Synthesis and Stabilization of Metallic Nanoparticles and Pre-Metallic Intermediates in PFPE/CO_2 Reverse Micelle Systems

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This paper presents the stabilization of silver nanoparticle intermediates synthesized in ammonium perfluoropolyether (PFPE-NH_4) reverse micelles using supercritical fluid (SCF) carbon dioxide. The effect of reducing agent type, reverse micelle water content, water core buffering, and bulk solvent type were all investigated as factors affecting stabilization of silver nanoparticle intermediates. Particles were characterized using in-situ UV-vis spectroscopy and transmission electron microscopy (TEM). Time-resolved spectral measurements were utilized to monitor both growth and persistence of particles. The intermediates were stabilized in PFPE-NH_4 reverse micelles as indicated by multiple UV-vis absorption bands which persist for periods of time measured to greater than 9 hours. Intermediate stabilization is facilitated by a unique environment existing as a result of PFPE-NH_4 surfactant presence and its local water environment.

INTRODUCTION

Nanomaterials currently show potential in a number of applications. Controlled organic synthesis as well as formation of metallic and semiconductor crystallites has been demonstrated in conventional liquid hydrocarbon solvents by exploiting reverse micelles as nano-scale reaction environments [1,2,3,4,5]. These unique environments result from organization of surfactants around a nanosized water core in contact with the hydrophilic headgroups of the surfactants. The size of the micelle core can be characterized by a W value which expresses the ratio of moles of water to moles of surfactant ($W = [H_2O]/[\text{surfactant}]$). Formation of nanometer sized particles by metal ion reduction within reverse micelle water cores has been demonstrated for copper, silver, and other metals [2,3,4,6,7]. Upon addition of reducing agent to the microemulsion, the metal ions in each reverse micelle are rapidly reduced to their ground state. The nanoparticle growth then occurs by intermicellar collision and exchange, leading to further particle growth [2,5,8,9,10]. This process of exchange and growth continues until the particles reach a size determined by the system where the surfactant aids in stabilization of the particles.

Several papers have focused on copper and silver nanoparticle production by reduction reactions within AOT reverse micelles in normal liquid alkane solvents [11,12,13,14]. These studies revealed the size of particles after a fixed reaction time to be primarily influenced by the micelle water content, W, the average number of metal ions and reducing agent molecules per micelle, and the continuous phase solvent type. Researchers [13,8,9] have found that the solvent properties can influence the dynamics of nanoparticle formation because of the different interactions between the solvent and the surfactant tails, and thus micelle-micelle interactions. Furthermore, Cason et al. [6] found that copper particle growth rates within AOT/alkane reverse micelles increased with higher water content, but that essentially the same particle size was eventually approached at all water contents in a given solvent. More importantly, it was found that the bulk solvent type significantly influenced the copper particle growth rates and final particle size. Thus, the ability to easily change the bulk solvent properties for desired particle characteristics appears promising and can be realized by supercritical fluids. Variations in supercritical solvent properties such as density, diffusivities, capacity for solutes, and dielectric constant, among others, can be effected by changes in temperature and pressure [15] to allow for regulation of reverse micelle collision rates and particle growth rates [7].

Recent investigation of silver and copper nanoparticle production in compressed and SCF alkanes showed these solvents provide effective media for nanoparticle synthesis [7]. Moreover, the importance of solvent density was recently demonstrated as a means of balancing steric repulsion forces and attractive van der Waals forces in order to disperse dodecanethiol-coated nanoparticles in supercritical ethane [16]. It would be desirable to replace the alkane solvent with supercritical CO_2 for environmental, economical, and safety reasons. Traditional hydrocarbon surfactants, however, are relatively insoluble in sc-CO_2 [17]. Fortunately, researchers have overcome this obstacle by employing surfactants with a fluorinated, CO_2-philic tail and a water soluble head group for use in sc-CO_2/water microemulsions [18,19,20,21,22,23,24,25]. These surfactants have proven capable at forming reverse micelles in supercritical CO_2 and have been shown to effectively solvate water soluble compounds in their bulk water core.

This paper presents the results of an investigation into the formation of silver particles within PFPE/sc-CO_2 reverse micelles. This study will investigate the formation of silver nanoparticles and silver intermediates within PFPE/sc-CO_2 reverse micelles as evidenced by multiple UV-vis absorption bands indicative of silver intermediates. We will show that silver intermediate stabilization is dependent upon a unique environment existing in the PFPE/sc-CO_2 reverse micelle. Specifically, we will demonstrate the effect of reducing agent, W, water core buffering, water core acidity, PFPE surfactant presence, and the addition of co-surfactants such as AOT on the stabilization of silver intermediates and silver nanoparticles.

