Metallic Nanoparticles from Spontaneous Reduction of Silver(I) in DMSO. Interaction between Nitric Oxide and Silver Nanoparticles

G. Rodríguez-Gattorno,[†] D. Díaz,^{*,†} L. Rendón,[‡] and G. O. Hernández-Segura[†]

Facultad de Química, Universidad Nacional Autónoma de México, Coyoacán, México DF, 04510 Mexico, and Instituto de Física, Dpto. de Materia Condensada, Universidad Nacional Autónoma de México, Coyoacán, México DF, 04510 Mexico

Received: July 12, 2001; In Final Form: November 29, 2001

Here we report a novel pathway for the synthesis of silver nanoparticles. Spontaneous reduction of silver 2-ethylhexanoate [Ag(ethex)] takes place in dimethyl sulfoxide (DMSO) at room temperature. The reaction is slow and markedly depends on temperature leading to the formation of silver nanoparticles (NPs) with a surface plasmon resonant band maximum centered at 424 nm. Colloidal silver is not stable in DMSO without stabilizing agents. When sodium citrate $(1 \times 10^{-4} \text{ M})$ is utilized as a capping agent, the surface plasmon shifts to 414 nm and the surface-modified silver nanoparticles are stable for more than 6 months. The resulting nanoparticles are quite stable but at the same time reactive enough for catalytic purposes. An HR-TEM study shows a nanoparticles size distribution centered in 4.4 nm of diameter (SD = 1.2) and a considerable number of defects such as stacking faults and twined particles. From *ab initio* quantum mechanical calculations, we propose a possible precursor for the spontaneous reduction of [Ag(ethex)] in DMSO. In addition, the interaction between NO and silver nanoparticles was tested. UV-visible spectra show the oxidation of silver and the reduction of NO at room temperature. The most probable products of this reaction are N₂O, molecular nitrogen, and oxygen. Therefore, we have a simple catalytic colloidal system for NO.

Introduction

Different chemical methods have been used for the synthesis of metallic nanoparticle (NP) dispersions, the most common involving the use of an excess of reducing agents such as sodium citrate¹ or sodium borohydride.^{2,3} Other simple methods involve the reduction of metallic salts by the solvent used to prepare colloidal dispersions. For example, Toshima et al. have reported a well-established method to obtain metallic and bimetallic nanoclusters using alcohols in the presence of poly(N-vinyl-2pyrrolidone) (PVP).4-7 Vasan and Rao prepared Ag-Pd and Cu-Pd nanoparticle alloys by using methanol or ethanol,⁸ and Ayyappan et al.⁹ obtained Ag, Au, Pd, and Cu nanoparticles by the reduction of metallic salts in dry ethanol. More recently, Pastoriza and Liz-Marzan¹⁰ reported the preparation of silver particles by the spontaneous reduction of AgNO₃ in N,N'dimethylformamide. These contributions represent some of the simplest ways to obtain colloidal dispersions because they require a minimum number of components, thus avoiding undesirable excess of reducing agents and reaction byproducts. Dimethyl sulfoxide (DMSO) is a relatively inexpensive, stable, environmental compatible, and very useful solvent in organic and inorganic synthesis due to its specific chemical and physical properties. The dielectric constant of DMSO $(46.7)^{11}$ is high enough to allow charge separation; consequently, it becomes a good solvent for ionic solids, polar and polarizable molecules.¹² DMSO is miscible with water in all proportions. In general, sulfoxides are potential reductors by oxidizing itself to sulfones.¹³ Despite DMSO being one of the few solvents for

which many applications have been found (e.g. physical chemistry, medicine, and biology), there is little information about the synthesis of metal nanoparticles in this medium. A previous paper¹⁴ demonstrated the feasibility of using the 2-ethylhexanoate anion as a capping agent of CdS nanoparticles in DMSO; this synthesis pathway is used in the present paper.

Here we investigated the preparation of silver nanoparticle dispersions by the simple dissolution of silver 2-ethylhexanoate in DMSO. To ensure stability of the silver dispersions, sodium citrate was used as an additional stabilizing agent. The advantages of such a nanoparticle synthesis method can be found in the applications of silver nanoclusters as catalysts (most organic reactions take place in nonaqueous solvents), and in the study of the changes in surface chemistry the adsorption of different moieties depends on the surrounding medium. Even more, it has been known since ancient times that metallic silver colloids act as an efficient bactericide, while DMSO has the ability to easily penetrate the biological membranes; both combined properties (i.e. silver nanoparticles suspended in DMSO) could find application in the preparation of very effective disease-fighting drugs.^{15–18}

In addition, the novel reaction presented here opens new possibilities in the field of solvent exchange, which represents one of the main challenges in metal colloids with nanometer size range. This should allow for dispersions of the particles in both polar and nonpolar solvents thus avoiding particle aggregation during the process.

