Synthesizing silver halide nanoparticles in supercritical carbon dioxide utilizing a water-in-CO_2 microemulsion

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Ionic species can be stabilized in the water core of a water-in-CO_2 microemulsion in supercritical fluid CO_2; by mixing two microemulsions containing Ag^+ and X^- ions separately, silver halide (AgX) nanoparticles were synthesized in supercritical CO_2; the water-in-CO_2 microemulsion may provide a reaction system for a wide range of nanoparticle syntheses involving ionic species in supercritical CO_2.

Reverse micelles and microemulsions formed in liquid and supercritical carbon dioxide (CO_2) allow high polar compounds to be dispersed in this nonpolar fluid.[1] A recent report demonstrated that silver ions in the water core of a water-in-supercritical CO_2 microemulsion could be reduced to nanosized metallic silver particles by a reducing agent dissolved in the fluid phase.[2] The rate of formation of silver nanoparticles in the water-in-supercritical CO_2 microemulsion is fast, suggesting the microemulsion is dynamic in nature.[3] By collision, exchange of contents between two water-in-supercritical CO_2 microemulsions probably would take place effectively. This suggests the possibility of performing nanomaterials synthesis in supercritical CO_2 by mixing water-in-CO_2 microemulsions containing different ions in the water cores. The water-in-CO_2 microemulsion system thus may function like a 'nanoreactor' for a wide range of chemical syntheses involving ionic species as starting materials in supercritical CO_2.

Recently, Ida *et al.* found that the ionic conductivity of silver iodide increased significantly as the particle size decreased to the nanometer-size range.[4] Silver chloride and silver bromide are indirect gap semiconductors and silver iodide is a direct gap semiconductor. Much attention has been paid to the changes in band gap energies for small semiconductor particles as the particle radius decreases.[5] Rosseti *et al.* explained the particle size dependence of the excited state electronic properties of silver iodide and silver bromide as a consequence of electron and hole localization in the small crystallites.[6] Water-in-oil microemulsion technology has been used to synthesize a variety of nanoparticles. Usually, nanometer-sized particles with a high degree of monodispersity can be obtained using this technology.[7] Formation of nanoparticles in supercritical fluids offers significant advantages over conventional liquid-phase systems including rapid separation of solvent and the possibility of depositing the particles *in situ* in porous materials utilizing the unique properties of the supercritical fluid phase.[2]

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) obtained from Sigma, was purified using a method described by Williams *et al.*[8] The perfluoropolyether–phosphate (PFPE-PO_4) received from Ausimont has a general structure of $CF_3O[OCF(CF_3)CF_2]_n(OCF_2)_mOCF_2CH_2OCH_2CH_2OPO(OH)_2$ with an average molecular weight of 870. The carbon dioxide, SFE grade, was obtained from Oxarc.

Two homemade high-pressure vessels were utilized for the synthesis. One vessel (9.5 ml volume) was equipped with a fiber-optic system (5 mm pathlength) connected to a CCD array UV–VIS spectrometer. The high-pressure fiber-optic spectroscopy cell is described elsewhere.[3] The other vessel was a 15 ml high-pressure view cell with sapphire windows.[2] Each system could be isolated from the other by Valco high-pressure valves. A schematic diagram of the entire supercritical fluid system used for this study is shown in Fig. 1.

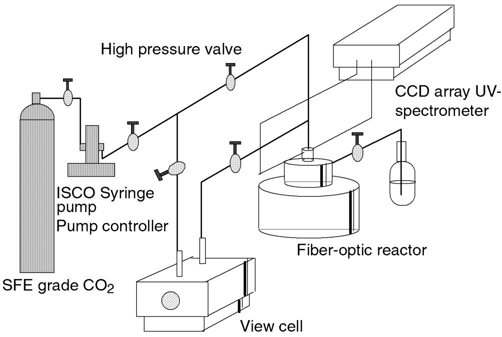

Fig. 1 Schematic diagram of the supercritical CO_2 microemulsion reaction system.