EXPERIMENTAL SECTION

Materials. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and 10 N sodium hydroxide (NaOH) buffer were purchased from Fisher Scientific. Sodium Borohydride 99% and silver nitrate 99.9999% were purchased from Aldrich. Sodium Triacetoxyborohydride 97% and Isooctane were acquired from Acros. Carbon Dioxide was obtained from BOC gases. Deionized water was used in all experiments requiring water. The ammonium carboxylate perfluoropolyether of general formula $X(CF_2CF(CF_3)O)_nCF_2\text{-}COO^- NH_4^+$ (where X is F or Cl) and average molecular weight of 667 (for X=CF_3O) or 632 (for X=Cl) was synthesized according to previously reported methods [26]. Experiments were initially conducted using a completely fluorinated PFPE, but use of the PFPE containing chlorine was eventually necessitated by commercial availability. Use of each is designated in the discussion.

A silver functionalized Cl-PFPE (Cl-PFPE-Ag) was synthesized according to Bio-Rad Labs recommendations (D. Hardy, personal communication, June 2001) by adding 14.8 N ammonium hydroxide (NH_4OH) to the carboxylic acid form of Cl-PFPE until a pH of 4.5 was achieved. The pH was elevated to provide a pKa appropriate for silver exchange with the acidic hydrogen. Subsequently, a 2 molar aqueous $AgNO_3$ solution was added to the mixture for a maximum fractional exchange of approximately 30%. The solution was allowed to mix for 14 hours after which time the mixture was finally neutralized with NH_4OH and then dried.

Particle Formation. The reactions were performed in a constant volume (96 mL) stainless steel reactor fitted with two quartz windows for UV-vis analysis a PTFE insert was used on some occasions to hold an additional quartz window, reducing the optical path length from 3.2 to 1.9 cm and the vessel volume to 87 mL. Desired amounts of surfactant, silver nitrate, deionized water, and NaOH (where noted) were initially loaded into the vessel. Bulk solvent (e.g. CO_2) was then loaded to the desired pressure using an ISCO high-pressure syringe pump. Vessel contents were allowed to mix for several hours at the desired temperature and pressure, after which the reducing agent was displaced into the vessel via the bulk solvent. Pressure within the vessel was monitored to within +/- 0.7 bar using a pressure gauge and temperature was maintained to within 0.1°C using a heating tape, platinum RTD, and an Omega controller. Particle growth could then be monitored by collecting UV-Vis spectra on a Varian 3E spectrophotometer as a function of time.

Silver nanoparticles were produced in compressed liquid propane at 37°C, 200 bar, and a W of 10 with AOT, $AgNO_3$, and $NaBH_4$ concentrations of 100, 1, and 3 mM, respectively. Synthesis of silver particles in water-in-CO_2 reverse micelles was accomplished at temperatures between 36 and 37°C, pressures ranging from 200 to 325 bar, and molar water to surfactant ratios, W, between 0 and 10. In this paper we report the uncorrected W value for the solubility of H_2O in CO_2 since the partitioning of H_2O between CO_2 and the reverse micelle cores has not been measured. The PFPE concentrations ranged between 1.4 wt.% (20 mM) and 2.2 wt.% (30 mM) while $AgNO_3$ concentrations ranged from 0.4 to 1.1 mM. Reducing agent concentrations extended from 0.5 to 3 mM for $NaBH_4$ and from 0.2 to 0.3 mM for $NaBH(OAc)_3$. Transmission electron microscope analysis was performed using a Zeiss EM 10 TEM. Sample grids were prepared either by depressurizing the vessel and placing a drop of particle mix redispersed in ethanol on a nickel grid or by rapidly expanding the reactor contents through a 100 μm capillary tube onto a TEM grid.

RESULTS AND DISCUSSION

Ag in Liquid AOT/Alkane Systems. Previous studies have shown the feasibility of silver nanoparticle production within reverse micelles using the surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT). Silver particles have been shown to demonstrate a characteristic absorbance near 400 nm and a typical decrease in bandwidth and increase in peak intensity as particles increase in size [14]. The peak full width at half max has been found to vary linearly with the inverse of the particle diameter, thus providing a valuable method of in-situ particle size characterization [14]. We have shown the same characteristic peak to result for silver nanoparticles formed in compressed propane/AOT reverse micelles.

