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Formation and Stabilization of Silver Nanoparticles through Reduction by N,N-Dimethylformamide

Isabel Pastoriza-Santos and Luis M. Liz-Marzán*

Departamento de Química Física e Química Orgánica, Universidade de Vigo, Apdo. 874, 36200 Vigo, Spain

The reduction of Ag^+ ions in N,N-dimethylformamide (DMF) is shown to take place spontaneously at room temperature. When no other additives are present in the system, the slow reduction leads to silver deposition on the glass walls of the container, while in the presence of 3-aminopropyltrimethoxysilane (APS) stable dispersions of silver nanoparticles are obtained. Even though the reduction can be performed at room temperature, higher temperatures markedly increase the reaction rate and improve the monodispersity of the colloid. The reduction rate and morphology of the colloidal particles also depend on the ratio [Ag]/[APS]. The reduction takes place both with nitrate and perchlorate as counterions, which confirms that DMF plays the role of a reducing agent. Additionally, when excess APS is used, a thin, homogeneous silica shell is formed on the silver particle surface.

One of the main applications of metal nanoparticles is found in catalysis.[1,2] Since most of the reactions to be catalyzed take place in organic solvents, it is desirable to design synthetic methods which lead to the stabilization of metal nanoparticles in such solvents. This can be accomplished through the reduction of the metallic salts or complexes "in situ", or by transfer of aqueous colloids into the organic phase,[3,4] normally after surface modification.[5–7] In both cases, the reduction can be driven by a chemical reducing agent,[8–11] an electron scavenger for the formation of radicals promoted by γ,[12] UV,[13] or ultrasound[14] irradiation, or a thermal method such as prolonged reflux.[15]

N,N-Dimethylformamide (DMF) is one of the standard organic compounds used as a solvent for various processes, including the preparation of colloids[16–18] which usually contain metals in their composition. The oxidation of DMF has been studied with respect to the production of hydrogen from water–DMF mixtures[19] and even for the reduction of Ni(IV) to Ni(II) in alkaline medium.[20] These studies show that DMF can be an active reducing agent under suitable conditions. We show here the ability of DMF to reduce Ag^+ ions to the zerovalent metal, even at room temperature and in the absence of any external agent. Such a redox process should be taken into account when handling solutions of metal ions in DMF, because it can also be of importance for metals other than silver. Furthermore, by means of a silane coupling agent,[21] dispersions of silver nanoparticles can be prepared which remain stable for months. We have also observed that the relative amount of this coupling agent, as well as the temperature, influences noticeably both the reaction rate and the morphology of the colloids obtained.

Experimental Section

Materials. $AgNO_3$, $AgClO_4$, and 3-(aminopropyl)trimethoxysilane (APS) were purchased from Aldrich. N,N-Dimethylformamide (DMF) was Fluka (Pure grade). Ethyl alcohol was Scharlau (Pure Grade). All chemicals were used as received. For the preparation of aqueous solutions, Milli-Q deionized water (18 MΩ) was used.

Particle Preparation. Simple addition of aqueous solutions of $AgNO_3$ or $AgClO_4$ (typically microliter volumes) to DMF leads to the slow reduction of silver ions to silver metal, as manifested by a gradual yellowish coloration of the solution. No stirring is necessary after an initial shaking to homogenize the solution. Preparations at 60 °C were performed in a thermostated water bath, while at 100 °C a paraffin bath placed on a hotplate was used. During high temperature preparations, care must be taken regarding DMF vapor, which is harmful, and readily dissolves plastic micropipet tips. As it will be shown below, the time needed for completion of the reaction mainly depends on [Ag]/[APS] ratio (R) and temperature, ranging from several weeks at room temperature to a few seconds at reflux, for Ag and APS concentrations between 10^{-4} and 10^{-3} M.

Experimental Techniques. Transmission electron microscopy (TEM) was performed with a Philips CM20 microscope operating at 200 kV, equipped with a setup for element analysis

* To whom correspondence should be addressed. E-mail: lmarzan@uvigo.es.

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by X-ray energy dispersion (EDS) EDAX PV9900. Sample preparation for TEM was performed by diluting $10\times$ the DMF dispersion with ethanol to minimize the damaging of the Formvar coating by DMF (this dilution did not have any apparent effect on the aggregation state of the particles during the time scale involved in the preparation of the grids). UV−visible spectra were measured in 10 mm optical path length quartz cuvettes with a HP 8453 spectrophotometer. A blank was measured with pure DMF before each measurement. Dc conductivity was measured with a Crison 2202 conductimeter calibrated with standard KCl 0.1M solution.