The reverse micellar solutions were prepared by using sodium bis(2-ethylhexyl) sulfosuccinate [AOT] (12.8 mM) and the cosurfactant perfluoropolyether phosphate [PFPE-PO_4] (25.3 mM) at the water-to-surfactant ratio, $W = [H_2O]/[AOT] = 12$. The $AgNO_3$ was made to 3.3 mM and NaI, NaBr and NaCl were made to 6.6 mM. The silver nitrate solution was always placed in the 9.5 ml fiber-optic cell and the sodium halide solutions were placed in the 15 ml view-cell. Each solution was stirred for 1 h in the pressurized vessel to ensure the formation of a homogeneous optically transparent microemulsion. For the supercritical fluid carbon dioxide experiments, the vessels were first both pressurized to 80 atm. At the end of 1 h, the 15 ml vessel was pressurized to 200 atm and the microemulsion containing the halide solution was pushed into the fiber-optic cell by opening an interconnecting valve and the spectra were recorded.

Fig. 2 shows the UV–VIS absorption spectra of silver halide nanoparticles observed in the supercritical fluid CO_2 experiments. The spectra for silver iodide show a broad band in the approximate range 410–450 nm. The peak wavelength of the absorption band increased with time after the mixing, varying from *ca*. 422 to 429 nm. About 30 s after the mixing, the peak wavelength reached approximately a constant value at 429 nm and the peak absorption intensity also became constant for the remainder of the experiment. These spectra are consistent with the UV–VIS spectra previously reported by Sato *et al*. for nanosized silver iodide particles formed in an AOT/isooctane reverse micelle system.[9] For silver bromide, we observed shoulder peaks in the range 300–350 nm. Again the observed spectra are consistent with the previously reported observations for silver bromide nanoparticles.[9] The spectra of silver chloride showed an absorption threshold shorter than silver bromide, also in agreement with the literature report.[9]

The size of the silver halide nanoparticles can be estimated by first calculating the band gap energies for the semiconductors. For direct allowed transitions, such as silver iodide, the following equation has been derived by Ravich *et al.*[10]

$$\sigma h\nu = K(h\nu - E_g)^{1/2} \qquad (1)$$

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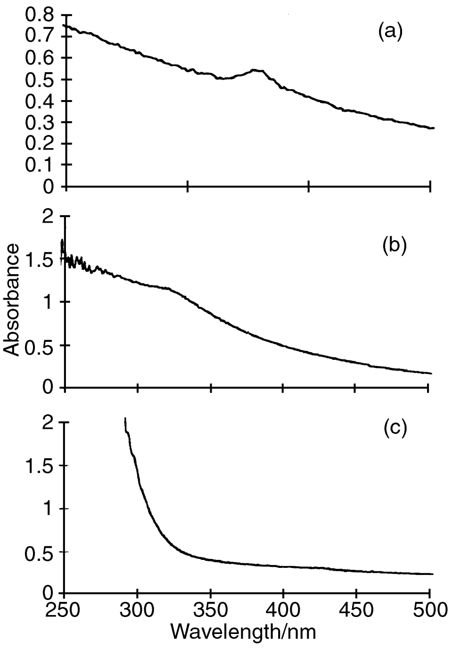

Fig. 2 Absorption spectra of AgX nanoparticles synthesized in the water-in-supercritical CO_2 microemulsion: (a) AgI, (b) AgBr and (c) AgCl.

and for indirect gap semiconductors, like silver bromide and silver chloride,

$$\sigma h\nu = K'(h\nu - E_g')^2 \qquad (2)$$

In these equations, σ and $h\nu$ are the absorption coefficient and the photon energy, respectively, K and K' are proportionality constants, and E_g and E_g' are the band gap energy and the indirect energy transition threshold, respectively.

