

# Radiolytically Induced Formation and Optical Absorption Spectra of Colloidal Silver Nanoparticles in Supercritical Ethane<sup>†,‡</sup>

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Received: August 4, 2000; In Final Form: October 30, 2000

Colloidal silver nanoparticles were synthesized in supercritical ethane at 80 °C and 80–120 bar, with methanol as cosolvent. Solvated electrons, produced by a pulse of 20 MeV electrons, reduced the silver ions. The time-resolved technique of pulse radiolysis was employed to characterize the reduction products and colloidal metallic particles. The absorption spectra of small silver clusters ( $\text{Ag}_2^+$ ,  $\text{Ag}_3^+$ ,  $\text{Ag}_4^{2+}$ , etc.) were detected at short times after the pulse. Colloidal metallic silver particles were identified by their characteristic plasmon absorption at 1–10 s after the pulse. Colloidal particles are stable for hours in supercritical ethane. The particles are less than 10 nm in diameter. Their size was determined using transmission electron microscope after precipitation from the solution.

## Introduction

Metal nanoclusters are important materials because of their role in surface-enhanced processes. The unique properties of metal clusters, such as collective electronic and lattice excitations, depend on the size and geometry of the particle,<sup>1</sup> and can be used in various applications from catalysis<sup>2,3</sup> to micro-electronics.<sup>4</sup>

Because of the unusual microscopic solvation of solutes and cosolvents, which affects the reaction kinetics,<sup>5</sup> supercritical fluids can provide great chemical flexibility and synthetic tunability for preparation of nanoparticles. In addition, the use of supercritical fluid as a medium for chemical reactions has prompted interest for in situ synthesis of catalysts, including metallic and semiconductor particles. Thus, nanometer- and micrometer-sized particles of metal oxides ( $\text{TiO}_2$ ),<sup>6</sup> hydroxides ( $\text{Al}(\text{OH})_3$ ),<sup>7</sup> and sulfides ( $\text{CdS}$ )<sup>8</sup> have been synthesized in reverse micelles and microemulsions in supercritical alkanes or carbon dioxide. Chemical reduction of silver<sup>9,10</sup> and copper<sup>11</sup> cations by borohydride or hydrazine was performed in water-in- $\text{CO}_2$  and water-in-ethane AOT reverse micelles under supercritical solvent conditions, resulting in the formation of metallic particles of 15–20 nm in diameter. The growth of silicon nanowires in hexane under elevated temperature (500 °C) and pressure (270 bar) was recently reported,<sup>12</sup> demonstrating that the thicknesses and orientations of nanowires depend on pressure in supercritical alkane.

We combined radiolytically induced reduction of silver cations with supercritical solutions to synthesize silver clusters. We used pulse radiolysis as a tool both for generating silver clusters in supercritical fluids and for examining their optical properties. Radiation chemistry has been shown to provide an excellent method for studying optical properties associated with surface plasmon absorption of metallic silver colloids.<sup>3,13,14</sup> There are many advantages of using supercritical fluids as a

reaction medium; the major one is the possibility to control size of particles combining pressure, temperature, and the time for termination of reaction by evacuation of gas from the cell. In this paper we report on the controlled growth and recovery of silver clusters in supercritical ethane (sc- $\text{C}_2\text{H}_6$ ) in the presence of methanol as a cosolvent.

## Experimental Section

**Materials.** Silver perchlorate and methyl alcohol were of the highest purity commercially available and were used as purchased. The  $\text{C}_2\text{H}_6$  (99.95%) was purchased from AGA. The gas was passed through a filter (Pall Gaskleen, GLPV2SIVMM4) for removal of impurities such as ethylene, oxygen, water, etc.

**Methods.** Experiments were performed in a stainless steel high-pressure cell with an optical path of 5 cm and effective volume of 12.5 cm<sup>3</sup>. Two Suprasil windows (1 cm thick) were sealed to the cell using Teflon O-rings. Experiments were done at constant temperature of  $80.0 \pm 0.1$  °C as monitored with a temperature controller (Omega, model CN 1001R7D). Pressure in the cell was adjusted using a high-pressure piston pump (Eldex, model B-100-S), and monitored with a Cole-Parmer digital pressure meter (model 7350-38). The experimental arrangements were similar to those described previously.<sup>15,16</sup>

Pulse radiolysis experiments were performed using the Argonne 20 MeV linear accelerator with 4 ns electron pulses. Two different pulse radiolysis setups were used, one for short time resolution (up to 100  $\mu\text{s}$ ) and another for longer time resolution (from 1 ms to 10 s). In both cases transient species were detected optically.

