

Reduction of silver nanoparticles in DMF. Formation of monolayers and stable colloids*

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Abstract: We explore in this article the reduction of Ag⁺ ions by N,N-dimethylformamide (DMF), both in the presence and in the absence of a stabilizing agent. The reduction can lead to the formation of either thin films of silver nanoparticles electrostatically attached onto glass surfaces, or stable dispersions of silver nanoparticles if the silane coupling agent 3-aminopropyltrimethoxysilane (APS) is present. The different parameters affecting the reduction process are discussed, and the reducing ability of DMF is compared with that of ethanol, which is often used for the production of catalytically active metal colloids.

INTRODUCTION

Several examples exist on the reduction of metallic salts by organic solvents. Probably the most popular one is ethanol, which has been long used by Toshima and coworkers for the preparation of metal nanoparticles suitable for catalytic applications [1–4]. Another interesting example is found in Figlarz's polyol method, which was initially developed for the formation of larger colloidal particles [5,6], though later was also adapted for the production of nanoparticles [7]. Methanol was also used for the preparation of silver colloids in basic conditions [8]. Related to these processes, we can also mention the reduction of noble metal salts by non-ionic surfactants, and more specifically by those with a large number of ethoxy groups, to which the reducing ability has been assigned [9,10].

In basically all these processes, some sort of external energy (thermal or electromagnetic) was necessary for the reduction to actually take place. It was also recently shown that both N,N-dimethylformamide (DMF) [11,12] and formamide [13] can act as powerful reductants for silver or gold salts. We are reporting here on the basic features found for the reduction of silver salts by DMF, as well as the different results obtained under different conditions. We compare our results with some other literature results for metal colloid formation by reduction with organic solvents. The importance of this study not only relies on providing a novel reaction medium for the preparation of non-aqueous metal colloids, but also on showing the possibility to obtain unwanted byproducts during other synthetic procedures involving DMF as a solvent and metal salts or complexes as reactants.

DMF AS A REDUCTANT

N,N-dimethyl-formamide (DMF) is one of the usual organic compounds used as a solvent for various processes. The oxidation of DMF has previously been studied with respect to the production of hydrogen from water–DMF mixtures [14] and, more related to the topic of this report, for the reduction of Ni(IV) to Ni(II) in alkaline medium [15]. These studies showed that DMF can be an active reducing agent under suitable conditions.

Several routes have been proposed [14] for the oxidation of DMF, which normally involve the evolution of H₂ or CO₂ gas.

Since no gas evolution was observed during the reactions performed at room temperature, we propose that the following reaction takes place during the process:

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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,



though this reaction is only favored at high temperature, while at room temperature the reverse reaction is preferred [14].

A basic difference of this reaction, as compared to the ethanol reduction method [1] is that it proceeds at a meaningful rate even when performed at room temperature and in the dark. This is readily observed as a yellow color shows up in the solution, which deepens as a function of time. It is also important to note that the reaction is performed without degassing the solutions or taking any special care with regard to the presence of oxygen, which is in contrast with the observations of Han et al. [13], who claim that the reduction of AuCl_4^- by formamide can only take place in an oxygen-free environment, and is actually frozen when oxygen is allowed to come in contact with the system. These authors claim similar observations for N-methylformamide and for DMF.

This reducing ability in mild conditions points toward a larger tendency of this solvent for the reduction of Ag^+ than that shown by ethanol or other organic solvents, which we actually demonstrate later in this paper (see "Reduction in Mixtures of Solvents").

REACTION AT ROOM TEMPERATURE

As we mentioned in the previous section, the reduction of silver salts by DMF can be monitored from the color evolution of the solution. Visual observation shows that, as the reaction proceeds, the color shifts from light yellow to dark brown, through orange and olive green, and then starts concentrating on the glass surfaces in contact with the solution, while the solution itself becomes increasingly clearer (the amount of stable Ag colloid in solution decreases) until it is completely transparent. This means that silver metal particles are formed in solution, which at some point stick onto glass surfaces. This process is probably driven by electrostatic attraction between the particles with excess positive charge (from adsorption of unreacted silver ions [16], and the negatively charged SiO_2 surface. Observation of such surfaces with an atomic force microscope shows that individual metallic silver particles are indeed attached onto the glass (see Fig. 1).