Results and Discussion

This section is broken into several subsections. In the first subsection, we propose a reaction route which we believe takes place in our system during the reduction process and describe the general phenomena which take place during the reduction at room temperature. Subsequently, the influence of several parameters on both the reaction rate and the morphology and stability of the particles obtained is described. This sets up the basis for establishing a mechanism for colloid formation.

A. The Reduction Process. Several routes have been proposed[19] for the oxidation of DMF, which normally involve the evolution of H_2 or CO_2 gas.

Since we do not observe any gas evolution for the reaction at room temperature, we propose that the following reaction takes place during the process:

$$HCONMe_2 + 2Ag^+ + H_2O \rightarrow$$
$$2Ag^0 + Me_2NCOOH + 2H^+ \quad (1)$$
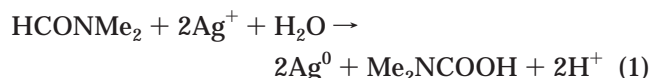
This mechanism is supported by a measured increase of conductivity as the reaction proceeds, which indicates that the larger Ag^+ ions are progressively exchanged for the more mobile H^+ ions.

Actually, the carbamic acid formed can easily decompose as

$$Me_2NCOOH \rightarrow CO_2 + Me_2NH \quad (2)$$
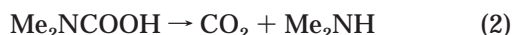
though this reaction is only favored at high temperature, while at room temperature the reverse reaction is preferred.[19] ^{1}H NMR measurements on the final (basically particle-free) reaction product after reduction of 0.01 M $AgNO_3$ at 100 °C, only yielded the signals characteristic for DMF. At this high temperature (necessary for completion of the reaction in a reasonable time period), not only decomposition of the carbamic acid but also evaporation of the amine are expected.

When no stabilizing agent is present in solution, after some minutes to hours after silver salt addition, deposition occurs on the glass walls of the vessel, such that they become initially yellow, then brown, and eventually (depending on the initial silver concentration) shiny and metallike. Observation of the surfaces with a scanning electron microscope shows that metallic silver particles are indeed attached onto the glass. A full account of these phenomena will be published elsewhere.[22] On the contrary, if the silane coupling agent APS is present in solution previous to silver salt addition, no adsorption of metallic silver onto the beaker walls takes place whatsoever. This means that Ag nanoparticles are formed in solution, which are stabilized by APS, in a fashion similar to that reported for the equivalent mercaptosilane, MPS, during the
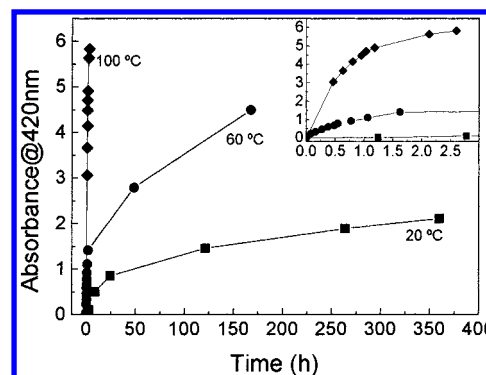
Figure 1. Kinetic traces for the formation of Ag particles in DMF solution with APS at different temperatures, with [Ag]/[APS] ratio = 1. The inset shows the traces for the initial stage of the reaction. [Ag] = 0.5 mM.

synthesis of gold nanoparticles in ethanol.[23] The following sections are devoted to the systematic study of this process of colloid formation.

B. Influence of Temperature. As mentioned above, the reduction of Ag^+ by DMF can proceed at room temperature. However, the process is so slow that even after 2 weeks the reduction of a 0.5 mM solution is not completed when APS is in solution. It was observed that increasing the reaction temperature, the reaction rate is greatly enhanced. The effect of temperature was followed by UV−visible spectroscopy for three different values of the [Ag]/[APS] ratio R (0.38, 1.0, 1.2), since (as will be shown below) this ratio also affects the reaction rate. For each R value, three identical samples were prepared and the reaction was followed at 20, 60, and 100 °C by measuring the UV−visible spectrum of aliquots extracted from the samples at selected time intervals. When the sample concentration became too high to measure reliable spectra, dilution with pure DMF was performed, and the spectrum was subsequently rescaled assuming validity of the Lambert−Beer law. This is the reason for the high absorbance values shown in the figures. The reactions performed at reflux were so quick that the time evolution could not be followed. As can be observed in Figure 1 for $R = 1.0$, the reaction rate increases dramatically (in orders of magnitude) upon temperature increase.