For short-time experiments, a monochromator (PTI, model 102) and photomultiplier (Hamamatsu R-1913) were used for wavelengths below 450 nm, and interference filters (bandwidth 10 or 40 nm) and silicon photodiode (EG&G, FND 100) were used for longer wavelengths (450 to 1000 nm). The electron pulses were collinear with the analyzing light beam, but in the opposite direction.

For longer times, a commercial OLIS RSM 1000 rapid scanning monochromator system was used. It consists of a subtractive double monochromator ( $1/4$  m,  $f/4.4$ ) with a rotating sector slit at the intermediate focal plane to scan the wavelength. A beam splitter and a pair of photomultipliers were used to measure the incident and transmitted light. A 250 nm-wide

<sup>†</sup> Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under contract number W-31-109-ENG-38.

<sup>‡</sup> The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U. S. Department of Energy.

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spectrum is acquired every millisecond. For these experiments a T-shaped pressure cell was used, having 5 cm optical path, but with an approximate 2 cm irradiation zone in the center where the electrons entered perpendicularly to the analyzing light.

The dose in the cell was measured using aerated solutions of thiocyanate and hexacyanoferrate(II).<sup>17,18</sup> The 'super Fricke' solution<sup>17</sup> was also used for dosimetry in long-time experiments. Details are published elsewhere.<sup>16</sup> The average dose absorbed in a sample was  $27.5\rho$  Gy, and  $20.5\rho$  Gy where  $\rho$  is density of sc-C<sub>2</sub>H<sub>6</sub> in g/cm<sup>3</sup>, for short and long time setups, respectively. The density of sc-C<sub>2</sub>H<sub>6</sub> was taken from the PVT relationship calculated using the BWR equation.<sup>19</sup> The effect of cosolvent was not taken into account for calculation of absorbed doses.

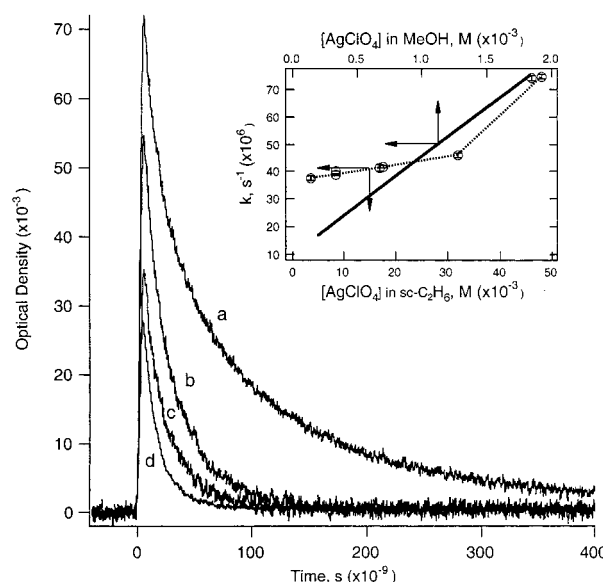
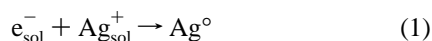
Solutions of silver perchlorate in methanol were prepared and deaerated prior to use. The desired volume of solution was added to the previously evacuated cell at temperature of 80 °C under the flow of ethane using an injector (Rheodyne, model 7030). The cell was then finally filled and pressurized with C<sub>2</sub>H<sub>6</sub>.

The size distribution and morphology of the collected particles were studied using a transmission electron microscope (TEM) from the Electron Microscopy Center for Materials Research at ANL (JEOL 100 CX and high-resolution electron microscope JEOL 4000). For preparative purposes, 5–10 consecutive pulses were used. The carbon-coated copper grids were placed on the window perpendicular to the electron beam or on the walls inside the cell. The silver particles were collected directly on the grids after depressurization of the cell. In some cases, particles deposited on the window were dispersed in methanol and then placed onto a grid.