Ag in PFPE-NH_4/sc-CO_2 Systems. Given our previous alkane results, the production of nanoparticles in PFPE-NH_4/CO_2 reverse micelles seems straightforward. However, extension of the micelle system to supercritical carbon dioxide resulted in spectra inconsistent with the previous trend of one plasmon band centered at 400 nm. Rather than the characteristic absorption spectra indicative of silver nanoparticles, multiple absorption bands were recorded. Figure 1 displays the typical absorption spectra for silver particles produced in PFPE-NH_4/CO_2 reverse micelles. Interestingly, the bands persist for extensive periods of time (to 9 hours), indicating stabilization of unexpected products. $NaBH_4$ was initially used as the reducing agent, so in order to reveal any link between the reducing agent and the multiple absorption bands, sodium

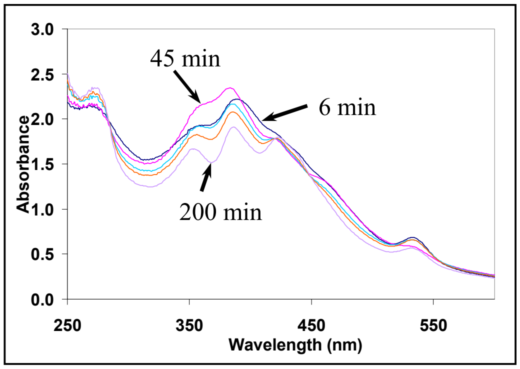


Figure 1: **UV-vis spectra of silver nanoparticles synthesized in PFPE-NH_4/CO_2 microemulsion**

triacetoxyborohydride was used as an alternate reducing agent. Despite the different reducing agent, multiple UV-Vis peaks, located at 275, 350, 380, 420, 470, and 530 nm, still persist. An additional experiment was performed whereby reducing agent was added to a system absent of silver nitrate and from which no absorption bands were observed. Taken together these results indicate that the reducing agent is not the sole cause of the absorption bands and also that they are the consequence of some silver derivative. The multiple absorptions likely imply the presence of stabilized silver intermediates as other researchers have seen similar peaks and have linked them to individual intermediates.

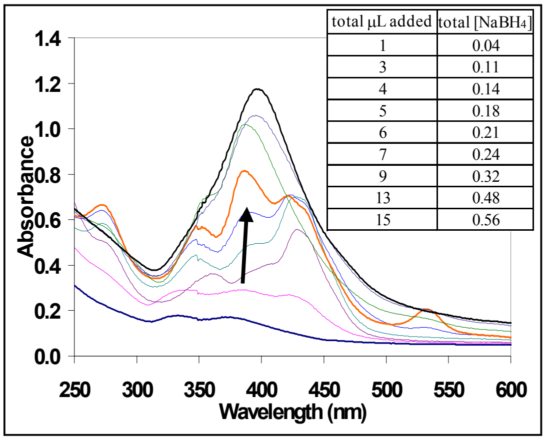
Absorption Band Identification. Many researchers have investigated silver particle formation on microsecond time scales and have identified silver intermediate UV-vis bands indicative of silver clusters comprised of small numbers of atoms. UV-vis peak location may also result from particle shape, size, and multiple particle environments, etc. [14,27]. The peak observed at 270 nm may indicate Ag_4^{2+}, as this location has been widely reported in the literature to denote Ag_4^{2+} presence [14,28,29]. The absorbance near 350 nm may be attributed to a wider range of intermediates ranging from metal silver atom (Ag^0) and oligomeric clusters at 360 [30]. Additional bands at 310 and 345 nm have been ascribed to clusters consisting of Ag_9^+ and/or Ag_8^{2+} [31]. In some of our experiments the 350 nm peak can be seen to fall as the peaks near 400 grows, which may indicate a large cluster such as Ag_9^+. Absorption bands observed at 390 and 420 nm may indicate the presence of silver nanoparticles situated within different regions as this absorbance varies between 380 and 420 depending upon the size, shape, and surrounding environment in which the nanoparticle is situated [14,28,32]. Consequently, the peaks observed at 390 and 420 may result from silver nanoparticles situated in different microenvironments such as the acidic, bulk water, and polar surfactant headgroup regions observed by Johnston and coworkers, [18,19] when using the methyl orange probe. Furthermore, shifts to 384 nm and 420 have been reported for silver nanoparticle near polyacrylate or of large size, respectively [32,31]. Therefore, there are many contributions that could result in the bands near 400 nm. The bands recorded at the 480 and 540 nm region are potential clusters of silver atoms and ions as others have observed clusters of silver atoms consisting of equal parts atoms and ions and of sizes ranging from 8 to larger than a Ag_4^{2+} dimer [31,32,33].

Ag Size Comparison in AOT/Alkane vs. PFPE-NH$_4$/sc-CO$_2$ Systems. Transmission electron microscopy was used to obtain images of the silver nanoparticles. Particles created in an AOT/Propane reverse micelle system show a mean particle diameter of approximately 3.8 nm with a 2.4 nm standard deviation, based on more than 720 particles. Applying the same technique to particles produced in the PFPE/CO_2 reverse micelles indicated a fairly even and narrow distribution of particles around 3.5 nanometers in diameter, based on 201 particles. Silver intermediates would likely be too small to appear on a TEM, but the presence of monodisperse particles at comparable sizes to particles produced in alkanes nevertheless demonstrates the feasibility of silver particle production in PFPE-NH_4/CO_2 reverse micelles.