Our results suggest the formation of a silver precursor species with a convenient LUMO energy, which favors the silver reduction process. To support the proposed mechanism for silver reduction in DMSO, we performed *ab initio* quantum mechanical computations arising to a simple silver complex structure as the most probable precursor species. We also explored the

^{*} To whom correspondence should be addressed. E-mail: david@ servidor.unam.mx.

[†] Facultad de Química.

[‡] Instituto de Física, Dpto. de Materia Condensada.

interaction between silver dispersions and nitric oxide (NO) under anhydrous, anaerobic conditions and at room temperature, by means of UV-visible spectroscopy.

Experimental Section

Materials. Silver 2-ethylhexanoate {[Ag(ethex)] (Strem Chemical, 99%)}, trisodium citrate dihydrated [Na₃Cit·2H₂O (Aldrich, 99%)], sodium 2-ethylhexanoate {Na[ethex] (Aldrich, 97%)}, sodium borohydride [NaBH₄ (Aldrich, 98%)], silver nitrate [AgNO₃ (Aldrich, 99%)], silver citrate hydrate [AgO₂-CCH₂C(OH)(CO₂Ag)CH₂CO₂Ag•xH₂O (Aldrich, 99%)], silver perchlorate monohydrate [AgClO₄•H₂O (Strem Chemical, 99%)], silver metavanadate [AgVO3 (Aldrich, 98%)], FeSO4·7H2O (Baker, 99.6%), NaNO₂ (Baker, 99.99%), and argon (Praxair Inc., 99.998%) were used as starting materials. These chemical reagents were used without further purification. DMSO used was Sigma (ACS reagent). It is strongly recommended to check the purity of DMSO, especially to avoid the presence of volatile contaminants. A procedure to eliminate the majority of the volatile contaminates from DMSO includes the use of a rotary evaporator at 50 °C during 2-3 h, under vacuum (10 mmHg). The electronic absorption spectra were collected in a Hewlett-Packard 8452A UV-visible spectrophotometer. An HR-TEM study was carried out in a JEOL 4000EX at 400 KV, depositing a drop of the sample over a carbon/collodion coated copper grid, no special care being taken to avoid aggregation.

The size distribution was obtained from a digitalized amplified micrograph by averaging the larger and smaller axis diameters measured for each particle. *Ab initio* quantum mechanical calculations of the type restricted closed-shell, Hartree–Fock with a 3-21G(*) split valence basis set were carried out; all the structures were previously optimized at the same level of theory, HF/STO3-21G(*)//HF/STO3-21G(*). These computations were performed using the version 1.5.2 of the PC-Spartan Plus program.¹⁹

Colloid Preparation. The required quantity of [Ag(ethex)] (0.001 25 g) was mixed with 50 mL of DMSO (previously saturated with argon) in an Erlenmeyer flask to a final concentration of 1×10^{-4} M. Stirring ensured the rapid solubilization of the silver salt. The colloidal dispersions were protected from light. Preparations at 60 °C were performed in a hot plate thermostat.

Glassware was cleaned with moderately concentrated nitric acid and then washed with Alconox detergent and wiped away with plenty of ultrapure water (18 M Ω , obtained from a Barnsted E-pure deionization system). Experiments of silver colloid dispersion interactions with NO were carried out in a sealed UV–visible cell filled with 3 mL of 2.5 × 10⁻⁴ M silver dispersion. NO was generated from the reaction between FeSO₄·7H₂O and NaNO₂.²⁰ The gas and silver dispersions were dried with previously activated Linde 4 Å sieves at 500 °C for 16 h.²¹ NO was dragged with an argon gas flow of 0.6 L/min. The quantity of NO was approximately controlled by careful additions of known quantities of the ferrous salt over the nitrite salt, yielding NO in an amount lower than 1 × 10⁻⁷ mol.