## Results and Discussion

The results and discussion will be divided into three sections: (1) the initial reaction of the electron with the silver ions, (2) the growth of the small silver particles, and (3) the formation of large silver particles. In the first section we discuss the initial reactions between an electron and a silver ion and how the alcohol clusters alter the reactivity. In the second section we discuss the further reactions of silver atoms and growth of silver clusters. In the third section we will focus on the formation of nanometer-sized metallic silver particles.

**Kinetics of the Initial Reaction Between the Electron and Ag<sup>+</sup>.** A pulse of high-energy electrons was used to initiate the ionization of ethane. The electrons formed from the ionization of ethane were solvated in preexisting clusters of methanol, and were identified by their characteristic absorption spectra.<sup>20</sup> It has been shown previously that methanol molecules form clusters in binary mixtures of alcohols in liquid alkanes,<sup>21</sup> and in supercritical CO<sub>2</sub> or ethane.<sup>22</sup> Experiments on the spectrum of the electron had been carried out both as a function of pressure and mole fraction of alcohol. It was found that the size of methanol clusters decreases with increasing the pressure of ethane. Both the radiation chemical yield and lifetime of solvated electrons were found to depend on the mole fraction of methanol and on the size of methanol clusters in supercritical ethane.<sup>23</sup> In our experiments on silver particles, we injected 0.4 mL of methanol solution containing various concentrations of AgClO<sub>4</sub> into the cell, which was then pressurized with ethane to 100 bar. This corresponds to 10% mole fraction of methanol, with the agglomeration number of approximately 6–8 molecules of methanol per cluster.<sup>21</sup> We have found that, once formed, solvated electrons are able to reduce silver cations, reaction 1.



**Figure 1.** Time profile of solvated electron signal detected at 650 nm in a 12.5 cm<sup>3</sup> sc-C<sub>2</sub>H<sub>6</sub> (100 bar, 80 °C) containing 0.4 mL of (a) 0 M, (b) 0.26 M, (c) 1.0 M, and (d) 1.5 M of AgClO<sub>4</sub> in CH<sub>3</sub>OH. (Concentrations of AgClO<sub>4</sub> in the cell are 0 M, 8.3 mM, 32 and 48 mM, respectively, and concentration of CH<sub>3</sub>OH is 0.79 M.) Inset: Dependence of the rate of decay on the concentration of AgClO<sub>4</sub> (O) in sc-C<sub>2</sub>H<sub>6</sub>. The full line presents rates obtained in liquid methanol solution at room temperature. Dose: 6.8 Gy.

The traces in Figure 1 present the decay of solvated electron at 650 nm in the absence and in the presence of different concentrations of AgClO<sub>4</sub>. The half-life of the solvated electron decreases with the concentration of silver cations, obeying a first-order rate law. However, the rate of reaction 1 was not linear with concentration of silver cations over the concentration range examined (see Figure 1, inset). If we analyze the low concentration linear region (0–30 mM) we obtain a value of  $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . (The high-concentration data are discussed below.) In the inset of Figure 1 the rate of reaction 1 measured in liquid methanol at room temperature is also presented. The reduction of silver cations is diffusion-controlled in liquid methanol.<sup>24</sup> The value for rate constant of  $5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  was determined for zero ionic strength. The value agrees with calculated diffusion-controlled rate constant in liquid methanol if the radii for solvated electrons and solvated silver cations,  $r(e_{\text{sol}}^-) = 2.5 \text{ \AA}$  and  $r(\text{Ag}_{\text{sol}}^+) = 4.18 \text{ \AA}$ , are used.<sup>24</sup> If the same reaction were diffusion-controlled in supercritical ethane, one would expect similar or even higher rates. However, as we showed above, the rate in sc-ethane is 2 orders of magnitude slower. To determine if there is a change in the characteristics in the electron-transfer reaction, we must discuss possible effects associated with the properties of supercritical solutions. These include the effects of low mobility of ionic species and low solubility in supercritical fluids.