The average diameter of the nanoparticle, d_p, can be estimated from the band gap energy, E_g,[9,11]

$$E_g = E_{g,\mathrm{bulk}} + (h^2/2d_p^2)[(1/m_e) + (1m_h)] - [(3.6e^2)/(4\pi\varepsilon d_p)] \qquad (3)$$

where m_e and m_h are the effective mass of an electron and a hole in a semiconductor, respectively. In eqn. (3), $E_{g,\mathrm{bulk}}$ is the energy of the band gap of the bulk semiconductor, ε is the dielectric constant of the semiconductor and e is the charge of an electron. The following parameters[8] were used for the calculations: for AgI, $E_{g,\mathrm{bulk}} = 2.83$ eV, $\varepsilon/\varepsilon_0 = 4.91$, and $m^*/m_0 = 0.2$; for AgBr, $E_{g,\mathrm{bulk}} = 2.5$ eV, $\varepsilon/\varepsilon_0 = 4.62$, $m_h/m_0 = 0.645$, and $m_e/m_0 = 0.215$. For the other symbols, ε_0 is the dielectric constant of vacuum, m_0 is the rest mass of an electron and m^* is represented by the following equation, $m^* = [(1/m_e) + (1/m_h)]^{-1}$.

The variation of AgI nanoparticle diameters with time during synthesis in supercritical CO_2 can be calculated using eqn. (3) and the UV–VIS spectroscopic data. The results for silver iodide showed a sharp increase in particle size in the first few seconds until a stable size of *ca.* 3.4 nm in supercritical CO_2 was reached. For silver bromide, we obtained a particle size *ca.* 3.0 nm. The size of the silver chloride particles could not be calculated since the effective mass of a hole is not available.

A rapid expansion of supercritical solution (RESS) method[12] was used to collect the synthesized silver halide particles. The size distribution of AgI particles collected on a copper grid by the RESS method is shown in Fig. 3. The particle sizes shown in Fig. 3 (*ca.* 3–15 nm) are larger than the calculated AgI size based on the spectroscopic method. Rapid expansion of the water-in-CO_2 microemulsion apparently can cause agglomeration of the AgI nanoparticles. Other methods of collecting the synthesized nanoparticles in supercritical CO_2 with minimum agglomeration are currently under investigation.

To obtain more information on the mechanism of silver halide nanoparticle formation in supercritical CO_2, the absorbance *vs.* time for the products AgI, AgBr and AgCl were investigated at 426, 325 and 300 nm, respectively. The time that required for the absorbance–time curve to reach a plateau was used as a measure of the completion of the reaction. The reaction time followed the order AgI (16 s) > AgBr (28 s) > AgCl (40 s). Similar experiments by mixing water/AOT/hexane microemulsions (containing Ag^+ and I^- separately) would require *ca.* 3 min to reach the plateau for the formation of the AgI nanoparticles. The formation of silver halide nanoparticles in the water-in-CO_2 microemulsion system involves several processes including collision, intermicellar exchange and reaction between silver ion and halide ion as shown in the graphical abstract. The intermicellar exchange process involves the distribution of silver nitrate and sodium halide from water droplets to the surfactant phase. This process should depend on the hydrophobicity of sodium halide, *i.e.* NaI > NaBr > NaCl. The observed reaction speed follows the order of hydrophobicity of sodium halide, suggesting that the most hydrophobic species probably reside close to the interface and exchange faster. The reaction between Ag^+ and I^- is expected to be very fast because of the large K_{sp} values for all AgX. The rate-determining step for the formation of silver halide nanoparticles in the water-in-supercritical CO_2 probably is the intermicellar exchange process.

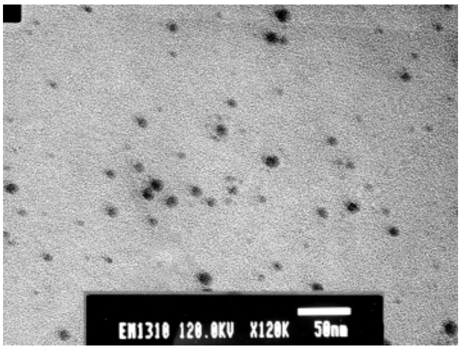

Fig. 3 TEM micrograph of the AgI particles collected on a copper grid using the RESS method.

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