The morphology of the resulting surfaces changes with time, and depends on parameters such as starting concentration, illumination conditions, or the specific silver salt used [12]. It is remarkable that by careful control of these parameters (small concentration and relatively short deposition time), quite homogeneous films of reasonably monodisperse nanoparticles can be obtained, as shown in Fig. 1. On the other end (larger concentration and longer deposition times), formation of larger agglomerates can be observed, which can even lead to electrically conducting films (see Fig. 2).

These changes in the morphology of the obtained films can also be observed through UV-visible spectroscopy. Figure 3 shows the spectra of films prepared by deposition from AgNO_3 solutions of different concentration, after a period of 24 h. It is clear that, for larger concentrations, the amount of deposited metal increases. It is also apparent from the figure that, for larger concentrations, even after just one day there is already contact between neighboring nanoparticles, which is reflected in the increased absorbance at high wavelengths.

If a suitable stabilizing agent is added to the Ag^+ solution in DMF, stable silver colloids can be obtained [11]. We have tested the silane coupling agent [17] 3-aminopropyltrimethoxysilane (APS) as a stabilizer, since it can readily complex to silver atoms through its amine functionality, so that silane groups would point toward solution, which would result in a favorable situation, as indicated by the stability of silica colloids in DMF [18]. It was indeed observed that with APS present, no adsorption of

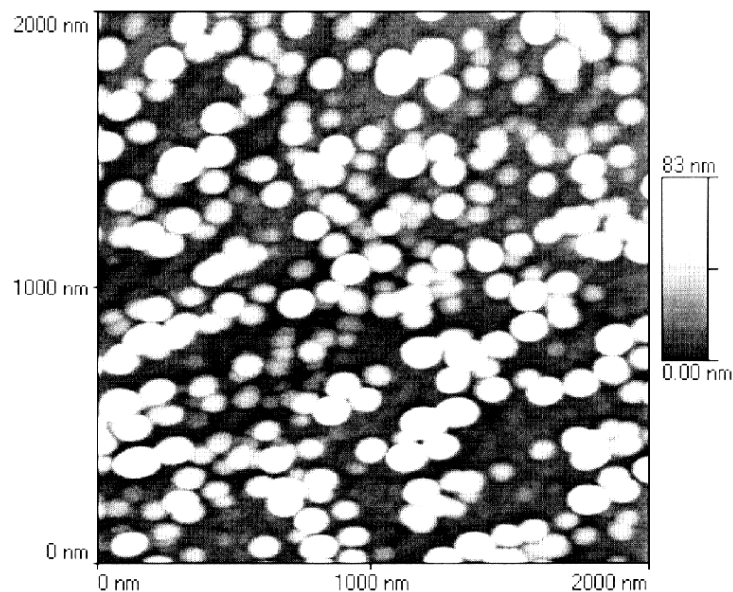


Fig. 1 AFM image of a typical glass surface after deposition of Ag nanoparticles reduced by DMF.