Results and Discussion

Since the oxidation of DMSO implies the formation of dimethyl sulfone,²² the following total reaction might take place during the reduction of [Ag(ethex)]:

$$2[AgOOCR] + (CH_3)_2SO: + H_2O \rightarrow 2 Ag^0 + (CH_3)_2SO_2 + 2H^+ + 2[:OOCR]^-$$



Figure 1. Evolution of UV–visible spectrum during the formation of silver NPs in DMSO, from the spontaneous reduction of [Ag(ethex)] $(1 \times 10^{-4} \text{ M})$ at room temperature. Numbers indicate the spectra for different times: (1) recently dissolved; (2) 10 min; (3) 27 min; (4) 80 min; (5) 120 min; (6) 240 min; (7) 420 min; (8) 24 h.

Here $R = -(C_2H_5)CH(CH_2)_3CH_3$.

Water is required for mass balance reasons; enough of it comes from the hydrated solvent. This reaction seems to take place conforming to a reported mechanism by initial complexation of the $(CH_3)_2SO$: to the metal ion species,

$$[AgOOCR] + (CH_3)_2SO: \Rightarrow [(CH_3)_2SOAgOOCR]$$

followed by electron transfer to form a sulfoxide radical cation $([(CH_3)_2SO']^+),$

$$[(CH_3)_2SOAgOOCR] \rightarrow Ag^0 + [(CH_3)_2SO^{\bullet}]^{+1} + [:OOCR]^{-1}$$

which then transfers a second electron,

$$[(CH_3)_2SO^{\bullet}]^+ + [AgOOCR] \rightarrow$$
$$[(CH_3)_2SO]^{2+} + Ag^0 + [:OOCR]^{-1}$$

Therefore, the cationic species $([(CH_3)_2SO]^{+2})$ is attacked by water forming the sulfone:

$$[(CH_3)_2SO]^{2+} + H_2O \rightarrow$$
$$[(CH_3)_2SOOH_2]^{2+} \rightarrow (CH_3)_2SO_2 + 2H^+$$

This happens in the same way with other transition metals (for example, Ce^{4+}) used to oxidize sulfoxides to sulfones.¹³

In addition, under darkness and in anaerobic conditions, the silver reduction reaction in DMSO takes place.

The silver reduction reaction becomes apparent after 10-15 min at room temperature (approximately 23 °C); the colorless and transparent DMSO solution turns from light yellow to yellowish-orange. Figure 1 shows the time evolution spectra of the typical surface plasmon resonant band for silver NPs resulting from the reduction of 1×10^{-4} M [Ag(ethex)] in DMSO. As can be seen, the process is slow, and after 24 h the relative increase of the half-width at the maximum of the peak becomes more significant than its increase in intensity. This implies an increment in particle size, easily verified by the gradual appearance of a silver precipitate. The reaction, however, cannot be observed at room temperature, after 1 week, when the silver salt concentration is as low as 0.5×10^{-4} M, probably due to the slowness of the reaction. Though raising the temperature can accelerate the progress of the reaction, the agglomeration of nanoparticles is also favored.



Figure 2. (a) Diagram of calculated HOMO and LUMO energies resulting from *ab initio* quantum mechanics computations HF/STO3-21G(*)// HF/STO3-21G(*) for several possible precursor species in the reduction of silver 2-ethylhexanoate in DMSO. In parentheses are the resulting point groups for each molecule. (b) Image shows a projection of the calculated LUMO surface for the [Ag(ethex)(DMSO)] species.

Other silver salts such as the nitrate, perchlorate, and metavanadate were also tested as silver sources, but DMSO does not reduce them even upon heating to 80 °C. However, silver citrate starts to reduce at 70 °C in DMSO. In this case, silver citrate yields silver nanoparticles that are stable for less than 12 h. To stabilize them it is necessary to add at least a 4-fold excess of citrate anions to the total silver concentration. An explanation can be that citrate acts both as reducing and stabilizing agent. During these preparations, it was found that silver nitrate was slowly reduced to silver nanoparticles in DMSO at room temperature but only in the presence of trisodium citrate, which suggests that it proceeds by the direct reaction between Ag⁺ and the citrate anion. The optical response in this case is similar to that reported by Rivas et al.²³ for particles ranging between 30 and 60 nm in diameter, where the absorption electronic spectrum displays an asymmetric plasmon resonant band centered in 434 nm. In water this reduction reaction is not observed at room temperature.

For the purpose of finding out which silver species acts as a precursor in the reduction process of this metal, we carried out the following experiment: A AgNO₃ solution (with final concentration 1×10^{-3} M) was mixed with equimolar Na[ethex] solution, in DMSO, at room temperature. After 5 min, the starting colorless solutions turned into a brownish-orange transparent dispersion. A wide plasmon band centered at 418 nm was developed in the electronic absorption spectra. These results suggest the formation of a silver—ethex coordination compound as the precursor species for the silver reduction reaction.