The clustering of methanol around salt ions (Ag<sup>+</sup> and ClO<sub>4</sub><sup>-</sup>) could be promoted in supercritical ethane compared to homogeneous liquid environment. The increased clustering would lead to a lower mobility. It has been shown that mobility of cationic and anionic species decreases with increasing pressure (density) in gaseous<sup>25</sup> and supercritical<sup>26</sup> CO<sub>2</sub>. The mobility of solvated species, both electrons and cations, may be additionally suppressed by clustering of solvent (ethane) molecules around cosolvent/solute. The radii at which such clustering occurs are up to 1.0 nm.<sup>26</sup> Diffusion in supercritical fluids, when a cosolvent is present is slower than in the neat supercritical fluid, mostly due to the slight increase of density when cosolvent is

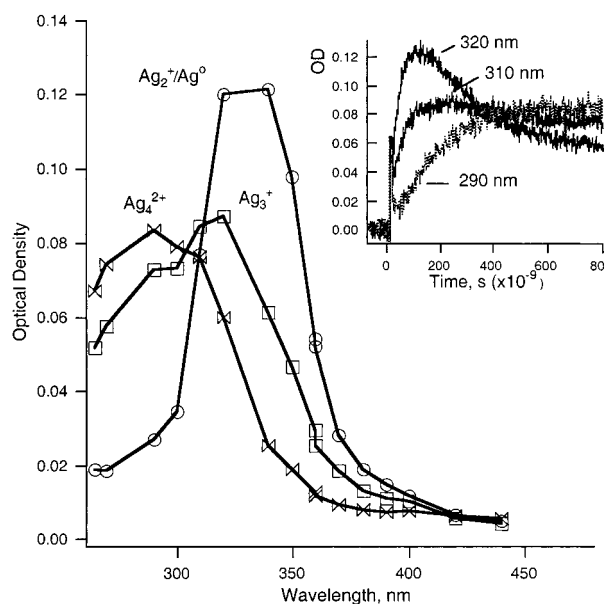
added to the solution at given pressure.<sup>27</sup> However, the mobility of neutral species is more than an order of magnitude higher in the supercritical ethane than in the neat methanol, and thus the effect of lower mobility of clustered species is unlikely to explain such low rate constants.

The concentration of solvated silver cations, as presented in the inset of Figure 1, may be smaller than assumed from calculations from bulk concentration. When the nonreactive salt (NaClO<sub>4</sub>) was added into solution the decrease in product (silver clusters) yield was observed. The "salting out" effect indicated that silver cations may not dissolve completely, especially at high salt concentrations. The concentration of silver cations in supercritical ethane may not be proportional to their bulk concentration in methanol. However, the clear change in the absorption magnitude and decay rates between the 8.3, 32, and 48 mM solutions show that more silver cations are being dissolved at higher concentrations.

The low mobility of clustered species and suppressed solubility in supercritical fluid could decrease the rate of reduction of silver ions, but for the reasons cited above, these effects would not change the apparent rate constant by 2 orders of magnitude. The most probable explanation for the decrease in rate is that the energy barrier at the boundary of the ethane and the clustered methanol inhibits the reaction, i.e., reaction 1 is not diffusion-controlled in the micellar-like supercritical fluid-cosolvent binary system. The electron-transfer reaction through interface of clustered species depends on the size, nature, and properties of preexisting cosolvent clusters.

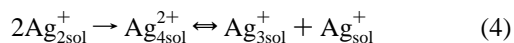
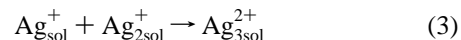
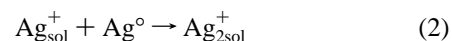
The sudden increase of the rate of reaction 1 for high concentration of silver cations can be explained by the nature of preexisting methanol clusters. The molecular ratio of methanol to silver perchlorate was in the range of 200:1 for 0.11 M AgClO<sub>4</sub> in MeOH (3.5 mM of silver cation, and 0.79 M of methanol in the total sample) to 16:1 for 1.5 M AgClO<sub>4</sub> in MeOH (48 mM of silver cation, and 0.79 M of methanol in cell). With a dose that produces micromolar concentration of solvated electrons, the probability that electron occupies an "empty" (empty from the salt) preexisting methanol cluster is high for a low concentration of salt. As the concentration of salt increases, the probability that an alcohol cluster does not have a silver ion decreases. At the highest concentration of silver used, almost all the alcohol clusters will contain silver ions. Therefore, there are two limiting conditions for reaction: one for low concentrations of silver ions, when reaction 1 occurs between two separated methanol clusters, one with solvated electron and the other with silver perchlorate. In the other case, when electrons and silver cations are in the same methanol cluster, their reaction will be very fast. The linear part of the curve in inset of Figure 1 for low concentrations of silver cations corresponds to the reaction of separated species of clustered electrons and clustered silver cations. The sudden increase of the rate for higher concentration of salt corresponds to the competition of the reactions of electrons and silver cations in the same and in the separate preexisting methanol clusters. The effect of ionic strength on the rate of reaction, and the effect of salt concentration on the size of preexisting clusters will also influence the kinetics of reaction at high salt concentrations.