Ag in Buffered PFPE-NH$_4$/sc-CO$_2$ Systems. As previously mentioned, micelles formed in supercritical CO_2, unlike AOT/alkane microemulsions, have acidic water cores due to the reaction of CO_2 with the water to form carbonic acid. The pH within PFPE/CO_2 reverse micelles has been determined to be between 3.1 and 3.5, [34] but since many reaction outcomes rely on pH, this presents an obstacle to the tunability of the micelle "nanoreactor." More recently, NaOH has been shown to effectively buffer the core pH to nearly 7 [35]. In light of these experimental findings, the reverse micelle water cores were buffered with NaOH to achieve an approximate pH of 6. Following reduction, the absorption spectra once again revealed the single absorption band indicating silver nanoparticles at 400 nm. The absence of strong multiple peaks at alternate locations may indicate a reduced concentration of Ag intermediates and an increased concentration of nanoparticle silver as a result of buffering. It should be stressed that this destabilization may result from a mechanism such as NaOH ion interference, rather than simply the raised core pH.

Ag in Ag-PFPE-NH_4/sc-CO_2 (W = 0) Systems. An experiment was performed with no water added to the system in order to determine the importance of the micelle water core, since without water, CO_2 cannot react to form carbonic acid. A small amount of silver functionalized surfactant (Cl-PFPE-Ag) was used along with Cl-PFPE-NH_4 to load silver into the microemulsion. The silver was then reduced by $NaBH_4$ (0.6 mM in vessel) and monitored to give the absorption spectra. Of interest were the peaks located at 275, 350 and 400 nm after only 1 minute , which after only 1 additional minute, diminished at 275 and 350 nm to give a more focused and intense band at 410 nm. Typical of nanoparticle synthesis in reverse micelles, the single band temporarily grows in intensity and decreases in width before the onset of particle agglomeration and precipitation, which is indicated by the broadening and flattening of the spectrum. As a result, we can conclude that the reverse micelle water core aids silver intermediate stabilization, particularly at 275 nm and 350 nm.

Ag in PFPE-NH_4/AOT/sc-CO_2 Systems. Addition of AOT to the PFPE- NH_4 reverse micelles was undertaken, similar to work by Ji et al. using a mixture of AOT and PO_4-PFPE [36]. Despite the different functional group on the PFPE surfactant, the spectrum we obtained coincides well with those obtained by Ji et al. which demonstrates a UV-vis spectrum with a wide bandwidth and an absorbance that decreases with time. Such spectra denote polydisperse particles that tend to agglomerate and precipitate as time progresses. Should intermediate stabilization result entirely from low pH, then multiple UV-vis peaks should persist regardless of AOT surfactant addition. Thus, this demonstrates that the PFPE/CO_2 environment is different from the AOT/PFPE/CO_2 environment such that the AOT, like the NaOH, is able to destabilize the intermediates of silver.



total μL added	total [$NaBH_4$]
1	0.04
3	0.11
4	0.14
5	0.18
6	0.21
7	0.24
9	0.32
13	0.48
15	0.56

Figure 2: UV-vis spectra of silver nanoparticles in PFPE-NH_4/HFE microemulsions

Ag in PFPE-NH_4/HFE Systems. Lastly, carbon dioxide's role in intermediate stabilization was examined using a liquid hydro-fluoroether (3M HFE 7100) to replace the CO_2. After verifying the presence of reverse micelles having a bulk water environment using methyl orange, silver ions solvated in the reverse micelles were incrementally reduced using 1 μL additions of $NaBH_4$/water solutions. Figure 2 shows the UV-vis spectra recorded after each additions as well as the microemulsion reducing agent concentration. Corresponding to incremental reductions, peaks form and then proceed to rise and fall in the same locations observed in CO_2 until a final single absorption band located at 400 nm persists. The water core pH in these HFE/PFPE-NH_4 reverse micelles is not acidic, since CO_2 is no longer present to form carbonic acid. Despite this elevated pH, the multiple UV-vis bands persist, thus suggesting that the ammonium PFPE surfactant in the reverse micelle environment plays a primary role in stabilizing silver intermediates. These results also demonstrate that stabilization is not simply an effect of low pH, as might be apparent from the results obtained after buffering CO_2 reverse micelles. Rather, in addition to elevating the pH, the added base also provides a counter ion that could disrupt the stabilizing interaction between the intermediate and the ammonium PFPE surfactant.

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