To support the silver—ethex precursor formation we carried out several *ab initio* quantum mechanic geometry optimizations at the restricted Hartree—Fock level and with the 3-21G (*) basis set, i.e., at the HF/3-21G(*)//HF/3-21G(*) level of theory, for the following molecules: $[Ag(DMSO)_4]^+$; $[Ag(DMSO)_2]^+$; $[Ag(H_2O)(DMSO)]^+$; $[Ag(ethex)_2]^-$; $[Ag(ethex)(H_2O)]$; [Ag-(ethex)(DMSO)]. All the calculated structures were previously optimized using the same calculation level. Some of the more relevant results are shown in Figure 2. We took in account the following experimental facts. It is well-known that the Ag⁺ ion shows a pronounced tendency to exhibit linear, 2-fold coordination.²⁴ However, the silver cation in DMSO can form di- and tetrasolvated species $[Ag(DMSO)_2]^+$ and $[Ag(DMSO)_4]^+$, as reported by Ahrland.²⁵ Since other silver salts soluble in DMSO (e.g. AgNO₃) are not reduced spontaneously in this solvent, it can be deduced that the anion 2-ethylhexanoate should be part of the most probable precursor species such as [Ag(ethex)-(DMSO)]. It is well-known that DMSO interacts with many different transition cations generating stable complex species, as $[Cu(DMSO)_2]^{2+}$, $[Hg(DMSO)_6]^{2+}$, $[Cd(DMSO)_6]^{2+}$, $[Mn-(DMSO)_6]^{2+}$, and many others.²⁶

In aqueous solutions, silver salts may generate $[Ag(H_2O)_2]^+$; however, the addition of DMSO to water may cause dehydration of the Ag⁺ ion to leave free coordination sites for DMSO molecules.²⁷ On the other hand, the interaction DMSO-H₂O is stronger than Ag⁺⁻H₂O; therefore, we reject the idea of possible formation of a complex containing coordinated water.

On the basis of Koopmans' theorem, the negative values of the HOMO and LUMO energies can be related to the ionization potentials and the electron affinity, respectively.^{28,29} From the results of our calculations, it is possible to propose the species that would act as precursor for silver reduction, on the basis of the fact that this precursor should have the highest LUMO energy and the lowest difference between HOMO–LUMO gap (hardness). In Figure 2, we show an energy scheme in which the calculated HOMO and LUMO energies were plotted for each possible precursor.

As can be seen, the highest LUMO energy corresponds to the $[Ag(ethex)_2]^-$ molecule but its formation is very unlikely because there are not sufficient ethex anions to complete this composition. The molecule [Ag(ethex)(DMSO)] is the next with an adequate value for the LUMO energy and is the only molecule for which we do not have arguments to discard as the most possible precursor for silver reduction in DMSO from silver 2-ethylhexanoate. At the right side of the energy diagram it is shown the LUMO surface of this molecule where one can observe that the charge acceptor site is centered over the silver atom, as can be expected.

Due to silver nanoparticles dispersions being unstable, it is necessary to use capping agents to stabilize them. Among the known stabilizers, trisodium citrate is a simple molecule with a well-defined composition, which is recognized as a good silver stabilizer.³⁰

Other stabilizers such as sodium dodecyl sulfate (SDS) and ammonium tetrathiomolybdate were tested, but the former does not work and, especially, the latter blocks the surface plasmon resonant band. Also was tested poly(*N*-vinyl-2-pirrolidone) (PVP) as capping agent, which shows a plasmon resonant band centered in 401 nm that shifts to higher wavelength in few days;



Figure 3. Electronic absorption spectra of silver nanoparticles in DMSO obtained from AgNO₃ (1×10^{-4} M) using a stoichiometric quantity of sodium borohydride and sodium citrate as a stabilizing agent (1×10^{-4} M): (1) after mixing; (2) 12 min; (3) 43 min; (4) 120 h. Top insert shows the spectral changes at different times of naked silver nanoparticles in DMSO obtained from AgNO₃ (1×10^{-4} M) by reduction with a stoichiometric quantity of sodium borohydride.

stability appears to be low because after 1 week the plasmon becomes broad and asymmetric. Finally, after 8 days the PVPcapped silver nanoparticles start to aggregate, which could be a result of the stronger interaction of PVP–DMSO in comparison with PVP–silver nanoparticles interactions. PVP is a good stabilizing agent for metallic nanoparticles; consequently, we do not discard the possibility that the stability, in the case of PVP–silver nanoparticles, could dependent on PVP concentration.

