present as a result of the $\text{CO}_2/\text{H}_2\text{O}$ equilibrium. Hence, for this experiment, we selected the less CO_2 -reactive $\text{NaBH}(\text{OAc})_3$ to perform the reductions in liquid and supercritical CO_2 . ($[\text{AgNO}_3] = 0.33 \text{ mM}$, $[\text{NaBH}(\text{OAc})_3] = 0.2 \text{ mM}$).

Before the reduction,¹¹ the system was stirred for about 1 h to ensure formation of an optically clear, homogeneous microemulsion. Reaction times were about 1–3 min following the introduction of the reducing agent. Inclusion of about 50 mM ethanol greatly improved the particle stability by a mechanism that is not well understood. The formation and stability of the Ag nanoparticles was monitored in situ by UV-vis spectroscopy which was described before.^{3b} The absorption bands originating from the surface plasmon resonance of nanosized Ag crystals¹² were recorded. The reported spectra represent difference-spectra

between the microemulsion before and after addition of the reducing agent. The precursor solution and the final Ag-particle solution contained *optically clear* microemulsions during the entirety of the reaction sequence.

Figure 1 shows the UV–vis absorption spectra of the Agnanoparticle microemulsion in (a) liquid CO₂ and (b) supercritical CO₂ collected at intervals of 20 and 10 min, respectively. Both spectra have a broad peak at ~400 nm, which is characteristic of nanosize Ag(0) particles. Bandwidth analysis² indicates that the particles have a size of about 4 nm. The intensity of this 400-nm band increased and reached its maximum in less than 3 min. Subsequently there was a gradual decrease in this band intensity over approximately 1 h especially for the supercritical CO₂ microemulsion, which is consistent with the slow flocculation of the nanoparticles. The 400-nm band persisted for many hours in liquid CO₂. This phenomenon can be explained in part by the lower viscosity and lower dielectric constant of supercritical CO₂ resulting in higher collision frequency and exchange rates between microemulsion droplets and stronger attractive interaction between the nanoparticles.

Particle samples were collect via the rapid expansion of supercritical fluid solution (RESS) technique using a 50- μ m i.d. (1.6-mm o.d.) PEEK restrictor in order to minimize the flocculation of particles during the depressurization. TEM was used to study the morphology and the size distribution of the collected particles. Figure 2 shows the TEM micrographs of the Ag particles collected by using the RESS process. The average size of the particles is approximately 5–15 nm, consistent with the particle size determined from the UV–vis spectra. There is a relatively high degree of polydispersity of the Ag particles, which is similar to what was observed during the formation of particles in liquid alkane microemulsions.¹² High-resolution images of these particles (not shown) gave clear evidence of a crystal lattice structure in agreement with the crystalline phase of Ag(0) that is observed in the liquid alkane synthesis. In these samples collected for TEM, the individual Ag particles were found to be embedded in the larger surfactant particles produced in the RESS expansion having sizes on the order of a few micrometers in diameter. The larger surfactant particles result from the agglomeration of many individual micelles, and they are typical of the morphology that is expected during the expansion and nucleation processes that occur via RESS under these conditions.

These results represent the first step to formation and stabilization of a range of different metallic particles in CO₂. The results are not only of interest for particle synthesis and catalytic reactions but also have implications in areas related to particle stabilization in parts cleaning.

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11. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was purified and dried as previously described.^{3b} The perfluoropolyether–phosphate ether (PFPE–PO₄) having a general structure CF₃O(OCF(CF₃)CF₂)_n(OCF₂)_mOCF₂CH₂OCH₂–CH₂OPO(OH)₂, an average molecular weight of 870, was used as received from Ausimont. Methods for acquisition of UV–vis spectra have been previously described.^{3b} All of the liquid and solid components, except for the reducing agent, were added directly to a 16-mL spectroscopy cell having a path length of 5 cm. The cell was flushed with small amounts of gaseous CO₂ to remove air, pressurized to about 400 bar, and then finally stirred for 1 h to dissolve the surfactants, water, and AgNO₃ and to form the microemulsion phase. The reducing agent solution (a suspension in dichloroethane) (60 μL) was rapidly injected into the cell using a small amount of pure CO₂ as the injection fluid.
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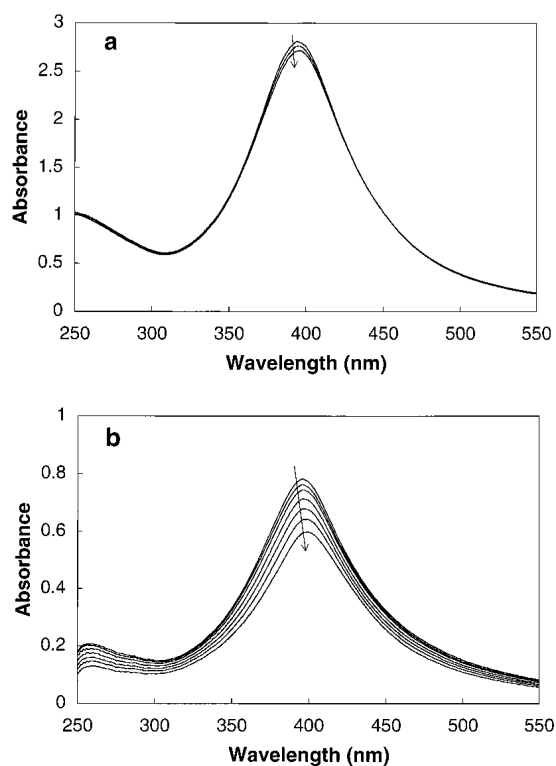


Figure 1.

Series of UV-vis spectra of Ag(0) nanoparticles dispersed in microemulsions formed in (a) liquid CO₂ (25 °C and 300 bar) and (b) supercritical CO₂ (35 °C and 367 bar) collected at intervals of 20 and 10 min, respectively. Spectra were acquired at evenly spaced intervals over the course of an hour after their formation.

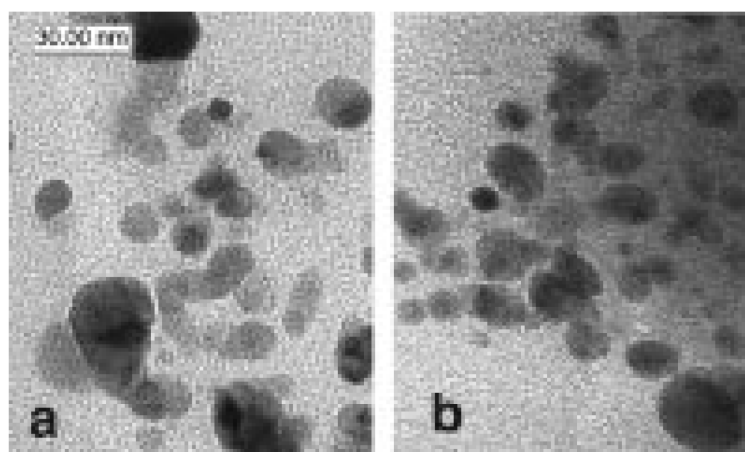


Figure 2. Transmission electron micrographs of silver particles synthesized in (a) liquid CO₂ (25 °C and 300 bar) and (b) supercritical CO₂ (35 °C and 367 bar).