The tendency shown in Figure 1 was observed for the other two molar ratios as well. However, it should be mentioned that a few experimental difficulties arise when performing these experiments. In the case of low temperature reactions, it is basically impossible to follow the reaction to completion, and in some cases aggregation processes were observed to occur after several weeks. In the case of high-temperature reactions with low APS concentration, the reaction was cooled just after the absorbance reached a plateau since, if the heating was maintained, aggregation and adhesion of the silver colloid particles onto the walls of the beaker took place. Absorbance values past that time would be unreliable.

The influence of temperature on the morphology and size of the resulting particles was studied with TEM. The results for different temperatures and R values are summarized in Table 1. At room temperature, we observe the formation of small silver particles, occasionally attached to the surface of larger spheres (Figure 2a), which presumably arise from the (acid catalyzed) hydrolysis and condensation of APS.[24] This is supported by a decrease of

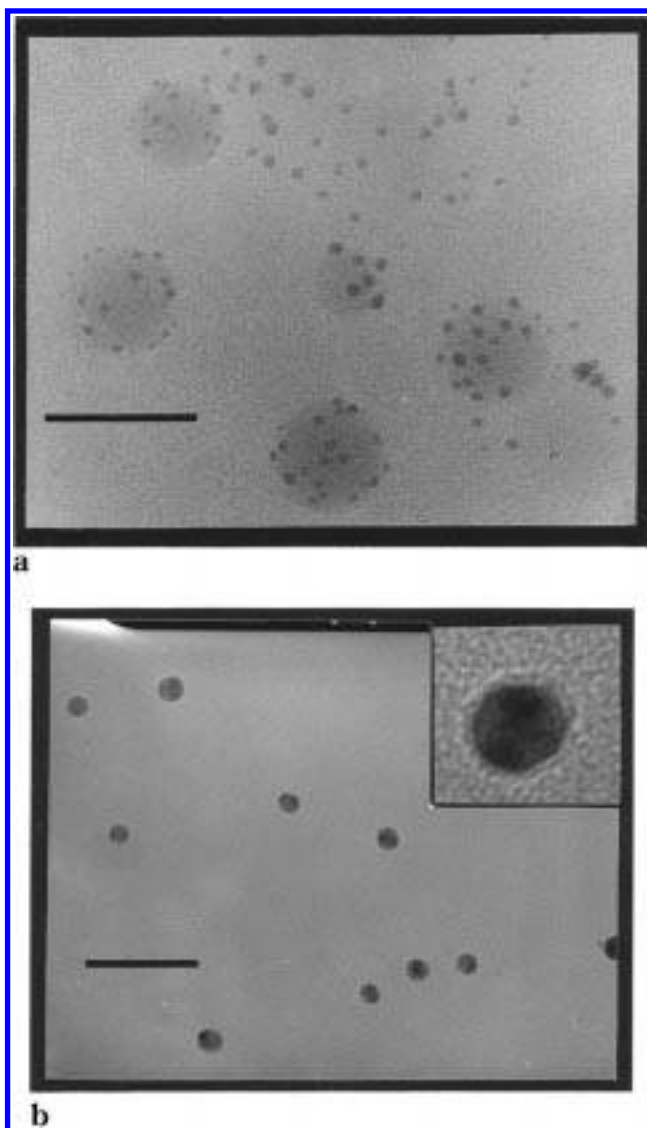(22) Pastoriza-Santos, I.; Liz-Marzán, L. M. Manuscript in preparation.

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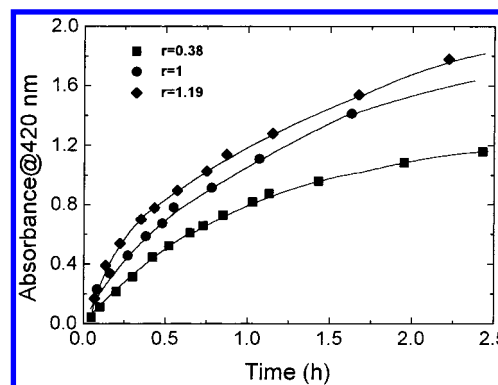
Table 1. Average Diameter of Ag Particles Prepared in DMF, for Several Values of the Molar Ratio *R* and of Temperature[a]

	diameter (nm)			
R	20 °C	60 °C	100 °C	156 °C
0.38	6.5 ± 1.5*	17.4 ± 3*		19.7 ± 2
	11 ± 2	8 ± 3		
1.0	13 ± 3	17 ± 4	17.4 ± 0.7	19.5 ± 3.8
1.2	7 ± 1.5*	12 ± 3	16.8 ± 0.4	19 ± 2
	14 ± 2	17.4 ± 3		
6.0	12 ± 2*			
	17 ± 2			

[a] When two populations exist, the most abundant one is marked with an asterisk.