To test the stabilizing effect of DMSO on the particles we decided to carry out the reduction of silver nitrate $(1 \times 10^{-4} \text{ M})$ using a conventional reductor, sodium borohydride;³¹ in 1:1 stoichiometric ratio, it produces NPs that are stable for less than 40 min (see insert in Figure 3). In addition, any attempt to stabilize the nanoparticles thus obtained using sodium citrate as a stabilizer resulted in dispersions containing larger particles, which precipitated after 5 days.

It is clear from Figure 3 (see insert) that citrate stabilizes the nanoparticles (in comparison with the same system without citrate) and also contributes considerably to the increase of the plasmon resonance band not only by raising the intensity but also by broadening it.

We prefer to introduce the capping agent at the very beginning of the reaction, keeping in mind that it is important to disperse the nanoparticles before they grow. A disadvantage of sodium citrate is its low solubility in DMSO, a difficulty that can be overcome by heating or dissolving it in a minimal amount of water. We decided to raise the temperature to 60 °C for 20 min to allow the rapid formation of silver nuclei. Under these conditions, the reduction of silver ethex would proceed via a simultaneous and cooperative reaction with DMSO and citrate ions.

Figure 4 shows the UV-visible spectra at different times for the formation of silver nanoparticles in DMSO using [Ag(ethex)] $(1 \times 10^{-4} \text{ M})$ as a starting material and trisodium citrate $(1 \times 10^{-4} \text{ M})$ as a capping agent. The stability of these NPs is outstanding since they remain stable for over 6 months. By examining the results already presented, one can summarize as follows: 2-ethylhexanoate behaves as a stabilizer since the resulting NPs are more stable than either of the naked ones obtained via the stoichiometric borohydride reduction.

Silver nanoparticles from silver citrate, with an excess of citrate, are as interesting as those obtained from 2-ethylhexanoate but with less stability, which leads us to the next statement.



Figure 4. Spectral variations with time during the silver NPs synthesis in DMSO from Ag(ethex) $(1 \times 10^{-4} \text{ M})$ in the presence of sodium citrate $(1 \times 10^{-4} \text{ M})$, heated at 60° C for 20 min: (1) 7 s after mixing; (2) 18 s; (3) 34 s; (4) 2 h; (5) 44 h. Top plot shows the variation of the intensity at the maximum of the plasmon resonance band versus time.

Sodium citrate acts as a stabilizer, but when combined with the starting material, 2-ethylhexanoate, the silver nanoparticles are stable for longer periods (compare Figures 3 and 4).

Otherwise, the absorbance at the maximum of the plasmon resonance band was plotted against time for further clarity; see the upper insert in Figure 4. The absorbance increased up to a maximum value of 1.5 after 40 h. After this time the absorbance decreased by 17% of the maximum value, becoming constant after 11 days of preparation. No substantial changes in width at half-height are noticed in the UV-visible spectra (88 ± 2 nm). This means that no important variation occurs in size or size distribution of the silver NPs. These variations could be related with two possible events: small displacement in size distribution or slow equilibrium of absorption over the surface of the nanoparticles. To validate this interpretation concerning with such spectral variations it is necessary to carry out more experiments supported by HR-TEM.

To rationalize our spectroscopic results with the nanoparticle size distribution we performed Mie's standard calculations to simulate the electronic absorption spectrum by using the Drude correction of the dielectric constants³² for the damping of electrons at particle size near or under 5 nm. The calculations were performed with the Mietab v.6.38 software.³³ Routines of this calculations have been previously described in detail.³⁴ Contributions from particle size distribution were taken into account, by assuming that HR-TEM micrographs approximately describe our dispersion in this sense.³⁵ The calculated absorption maximum appears at 411 nm, differing by only 5 nm from the experimental one (416 \pm 2 nm), while the width at half-height is 57 nm compared to 88 nm for the experimental value. These differences have been attributed to the nature of the molecular interactions of the surrounding medium with the surface of the particle.^{36,37} The red shift of the peak position in our dispersions with respect to classical aqueous silver colloids is predictable since the higher refractive index of DMSO (1.4170) can be compared to 1.333 for water at 20 °C.38 Additionally, Wang et al. reported the same optical behavior (plasmon centered at 413 nm and a full width at half-maximum of 90 nm) for nanoparticles of similar sizes capped with unsaturated carboxylates;³⁹ then, we cannot discard the possibility that the position of the peak is significantly influenced by the interaction of metallic silver with the carboxylic groups of citrate and 2-ethylhexanoate anions. Therefore, the silver molecular surroundings, solvent and capping agents, determinate the plasmon resonance band position.