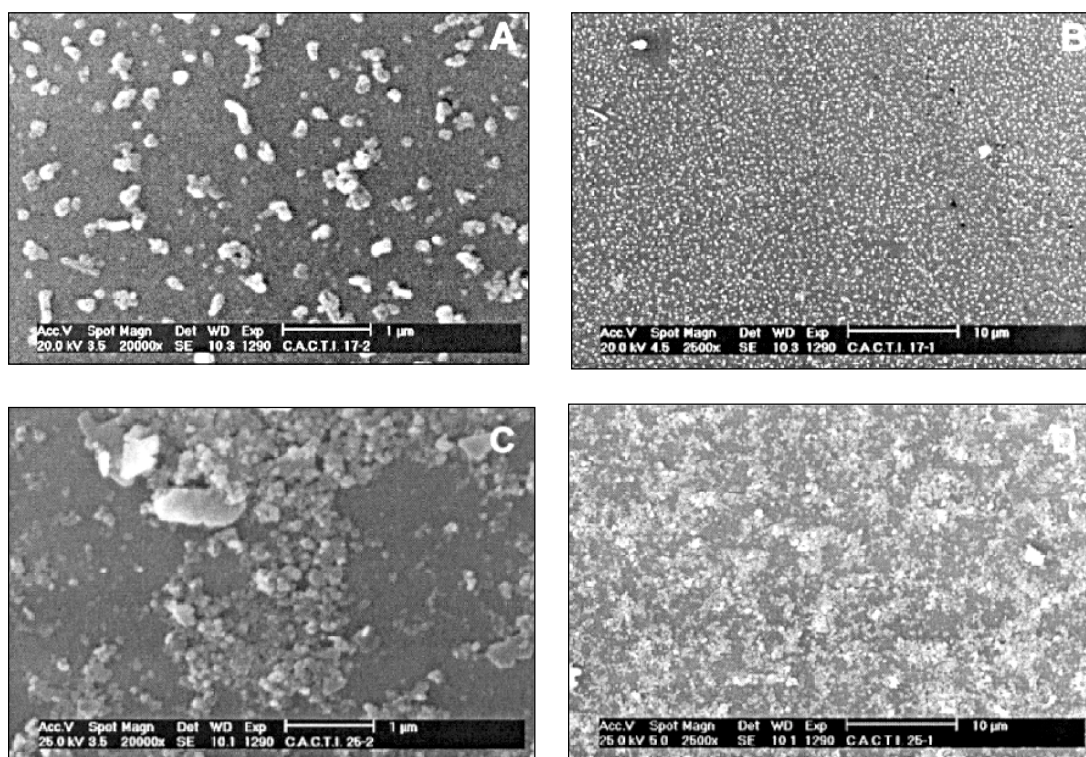


Fig. 2 Scanning electron micrographs showing the morphology of thin films deposited from DMF solutions of AgNO_3 with starting concentrations 0.5 mM (A,B) and 2.0 mM (C,D).

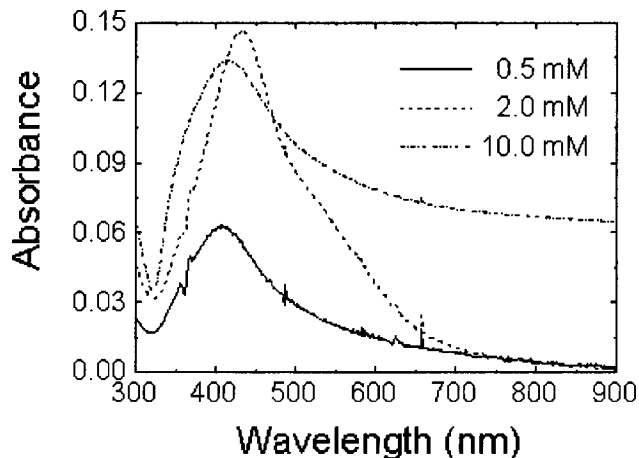


Fig. 3 UV-visible spectra of films deposited from AgNO_3 solutions for a period of 24 h.

metallic silver onto the walls of the beaker took place whatsoever. This means that Ag nanoparticles formed in solution were stabilized by APS, in a similar fashion to what was reported for the equivalent mercaptosilane MPS, during the synthesis of gold nanoparticles in ethanol [19]. This stabilizing action seems to start as an initial complexation of APS to Ag^+ ions, which is reflected in a marked decrease of the reduction rate. However, we have observed by transmission electron microscopy that the colloids prepared at room temperature consisted of larger silica spheres onto which small silver nanoparticles are randomly attached [11].

It should be finally pointed out that when the reaction was performed in anaerobic conditions, no increase of the reaction rate was observed, which is in contradiction with ref. 13. Actually, in the presence of oxygen, the prepared colloids were found to be both more homogeneous in size and shape, and more stable.