Figure 3. Kinetic traces for the initial stages of the formation at 60 °C of Ag particles in DMF solution with APS, for several [Ag]/[APS] ratios. [Ag] = 0.5 mM.

particles were observed to be surrounded by a thin, homogeneous shell (Figure 2b), which was identified by EDS as silica. The different morphology obtained for low and high temperature reactions with excess APS can be easily related to the respective reaction rates for silver reduction and APS condensation. At room temperature, silver reduction is so slow that silica nuclei can form and grow in solution, on which (slowly formed) silver particles attach. On the other hand, at high temperature, silver formation is so quick that silica polymerizes directly onto the (APS-coated) silver particle surface.

Finally, we should mention that TEM observation of high temperature samples at several times during the reaction showed the existence of two distinct populations at intermediate stages of the reactions, while in the end only the largest particles survive. This is an indication that high temperature favors Ostwald ripening, so that larger particles grow at the expense of the smaller ones.

C. Influence of the Ratio [Ag]/[APS]. The observation that when no APS was present, the reduction of silver by DMF was notably faster (though no stable colloids were obtained) suggested that complexation of the amino group of APS to silver ions occurred before the reaction, therefore influencing the reaction rate. To further characterize the influence of APS on the rate of the reduction process, kinetic traces were compared for reactions performed at the same temperature with different values of *R*. In Figure 3, the initial traces are shown for a temperature of 60 °C (optimal temperature for kinetic measurements to avoid undesired effects). The reaction rate was indeed observed to increase for larger *R* values, i.e., for a larger number of Ag^{+} ions per APS molecule.
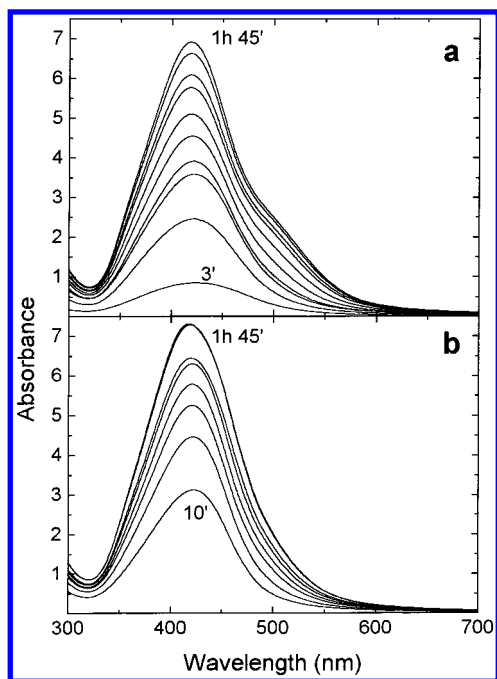
TEM showed a slight decrease in particle size for increasing ratios, though this trend is not very clear, as can be observed from the data shown in Table 1.

D. Influence of the Counterion. All the previous results were obtained using AgNO₃ as the precursor salt for supplying Ag^{+} ions to the solution. The problem of this salt is that nitrate can undergo photolytic reactions which cause silver nuclei to form. Nitrate supplies hydrated electrons in the presence of light through charge-transfer-to-solvent (CTTS) processes,[25] so that the nucleation process will be affected. We had anyway previously confirmed that the photochemical was not the main reduction process, since particle formation took place in the dark as well.