Figure 5. HR-TEM micrographs of the citrate- and 2-ethylhexanoatestabilized silver nanoparticles in DMSO from Ag(ethex). The arrows point out some defects present in nanoparticles. The sample stabilized after 11 days. The insertions show the corresponding diffraction pattern $(d_{hkl}$ calculated match with metallic silver) and a magnification of a single silver nanoparticle oriented along the 110 direction.



Figure 6. Size distribution in the sample illustrated in Figure 6. A total of 250 particles were counted. Particles not well defined in the largest lumps were not considered.

TABLE 1: Approximate Dispersion CharacteristicsEstimated from the Size Distribution in Figure 6, AssumingSpherical Particles

concn	cluster concn	tot. surf	surf/vol	% of atoms at the surf
(atoms/mL)	(particles/mL)	(m ²)	ratio (m ⁻¹)	
6.02×10^{16}	8×10^{11}	5×10^3	1×10^8	24

Another explanation for the overenlarged plasmon bands has been proposed by Henglein, who argues that this is due to the lattice imperfections that would act as potential barriers for electrons in the conduction bands by shortening its pathway, i.e., by increasing the damping of the electrons.⁴⁰

Figure 5 shows HR-TEM micrographs of silver nanoparticles capped with sodium citrate in DMSO, prepared from [Ag(ethex)] and measured after 11 days. Roughly spherical nanoparticles can be observed. By counting over 250 particles, we were able to obtain the particle size distribution shown in Figure 6. Large lumps, probably formed during sample preparation, were not considered.

From the size distribution in Figure 6, it is possible to obtain the features of the dispersions that are summarized in Table 1. Parameters are approximate because they were calculated on the assumption that the particles were spheres. The metallic



Figure 7. Electronic absorption spectra of silver NPs $(2.5 \times 10^{-4} \text{ M})$ after additions of equal quantities of NO. The top insert shows the spectrum of NO dissolved in anhydrous DMSO. Key: (1) dispersion as prepared; spectra 2–7 correspond to equal successive additions of NO.

silver concentration is 1×10^{-4} M (i.e. quantitative reaction), and the cell parameters correspond to those known for bulk silver (a = 4.06 Å).

In accordance with the report of Henglein,³⁰ we found in our samples a considerable number of particles that present massive defects, such as multiple twinning and stacking faults, which gives strong support to Henglein's proposition. In general, many of the defects are destroyed during the sample observation as a consequence of the unavoidable increase in temperature during the observation process. Thus, it is not possible to get a quantitative relationship between defects and optical response; however, we do not discard the possibility that citrate species allow the generation of such defects, this statement so far remaining only a suggestion.

Interaction of Silver Nanoparticles with NO. The adsorption and reactions of NO on various macrocrystalline transition metal surfaces has received considerable attention. The presence of an unpaired electron in the 2π molecular orbital of NO makes its behavior much more complicated and less understood than that of CO. NO is also technologically important in air pollution and as a strong oxidizing agent. Besides, the majority of the chemical model systems to study the interaction between metallic silver and NO_x utilize silver macrocrystals under high vacuum and low temperatures, or else the silver is deposited over a solid support as alumina or zirconia. In the previous case, the interaction with NO_x takes place under higher temperatures.^{41–44} Reports related with the interaction of NO_x and colloid dispersions are too scarce in the literature. In 1999, Henglein reported the interaction of N₂O with metallic lead nanoparticles at room temperature.45

Very stable capped silver nanoparticles have been synthesized; it was an important question to evaluate their catalytic activity. Are they reactive enough for catalytic purposes? To test silver NPs reactivity with NO it was necessary to remove any remaining water in the reaction system. To keep NO gas and silver colloids dry, pretreated 4 Å zeolites were used.

Nitric oxide in water generates an acidic medium, which leads to spontaneous silver NP agglomeration. Figure 7 shows the electronic absorption spectra of a silver colloid dispersion reacting with NO. In this case, the silver concentration was 2.5×10^{-4} M, allowing the collection of several spectra on consecutive additions of NO. When water is removed from dispersions by using zeolites, the silver nanoparticles react with the NO until the silver metal is completely dissolved. The

After six additions of NO, the spectrum is similar to that of NO in DMSO as a consequence of an excess of the dissolved gas (for comparison purposes, the spectrum of NO in DMSO was inserted in the upper part of Figure 7).