REACTION AT HIGHER TEMPERATURE

Due to the slow reduction rate at room temperature in the presence of APS, it seemed more advantageous to perform the reduction at higher temperatures. The rate was indeed observed to strongly increase with temperature, so that at 60 °C the reduction was completed in some 2 days, while at 100 °C it took just a few hours, and it was basically instantaneous at reflux (152–154 °C). This effect is shown in Fig. 4 for an equimolar solution of AgNO_3 and APS in DMF [20]. Though the ratio Ag^+/APS also played a role on the reduction rate, for several values of such a ratio the effect of temperature was found to be similar.

Interestingly, when the reduction is performed at high temperature in the presence of APS, the obtained silver particles were observed to be surrounded by a thin, homogeneous shell (Fig. 5), 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.

A different approach to high-temperature reduction is the use of microwave heating. Several examples have been reported on the microwave-induced formation of nanoparticles in solution [21,22]. The advantages of this method are based on a quick and very uniform heating of the whole sample with no need of stirring, so that the reaction should take place simultaneously through the volume of the sample. In the case of DMF, this method is experimentally more difficult to implement, due to the possible harm of the oven. The reaction must thus be carried out in successive short exposures, with

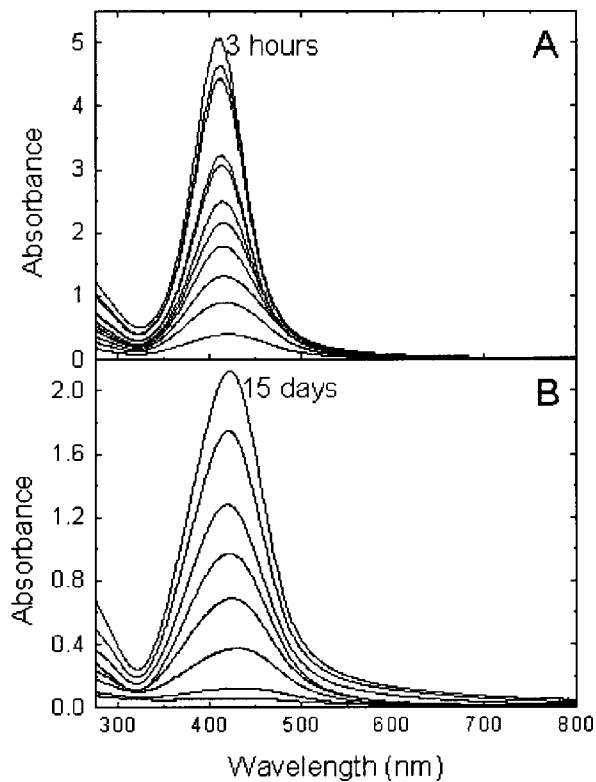


Fig.4 Time evolution of UV-visible spectra of Ag colloids during reduction in the presence of APS. $[AgNO_3] = [APS] = 0.5$ mM. (A) reaction at 100 °C; (B) reaction at room temperature.

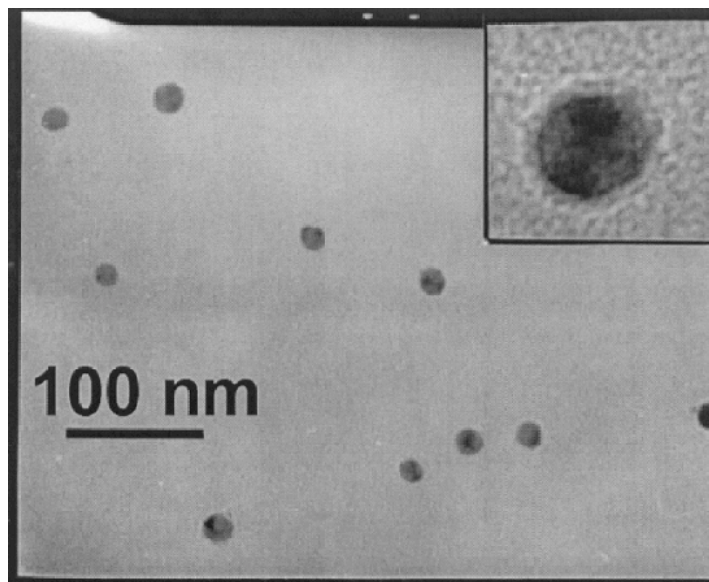


Fig. 5 Transmission electron micrograph of Ag particles prepared in DMF at reflux. The inset is a close-up of one of the particles, showing the thin, homogeneous silica shell more clearly. $[APS] = [AgNO_3] = 0.5$ mM. Reproduced from ref. 11.