**Early Time Species.** The formation and properties of colloidal metallic silver in aqueous solutions have been studied previously by pulse radiolysis, and the nature and absorption spectra of the intermediate clusters (Ag<sub>2</sub><sup>+</sup>, Ag<sub>4</sub><sup>2+</sup>, Ag<sub>2</sub>, etc.) have been established.<sup>13,28–32</sup> We have been able to identify the same silver clusters and observe their formation as a function of time in the pulse radiolysis of sc-C<sub>2</sub>H<sub>6</sub> containing AgClO<sub>4</sub> in



**Figure 2.** Transient absorption spectra detected (○) 0.1 μs, (□) 0.35 μs, and (×) 0.8 μs after the pulse in solution of sc-C<sub>2</sub>H<sub>6</sub> (100 bar, 80 °C) containing 8.3 mM AgClO<sub>4</sub> and 0.79 M CH<sub>3</sub>OH. Inset: Time profiles of signals at different wavelengths. Dose: 6.8 Gy.

methanol. The absorption spectra are presented in Figure 2. The early steps in the formation of metallic silver include reduction of silver ion by the solvated electron, reaction 1, and further formation of cluster species, reactions 2–4.

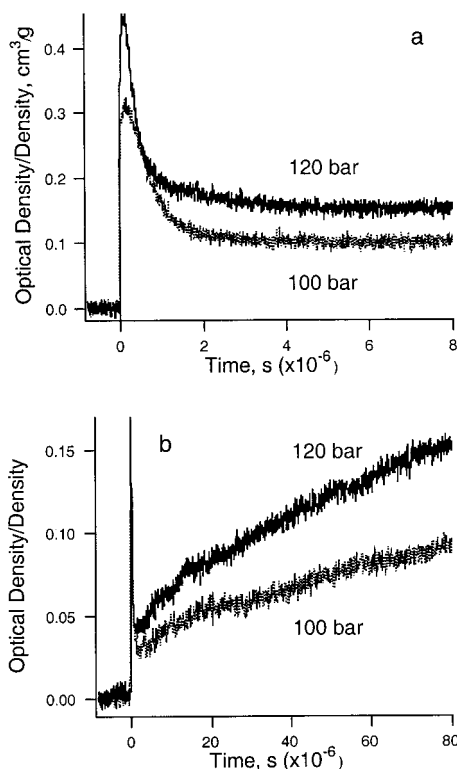


In our experiments the concentration of silver ions was kept relatively high to successfully scavenge solvated electrons, thus the spectrum observed at 0.1 μs after the pulse corresponds mostly to the dimer ion (Ag<sub>2</sub><sup>+</sup>) with superimposed absorption bands of the metal atom (Ag<sup>0</sup>). The positions of absorption maxima for metal atom and dimer ion are reported for aqueous solutions to be at 360 and 310 nm, respectively.<sup>31</sup> The spectral resolution of the different intermediates over time is similar or better than reported for aqueous solution;<sup>13,30</sup> however, as the inset of Figure 2 clearly indicates, it is not possible to completely resolve the species. We do, however, see the different concentrations that are present at different times. We were able to follow disappearance of very small intermediate clusters, and formation of higher order silver clusters, so-called oligomeric clusters, which accommodate up to eight electrons (Ag<sub>8</sub>, Ag<sub>9</sub><sup>+</sup>) at times of tens of microseconds, as followed at 320 and 360 nm.<sup>29</sup>