The colloid is not regenerated upon heating the dispersion used in this experiment. Under our reaction conditions, it was not possible to determine the NO and silver stoichiometric coefficients exactly because the NO concentration was not accurately known. We are certain that there is a reaction between NO and Ag NPs, where the reduction of NO takes place; therefore, the products are most probably N₂O or N₂, as previously reported in studies of NO dissociation over metallic silver.42

Conclusions

A new and reproducible method for the synthesis of silver nanoparticles is reported in this work. Very stable capped silver nanoparticles with average diameter close to 4.4 nm and narrow size distribution are prepared by addition of silver 2-ethylhexanoate to DMSO in the presence of trisodium citrate as a stabilizer. Probably DMSO and citrate ions act as simultaneous reducers of this silver salt. Our experimental and theoretical results suggest that, in these colloidal DMSO dispersions, the silver reduction takes place through a precursor species such as [Ag(DMSO)ethex]. High concentration of defects, such as stacking faults and twins, and citrate species interacting in nanoparticles surface would be responsible for the modification in the optical response of silver nanoparticles by enhancing damping during plasmon resonance, thus overenlarging the width of electronic absorption spectra.

UV-visible spectra show that silver nanoparticles in DMSO react with NO, thus causing the dissolution of metal when the dispersion is dry. Therefore, we have found a novel, simple, and inexpensive chemical model system to study the interaction of NO with metallic silver under anhydrous, anaerobic, and room-temperature conditions. Ongoing research is concerned with the reduction of different silver salts in DMSO, in the presence of different solid supports.

Acknowledgment. The authors thank the DGAPA-UNAM for financial support through projects IN-100398 and IN-107700. G.R.-G. thanks the DGEP-UNAM for a scholarship. The authors express their gratefulness to Drs. A. R. Vázquez-Olmos, E. Zeller, J. Robles-García, and S. E. Castillo-Blum for their revision and suggestions to this work. Also, we want to thank to Mr. L.-A. Ortiz-Frade for his help in the experimental part.

References and Notes

- (1) Lee, P. C.; Miesel, D. J. Phys. Chem. 1982, 86, 3391.
- (2) Creigton, J.; Blatchford, C.; Albrecht, M. J. Chem. Soc., Faraday Trans. 1979, 75, 790.
- (3) Shirtcliffe, N.; Nickel, U.; Schneider, S. J. Colloid Interface Sci. 1999, 211, 122.
- (4) Toshima, N.; Harada, M.; Yonezawa, T.; Kushihashi, K.; Asakura, K. J. Phys. Chem. 1991, 95, 7448.
- (5) Toshima, N.; Harada, M.; Yamazaki, Y.; Asakura, K. J. Phys. Chem. 1992, 96, 9927.
- (6) Toshima, N.; Yonezawa, T.; Kushihashi, K. J. Chem. Soc., Faraday Trans. 1993, 89, 2537.

(7) Hirai H. J. Macromol. Sci., Chem. 1979, A13, 633. (d) Hirai, H.; Nakao Y.; and Toshima, N. J. Macromol. Sci., Chem. 1979, A13, 727.

(8) Vasan, H. N.; Rao, C. N. R. J. Mater. Chem. 1995, 5, 1755.

- (9) Ayyappan, S.; Srinivasan Gopalan, R.; Subbana, G. N.; Rao, C. N. R. J. Mater. Res. 1997, 12, 2, 398.
 - (10) Pastoriza-Santos, I.; Liz-Marzan, L. M. Langmuir 1999, 15, 948. (11) Steiner, E. C.; Gilbert, J. M. J. Am. Chem. Soc. 1965, 87, 382.
 - (12) Parker, A. J. In Advances in Organic Chemistry; Raphael, R. A.,
- Taylor, E. C., Wynnberg, H., Eds.; Wiley Interscience: New York, 1965; Vol. 5, pp 1-46.

(13) Hoyle, J. Oxidation of Sulphoxides and Sulphones. In The Chemistry of Sulphones and Sulphoxides; Patai, S., Rappoport, Z., Stirling, C., Eds.; Wiley: New York, 1988; p 969.

(14) Díaz D.; Rivera M.; Tong Ni; Rodríguez J. C.; Castillo-Blum S. E.; Nagesha D.; Robles J.; Alvarez-Fregoso O. J.; Kotov N. A. J. Phys. Chem. B 1999, 103, 9854.