Photolytic side effects do not arise with AgClO₄, so that an experiment with this salt should provide a conclusive proof about the nature of the reduction process, and also

Figure 2. Transmission electron micrographs of Ag particles prepared in DMF: (a) reduction at room temperature; (b) reduction at reflux, where the inset is a close-up of one of the particles, showing more clearly the presence of a thin, homogeneous silica shell. [APS] = 0.5 mM, and [Ag] = 0.5 mM. Scale bars: 100 nm.

the relative amount of these organosilica spheres with increasing [Ag]/[APS] ratio. For *R* = 1.2, very few spheres were observed, but two distinct populations of silver particles exist. When increasing temperature, the average particle size increases, the particles become more monodisperse, and organosilica spheres are not formed any more. However, again for small *R* values, the silver

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Figure 4. Time evolution of the UV−visible spectra during the formation of Ag particles in DMF with [Ag]/[APS] ratio = 1: (a) from $AgNO_3$; (b) from $AgClO_4$. [Ag] = 1 mM.

lead to more homogeneous colloids through a cleaner reaction. When $AgClO_4$ was used, particle formation was observed with comparable reaction rates under similar conditions. This is a clear indication that DMF is the effective reducing agent and nucleation occurs just due to increasing Ag^0 concentration as the reduction proceeds.

Although no strong changes were observed in the reaction rates due to the different counterions, the shapes of the UV−visible spectra are different for colloids obtained from both salts, displaying the ones obtained from $AgClO_4$ sharper and more symmetrical plasmon bands (see Figure 4, and note that, again, rescaling after sample dilution is responsible for high absorbance values). This points toward a more uniform size distribution in the perchlorate system, which was confirmed by TEM, where basically no trace of large particles was found on the grids, unlike for nitrate colloids.

From the same figure, one can see that in both cases the plasmon band position blue shifts during the reaction. A plausible explanation for this effect is that initially the particle surface is positively charged due to the adsorption of unreacted Ag^+.[26,27] As the reaction proceeds, the ion concentration decreases, and so does the positive surface charge. The band position for the final perchlorate colloid is centered at 416 nm, i.e., red-shifted with respect to standard aqueous silver colloids. The two major factors responsible for this red shift are the higher refractive index of DMF[28] (1.428 as compared to 1.333 for water) and the presence of the silica shell surrounding the silver particles, which increases further the local refractive index around the surface.[29] Calculations based on Mie theory[30] predict a similar shift between (silica-coated) silver particles dispersed in water and in DMF.

E. The Stabilization Mechanism. We discuss here a few aspects of the stabilization process which were not addressed above. The adsorption of APS onto the particle surface is driven by the large complexation constant of amines with silver. Such a complexation is also the reason for the noticeable reduction in reaction rate observed with increasing APS concentration. Additionally, TEM shows that, for small *R* values, (organo)silica is formed during the reaction as well, which is shown either as independent spheres (on which some Ag particles are attached) or as a thin shell coating the final Ag particles. The silica shell is likely to form in this case from the hydrolysis and polymerization of APS molecules,[24] which is catalyzed by the acid environment generated during the reduction (see eq 1), while it is known[21] that in basic media six- and eight-membered rings are formed, which can remain as such for long periods of time. These two different ways for silica precipitation as a function of temperature can be related to the change in reaction rate. At low temperature, the silica polimerization rate is noticeably higher than silver particle formation, so that independent silica nuclei form in solution. Conversely, at high temperature the formation of Ag particles is so fast that they serve as nuclei on which silica polymerizes.

This means that, for particles prepared at high temperature, the final outer particle surface is similar to that of standard silica particles. As mentioned in the Experimental Section, for the preparation of the TEM grids, the samples had to be diluted with ethanol to prevent dissolution of the polymer film on the grids. No aggregation was ever observed on the grids, which shows that the particles are stable in ethanol. This was confirmed by UV−visible spectroscopy, where just a small blue shift was observed, which can again be attributed to the change in solvent refractive index (in this case toward smaller values).

Given the relatively high monodispersity achieved by this reduction process, and given the fortunate fact that homogeneous silica coating takes place at the time of reduction, the method promises itself as a convenient alternative to the preparation of silica coated silver particles.[7,29]

Conclusions

It was shown that DMF is a remarkably powerful reducing agent for silver ions. Colloidal silver particles in the nanometer size range were synthesized by reduction with DMF, using the silane coupling agent APS as a stabilizer.

The reaction rate is strongly influenced by temperature and by the [Ag]/[APS] ratio, which also affect the monodispersity and particle size of the colloids. When sufficient APS is used at high temperature, a thin silica shell is deposited on the particle surface, due to the acid catalyzed condensation of APS. With regard to the optical properties of the dispersions, the silver plasmon absorption band is shifted toward longer wavelengths in virtually all cases, due to the high refractive index of DMF, and to the silica surface coating.

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