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Reverse micelle synthesis of silver nanoparticles in gas expanded liquids

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ABSTRACT

The tunable solvent properties of gas expanded liquids (GXLs) have been previously used for the fractionation and separation of polydispersed ligand-stabilized metal nanoparticles into distinct monodispersed fractions. This work employs CO_2 expanded hexane for silver nanoparticle synthesis within an AOT reverse micelle system where the tunable GXL solvent properties are used to control the nanoparticle size and polydispersity. The objective of this project is to answer two questions: (1) can nanoparticles with narrow and well-defined size distributions be synthesized in GXLs? and (2) how do the solvent properties impact the resulting nanoparticle size? In the reverse micelle synthesis, the AOT surfactant provides a nano-scale aqueous micelle core for nanoparticle nucleation, as well as, acts as a nanoparticle stabilizing ligand. Increasing the CO_2 partial pressure in a GXL impacts the surfactant–solvent interaction and results in the synthesis of different sized nanoparticles. At ambient pressures, the mean particle diameter synthesized was 6.1 ± 2.1 nm with $W = 40$ and 5.4 ± 2.0 nm with $W = 20$, where W is the molar ratio of water to AOT. At CO_2 partial pressures of 6.9 and 13.8 bar, there was no significant change in particle size, but decreases in the size distributions were observed. At CO_2 partial pressures ranging from 20.7 to 41.4 bar, steady decreases in the mean particle diameter and size distribution were observed with values of 4.0 ± 0.8 for $W = 40$ and 4.1 ± 1.0 for $W = 20$ at 41.4 bar. This demonstrates some degree of nanoparticle size tunability within the GXL solvent, where smaller particle diameters and size distributions are achieved at higher CO_2 compositions.

1. Introduction

Nanotechnology is based on materials built from particles less than a critical length. In the case of metallic nanoparticles, the unique chemical, optical, and physical properties depend heavily on size, shape, and polydispersity [1,2]. Preparation of monodispersed populations is often required to employ size-dependent properties, and many methodologies require post synthesis processing to obtain the desired size monodispersity. The objective of this work is to use tunable solvents to synthesize monodispersed populations of silver nanoparticles of a controllable size. Traditional silver nanoparticle synthesis methods can produce nanoparticles with wide size distributions or are limited in the tunability on the synthesized particle size. Since size greatly impacts nanoparticle properties, it is imperative to (1) control the synthesized nanoparticle size or (2) fractionate the synthesized nanoparticles into monodispersed populations. There are several post-synthesis methods to narrow size polydispersity and obtain a specific particle size fraction including liquid anti-solvent precipitation [3–5], chromatography techniques [6], and isoelectric focusing [7]. Sigman et al. used an ethanol/chloroform anti-solvent/solvent pair and centrifugation to size selectively precipitate and separate a polydispersed population of silver nanoparticles capped with dodecanethiol ligands into monodispersed particle fractions [5]. The addition of anti-solvent results in poorer solvent conditions and reduces the favorable solvent–ligand interactions and leads to nanoparticle precipitation. The reduced ability of the solvent/anti-solvent mixture to disperse the particles is due to the decreased steric repulsion of the ligands and inability to overcome the van der Waals attraction between particles. Larger particles have greater van der Waals attractive forces, and as a result, precipitate first upon increasing anti-solvent concentration [8,9]. Further additions of anti-solvent and subsequent centrifugation to provide an external force to accelerate precipitation leads to smaller particles precipitating out of solution. Successive incremental additions of anti-solvent can lead to narrow size fractions with standard deviations less than 5%.

Although the use of liquid anti-solvents for size fractionation will produce very narrow size distributions, copious amounts of anti-solvents are used, and the required centrifugation is time and energy intensive and not easily scalable. This leads to a large amount of waste and energy usage [3–5]. There is motivation then to develop greener techniques to obtain nanoparticle populations with narrow size distributions. Previous work using compressed

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and supercritical fluid solvents has shown that pressure and temperature tunable solvent properties can be used to control the size of dispersed nanoparticles during synthesis and post synthesis processing [10]. Shah et al. utilized the tunable density of supercritical ethane to obtain a size-selective dispersion of dodecanethiol coated nanoparticles [10,11]. This work illustrated that by changing solvent density, the dispersible particle size could be controlled where the largest particles were dispersed at the highest pressure. Ethane, for example, requires high pressures above 500 bar to synthesize and disperse copper nanoparticles of 3.4 nm in diameter [9]. Roberts et al. used the tunable solvent properties of GXLs to fractionate a polydispersed solution of silver Brust particles [12,13]. CO_2 partial pressure was used to tune the solvent strength of solution for nanoparticles, and narrow size distributions were obtained at different CO_2 pressures. CO_2 is used as an anti-solvent because it dissolves easily into organic solvents and expands their volume; therefore changing the solvent mixture properties [12,14]. For example, the composition of CO_2 in gas-expanded *n*-hexane can be adjusted from zero mole percent at ambient conditions to 81 mol% at 49.4 bar. CO_2 is a good choice for GXLs because it is a weak solvent, even at high pressures [15] and has no dipole moment and a very low refractive index [10]. GXLs provide a wide range of tunability with adjustments in pressure, which affords control over the size of nanoparticles achieved in post synthesis processing [9–12,16–19].