(15) Hill, J. Colloidal Silver. A Literature Review. Medical Uses, Toxicology & Manufacture, 2nd ed.; Clear Springs Press: Rainier, WA, 2000

(16) Thurman, R. B.; Gerba, C. P. The molecular mechanisms of copper and silver ion disinfection of bacteria and viruses. In CRC Critical Reviews in Environmental Control; CRC Press: Boca Raton FL, 1989; Vol. 18, p 295

(17) Deitch, E. A.; Marino, A. A.; Gillespie, T. E.; Albright, J. A. Antimicrob. Agents Chemother. 1983, 23, 356

(18) Santos, L.; Tipping, P. G. Inmunol. Cell Biol. 1994, 72, 406.

(19) PC-Spartan Plus, version 1.5.2; Wavefuntion Inc.: Irvine, CA, 1998

(20) Bruce King, R. Encyclopedia of Inorganic Chemistry; Wiley: New York, 1994; Vol. 5, p 2533. (21) Kissinger, P. T.; Heineman, W. R. Laboratory Techniques in

Electroanalytical Chemistry; Marcel Dekker Inc.: New York, 1984; p 377.

(22) Antelman, M. S. Encyclopedia of Chemical Electrode Potentials; Plenum Press: New York, 1982; p 250.

(23) Rivas, L.; Sanchez-Cortes, S.; García-Ramos, J. V. Morcillo, G. Langmuir 2001, 17, 574.

(24) Cotton, F. A.; Wilkinson, G. Advance Inorganic Chemistry, 4th ed.; Wiley: New York, 1980; p 968.

(25) Elding, L. I. A Celebration of Inorganic Lives: An Interview with Sten Ahrland (Lund University, Sweden). Coord. Chem. Rev. 1996, 153,

(26) Calligaris, M.; Carugo, O. Coord. Chem. Rev. 1996, 153, 83.

(27) Sreekumar, T. K.; Janardhanan, S.; Kalidas, C. Ber. Bunsen-Ges. Phys. Chem. 1991, 95, 9.

(28) Jensen, W. B. The Lewis Acid-Base Concepts. An overview; Wiley: New York, 1980; p 214.

(29) Atkins, P. W. Quanta. A Handbook of Concepts; Clarendon Press: Oxford, U.K., 1974; p 186.

(30) Henglein, A.; Giersig, M. J. Phys. Chem. B 1999, 103, 9533.

(31) van Hyning, D. L.; Zukoski, C. F. Langmuir 1998, 14, 7034.

(32) Johnson, P. B.; Christy, R. W. Phys. Rev. B 1972, 6, 4370.

(33) Miller, A. MieTab version 6.38 for Windows, 1998.

(34) van de Hulst, H. C. Light Scattering by Small Particles; Dover Publications: New York, 1981; Part II, Chapter 9.

(35) Note: Mietab Software provides extinction coefficient; therefore, to obtain absorbance values, classical Lambert-Beer law was applied using a total concentration $N = 7.8 \times 10^{11}$ part./cm³, calculated by assuming spheres of diameter equal to the particle size and taking into account partial contribution of each diameter from Figure 6.

(36) Charlé, K. P.; Schulze, W. Ber. Bunsen-Ges. Phys. Chem. 1984, 88, 350.

(37) Taleb, A.; Petit, C.; Pileni, M. P. J. Phys. Chem. B 1998, 102, 2214

(38) CRC Handbook of Chemistry and Physics, 75th ed.; CRC Press: Boca Raton, FL, 1995; p 3-207.

(39) Wang, W.; Chen, X.; Efrima, S. J. Phys. Chem. B 1999, 103, 7238. (40) Gutiérrez, M.; Henglein, A. J. Phys. Chem. 1993, 97, 11368.

(41) Ludviksson, A.; Huang, C.; Jänsch, H. J.; Martin, R. M. Surf. Sci. 1993, 284, 328.

(42) Carley, A. F.; Davies, P. R.; Roberts, M. W.; Santra, A. K.; Thomas, K. K. Surf. Sci. 1998, 406, L587.

(43) Citra, A.; Andrews, L. J. Phys. Chem. A 2001, 105, 3042.

(44) Keshavaraja, A.; She, X.; Flytzany-Stephanopoulos, M. Appl. Catal., B 2000, 27, L1.

(45) Henglein, A. J. Phys. Chem. B 1999, 103, 9302.