We have found that growth of silver clusters is slower in the ethane–methanol system than in pure liquid methanol solutions of silver ions. Compared to the rates reported for aqueous solutions,<sup>30,31</sup> the reactions in ethane–methanol system are at



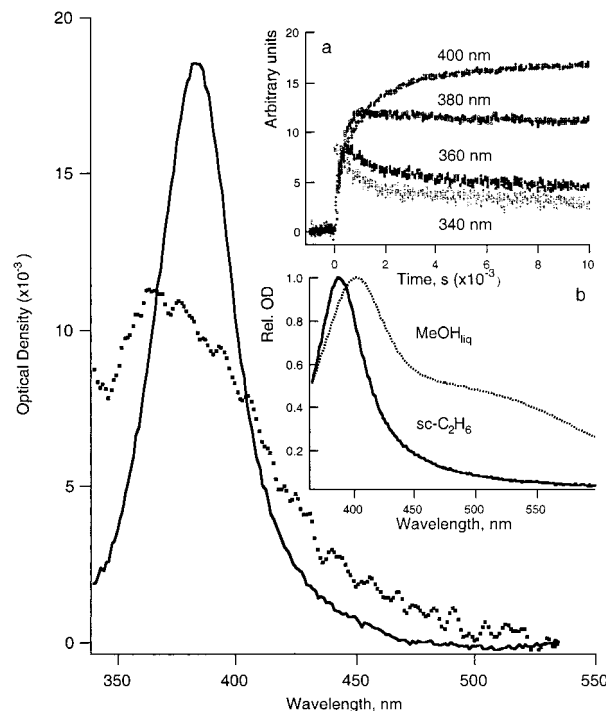


**Figure 3.** Time profiles of signals normalized to the unit density of ethane at (a) 320 nm (decay of dimer cation), and (b) 360 nm (formation of oligomeric clusters) in a solution of *sc*-C<sub>2</sub>H<sub>6</sub> (80 °C) containing 48 mM AgClO<sub>4</sub> and 0.79 M CH<sub>3</sub>OH: full line, 120 bar; dotted line, 100 bar.

least 2 orders of magnitude slower, assuming the total solubility of silver cations. As shown in Figure 3, the reaction rates increase with increasing density of supercritical ethane. In Figure 3, optical absorption signals of transient species (decay of dimer cation at 320 nm, and formation of oligomeric clusters at 360 nm) are presented for two different pressures. As the size of methanol clusters decreases with increasing ethane pressure one would expect the increase in solubility of solvated silver cations and/or silver clusters.<sup>23</sup> The effect is similar to the increased concentration and/or dose rate in the radiolysis of Ag<sup>+</sup> in aqueous solutions.<sup>33</sup>

The physical and transport properties of the binary system supercritical ethane–cosolvent that affect the rate and yield of bimolecular reactions are quite different than those in reversed AOT micelles in supercritical ethane.<sup>10,11</sup> Carson et al.<sup>11</sup> have explained the faster growth of silver and copper particles in supercritical fluids than in liquids by the weak interaction between ethane solvent and the surfactant tails of micelles, which results in higher collision frequencies and intermicellar exchange rates for growth of metallic nanoparticles.

**Metallic Silver Nanoparticles.** The interaction of oligomeric silver clusters with other silver clusters and/or with excess silver cations leads to the formation of colloidal metallic particles. These colloidal metallic silver particles absorb intensely in the region of 380–400 nm. The absorption is a typical Mie resonance, originating in the collective oscillations of the free conduction electrons in particles, and referred to as a surface plasmon absorption.<sup>1</sup> In Figure 4, the plasmon absorption of silver colloids obtained 1 s after the pulse is presented. The plasmon absorption band is blue shifted compared to the one obtained in reversed micelles and has a narrow bandwidth.<sup>9,10</sup> Such a narrow width of plasmon band had previously been observed for 7 nm Ag hydrosols in the presence of stabilizing



**Figure 4.** Transient absorption detected at 1 ms (dotted line) and 1 s (full line) in a solution of *sc*-C<sub>2</sub>H<sub>6</sub> (100 bar, 80 °C) containing 16 mM AgClO<sub>4</sub> and 0.79 M CH<sub>3</sub>OH. Inset (a): Time profiles of signals at different wavelengths. Inset (b): Relative transient absorption observed 10 s after pulse in supercritical ethane (full line), and in 5 mM AgClO<sub>4</sub> in liquid CH<sub>3</sub>OH (dotted line). Dose: 5.1 Gy.