intermediate cooling. This leads to colloids with more symmetrical visible spectra, which points to a narrower size distribution, which was confirmed by TEM. A full account of these results will be presented elsewhere.

REDUCTION IN MIXTURES OF SOLVENTS

As indicated in the introduction, some other organic solvents have previously been used as reductants for the formation of metal nanoparticles. We have tested the differences between DMF and ethanol for the reduction of silver under reflux. Therefore, we used the same silver salt and APS concentrations, in mixtures of DMF and ethanol with different compositions. As shown in Fig. 6 (see ref. 20), the trend is clear: the larger the concentration of DMF, the faster the reduction. Additionally, it was found that the minimum concentration of APS necessary to achieve stable dispersions is larger as we increase the ethanol content. The larger APS concentration accounts for a longer reduction time at reflux than was observed before.

The faster reduction rate obtained with DMF as compared to that with ethanol can be due to two distinct factors: i) the larger reducing ability of DMF, and ii) the higher standard boiling point, which is almost double for DMF than for ethanol. A more detailed comparative study is being currently per-

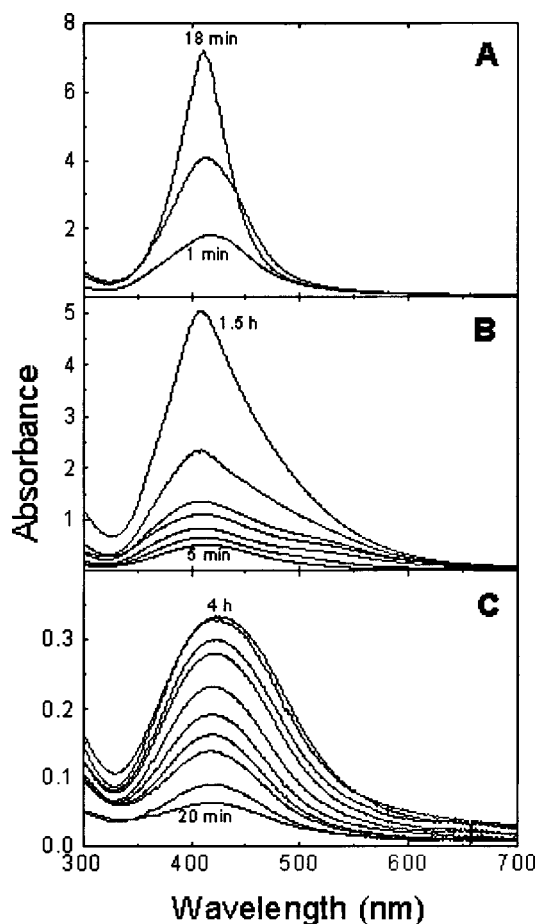


Fig. 6 Spectral evolution during the formation of Ag particles at reflux in pure DMF (A); a mixture of equal volumes of DMF and ethanol (B); and in pure ethanol (C). $[\text{AgNO}_3] = 0.75 \text{ mM}$; $[\text{APS}] = 2 \text{ mM}$.

formed, which includes other organic solvents, as well as other stabilizers, and will be published elsewhere.

CONCLUSIONS

It was shown that DMF is a remarkably powerful reducing agent for silver ions. Colloidal silver particles in the manometer 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 affects 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. Reduction experiments in mixtures of DMF and ethanol show an increase of reaction rate as the ratio DMF/ethanol increases, pointing toward a larger reducing ability of DMF.

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