Nanoparticle size control can also be achieved using surfactant-mediated reverse microemulsion techniques, in particularly the surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in proportions such a reverse micelle water-in-oil microemulsion is formed [2,20–23]. The AOT reverse micelle system has been used widely for the synthesis of metallic nanoparticles including silver. Synthesis variables in the system that have been investigated include the type and concentration of surfactant, metal precursor, and reducing agent, as well as the temperature, pH, bulk solvent and water-to-surfactant molar ratio (*W*-value) [2,20,22]. CO_2 has been used as an effective anti-solvent to recover nanoparticles synthesized via a reverse micelle method [18,19,24,25]. This work explores the use of GXLs as a tunable fluid medium for the reverse micelle synthesis of silver nanoparticles. It was our hypothesis that the nanoparticle–surfactant–solvent interactions can be adjusted by tuning the solvent strength with GXLs in order to control nanoparticle size and polydispersity. We were able to synthesize particles of controlled sizes using the pressure-tunable solvent properties of GXLs where the particle size decreases with increasing CO_2 partial pressure. As a result, GXLs provide a greener alternative to control the size of synthesized nanoparticles.

2. Materials and methods

The surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was obtained from Fisher Scientific and used without further purification. 98% *n*-hexane was purchased from Sigma Aldrich, sodium borohydride from EMD Chemicals, and 99.995% silver nitrate from Alfa Aesar. Industrial grade CO_2 was purchased from National Welders Supply.

2.1. Particle synthesis

The method for the synthesis silver nanoparticles via the AOT reverse micelle synthesis has been discussed previously [13,26]. In short, 4.80 ml of 0.1 M AOT in *n*-hexane was combined with 0.10 ml of 0.01 M aqueous silver nitrate ($W = [H_2O]/[AOT] = 40$) in a custom pressure cell. For a *W*-value of 20, 5.55 ml of 0.1 M AOT in hexane was combined with 0.10 ml of 0.01 M silver nitrate in water. The cell was sealed and pressurized. The CO_2 partial pressures used in this study were 6.9, 13.8, 20.7, 27.6, 34.5 and 41.1 bar and ambient conditions as a control. The pressure was controlled using a Teledyne ISCO D-Series Model 500HP syringe pump. 0.25 ml of 0.10 M ($W = 40$) or 0.10 ml of 0.25 M ($W = 20$) of aqueous sodium borohydride was then injected at constant pressure through a Valco VICI *W* type injection loop. The pressure cell was vented to create laminar flow to ensure that all of the $NaBH_4$ solution entered the cell. Following the reaction and nanoparticle synthesis, 0.10 ml of dodecanethiol was injected in the same fashion through an additional injection loop after 15 min of stirring via magnetic stir bar. The system was then depressurized, and a cloudy brown solution was removed from the pressure cell. The nanoparticles were crashed out of solution with ethanol, centrifuged, redispersed in 10 mL of fresh *n*-hexane containing 0.1 ml of dodecanethiol. Nanoparticle samples were deposited on copper grids (Ted Pella), and TEM images were obtained on a Hitachi 7600 TEM. The particle diameters were determined using ImageJ software and reported as the Max Feret and Min Feret (the maximum and minimum diameters of a given particle). Histograms were created using Origin 7, and statistical analysis was performed using Minitab 16.

3. Results

3.1. Nanoparticle synthesis with $W = 40$

A mean particle size of 6.1 ± 2.1 nm was synthesized with a *W*-value of 40 and ambient pressure, while particles with diameters of 5.9 ± 2.0 nm, 6.1 ± 1.4 nm, 5.3 ± 1.4 nm, 4.7 ± 1.2 nm, 4.6 ± 1.4, and 4.0 ± 0.8 nm were obtained with CO_2 partial pressures of 6.9 bar, 13.8 bar, 20.7 bar, 27.6 bar, 34.5 bar, and 41.4 bar respectively. Table 1 summarizes the results for both *W*-values with the mean particle size and the standard deviation for both the Max Feret (maximum diameter) and Min Feret (minimum diameter) for each particle, as determined by ImageJ. Differences between the Max Feret and Min Feret are indicative of the particle sphericity. The reported particle diameter error is representative of the distribution of measured particle diameters within the population and is determined from the standard deviation with a 90% confidence integral. Fig. 1 shows representative TEM images and particle diameter histograms for the seven different reaction pressures at $W = 40$. From the results it can be seen that the AOT reverse micelle synthesis in gas expanded hexane does indeed produce particles of lower polydispersity and smaller diameters with increasing CO_2 partial pressure at a *W*-value of 40. ANOVA with the Tukey's method was performed to determine if the mean particle size measured for each CO_2 pressure demonstrated statistical independence. It should be noted that the Tukey's method tests the hypothesis that

Table 1
Summary of results for TEM size analysis.

Pressure (bar)	*W*-value	Max diameter (nm)	Min diameter (nm)	Particles counted
Ambient	20	5.4 ± 2.0	4.3 ± 1.7	675
6.9	20	5.6 ± 1.5	4.2 ± 1.1	665
13.8	20	5.4 ± 1.4	4.1 ± 1.1	384
20.7	20	5.1 ± 1.3	3.9 ± 1.1	383
27.6	20	5.0 ± 1.3	3.8 ± 1.0	463
34.5	20	4.6 ± 1.0	3.4 ± 0.8	425
41.4	20	4.1 ± 1.0	2.0 ± 0.9	502
Ambient	40	6.1 ± 2.1	4.8 ± 1.8	544
6.9	40	5.9 ± 2.0	4.7 ± 2.12	290
13.8	40	6.1 ± 1.4	4.4 ± 1.3	574
20.7	40	5.3 ± 1.4	3.8 ± 1.1	396
27.6	40	4.7 ± 1.2	3.7 ± 1.1	529
34.5	40	4.6 ± 1.4	3.4 ± 1.0	584
41.4	40	4.0 ± 0.8	3.1 ± 0.7	445