polyphosphate anions using push–pull  $\gamma$ -irradiation technique.<sup>33</sup> It has been demonstrated<sup>33,34</sup> that the width of the plasmon absorption depends on the concentration and electronic structure of adsorbed species on the surface of metal particles (the so-called effect of chemical interface damping, CID<sup>1</sup>), and cannot be simply explained by a narrow size distribution. In other words, the bandwidth analysis for the particle size<sup>35</sup> cannot be applied in our case because we do not know the species at the particle/electrolyte interface. Thus, we relied only on the electron microscopy for the distribution and magnitude of particle sizes, which revealed particles less than 10 nm in diameter.

Colloidal particles were found to be stable in supercritical ethane for hours. Compared to liquid methanol, aggregation in supercritical fluid is suppressed (see inset b, Figure 4). When compared to the colloidal silver particles produced in aqueous solutions,<sup>28–33</sup> our method results in particles of similar sizes, but they are produced without stabilizers under the conditions of a high dose rate and a high concentration of silver cations. The advantage of using supercritical fluid approach over aqueous solution is in the formation of metallic particles with a “clean” surface, uncontaminated by surfactants and in easy collection of particles. One of the reasons for the generation of small and stable final particles in supercritical ethane may be due in part to the limited sizes of methanol droplets that can accommodate only certain size of colloids, and to the suppressed diffusion of silver clusters in this environment.

To use metallic silver particles it is necessary to remove them from high-pressure cell, and collect them on the surface or in a suspension. Possible applications require the determination of the size, morphology, and stability of collected particles. For synthetic purposes, solutions were exposed to 5–10 pulses, the plasmon absorption spectrum measured, cell evacuated, and particles collected and analyzed. No difference in plasmon absorption between the first and last electron pulse was detected.

The particles were collected after depressurizing the cell approximately 10 min after the irradiation. Two methods of collecting particles were used. In one method, carbon-coated copper grids were placed on the walls inside the cell. After depressurization of the cell, grids were removed, and analyzed. In this way silver nanoparticles were directly deposited onto grids. In the other method, nanoparticles that precipitated in the cell after evacuation of ethane were dispersed in methanol. A drop of methanol suspension was then placed on a TEM grid, methanol evaporated at room temperature, and particles were analyzed. We could not observe any significant difference in particle sizes for the two different methods of collections.

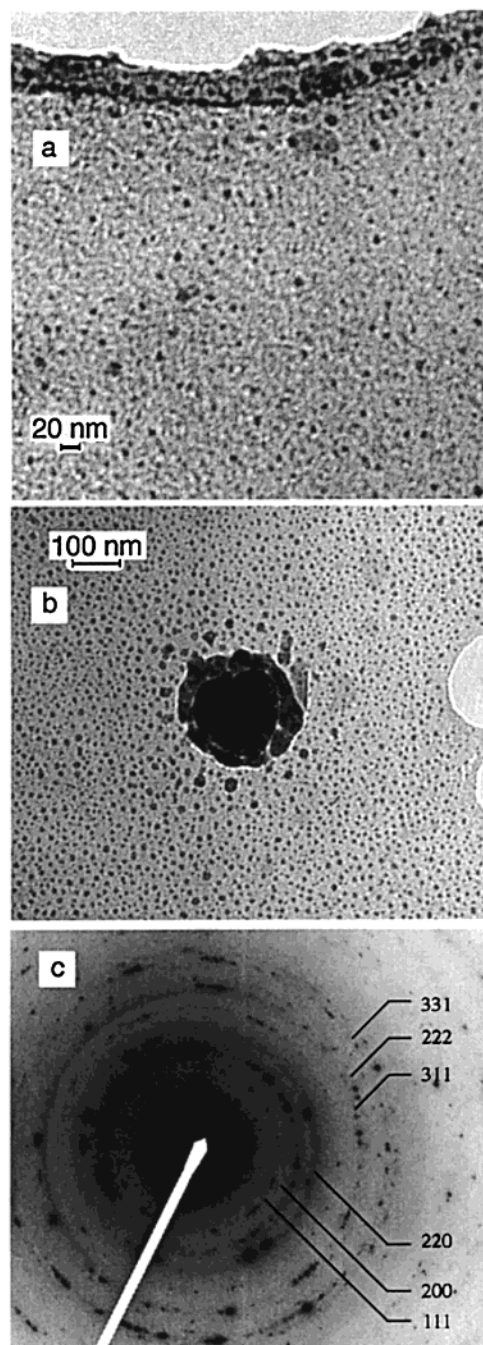
The particles were less than 10 nm in diameter, and their size depends on the pressure of supercritical ethane. Figure 5a,b show micrographs of silver particles synthesized at 80 bar (density of 0.142 g/cm<sup>3</sup>) and 100 bar (density of 0.209 g/cm<sup>3</sup>), respectively. The average size of particles is 8 nm for 100 bar, and less than 5 nm for 80 bar. The size dispersion is not large, with the exception of very few extremely large (200 nm in diameter) particles; one of them is shown in Figure 5b. It is to be expected that during depressurization of the cell some of the methanol clusters aggregate and form large droplets. The flocculation and clustering of the particles occur inside the methanol droplet, the size of particle being limited by the size of methanol droplet. It is worth noting that once collected, silver particles are stable for months. Compared to the particles produced by chemical reduction in supercritical CO<sub>2</sub>-reversed micelles,<sup>9,10</sup> our method results in metallic silver particles that are smaller in size and less polydispersed (8 nm at 100 bar, compared to 15–20 nm). Generally, smaller silver colloids are obtained by radiation-induced reduction of silver ions, than by chemical reduction in normal liquids.<sup>3</sup>

Electron diffraction revealed crystalline order that corresponds to the metallic silver structure (see Figure 5c). The spacings of the reflection planes were at 2.31, 2.05, 1.50, 1.24, 1.14, and 0.94 Å, which is within 5% of reported values for 111, 200, 220, 311, 222, and 331 reflections, respectively.<sup>36</sup>

We have found that the size of silver particles increases with increasing pressure of ethane solvent. Additionally, we have demonstrated by time-resolved measurement that silver clusters are relatively long-lived in supercritical ethane. This opens the possibility to control the size of particles by manipulating pressure, dose and the time when the cell is evacuated. Although they were prepared without surface stabilizers, metallic particles were stable both on air and in methanol suspension.

## Conclusion

Metallic silver nanoparticles (<10 nm) were synthesized by radiolytically induced reduction of AgClO<sub>4</sub> in methanol (10% mole fraction) dispersed in supercritical ethane. The electrons generated in radiolysis of ethane that escape geminate recombination, are solvated in preexisting methanol clusters. Reduction of silver cations by solvated electrons is the initial step in formation of metallic silver particles. The metallic silver nanoparticles were characterized in supercritical fluid solution by their plasmon absorption and after precipitation by electron micrographs. Time-resolved absorption spectra of small silver clusters (Ag<sub>2</sub><sup>+</sup>, Ag<sub>3</sub><sup>+</sup>, Ag<sub>4</sub><sup>2+</sup>) are detected in supercritical fluid at different times after the pulse. The spectra were compared to those in the liquid methanol. In preliminary measurements it was found that the particle growth in supercritical ethane proceeds at a slower rate than in the liquid methanol and depends on the pressure of supercritical solvent. It was also demonstrated that colloidal particles are more stable in supercritical fluid than



**Figure 5.** Electron microscopy of the silver metallic particles recovered after irradiation and depressurization of the cell. Solutions of sc-C<sub>2</sub>H<sub>6</sub> (80 °C) at (a) 80 bar and (b) 100 bar contained 16 mM AgClO<sub>4</sub> and 0.79 M CH<sub>3</sub>OH. Total dose: 34 Gy. (c) Electron diffraction pattern of the particles.

in the liquid solution. In this paper we have demonstrated that supercritical fluids present good medium for controlled growth of metallic nanoparticles.

**Acknowledgment.** We gratefully acknowledge Roseann Csencsits for assistance in obtaining and digitizing the electron microscope pictures. We acknowledge Sergey Chemerisov for assistance in the operation of the accelerator.

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