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Moderating effect of ammonia on particle growth and stability of quasi-monodisperse silver nanoparticles synthesized by the Turkevich method

Luiz F. Gorup, Elson Longo, Edson R. Leite, Emerson R. Camargo*

UFSCar – Federal University of São Carlos, Department of Chemistry, Rod. Washington Luis, km 235, São Carlos 13565-905, Brazil

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ABSTRACT

A new method to stabilize silver nanoparticles by the addition of ammonia is proposed. Colloidal dispersions of silver nanoparticles were synthesized by the Turkevich method using sodium citrate to reduce silver nitrate at high pH and at 90 °C. After approximately 12 min, a diluted ammonia solution was added to the reaction flask to form soluble diamine silver (I) complexes that played an important growth moderating role, making it possible to stabilize metallic silver nanoparticles with sizes as small as 1.6 nm after 17 min of reaction. Colloidal dispersions were characterized by UV-visible absorption spectroscopy, X-ray diffraction, and transmission electronic microscopy.

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1. Introduction

Stable colloids of silver nanoparticles have attracted considerable interest due to their practical applications, which range from surface-enhanced Raman spectroscopy [1], catalysis [2], and biosensing technology to their use as antibacterial agents [3–5]. In all these cases, particle size and size distribution play an important role in many physical and chemical properties. Silver nanoparticles are usually synthesized by bottom-up techniques using, for instance, templates [6], reduction by chemical [7,8] or electrochemical methods [9], sonochemical [10] and thermal or photochemical processing [11,12]. Chemicals such as surfactants, mercaptans, and polymeric compounds that include polyvinylpyrrolidone, polyvinyl alcohol, and some amino acids [13,14] are also widely used to prevent aggregation and precipitation of metal nanoparticles from the colloidal medium. Because of the green characteristics of the citrate reduction method, sometimes referred to as the Turkevich method that involves the use of nontoxic substances and minimum waste generation, it is the most popular route to obtain spherical silver nanoparticles [15,16]. In this method, silver and citrate salts are basically stirred together in water at a controlled pH and after an induction period, metallic nanoparticles are formed, which can be monitored by observing the characteristic plasmon band at around 425 nm in the visible spectrum. Although variables such as temperature, molar ratio of silver to citrate, and total concentra-

tions can strongly affect particle size and size distribution, the synthesis of stabilized silver nanoparticles of sub-10 nm size with narrow size distribution remains a challenge, particularly considering their potential applications in emerging areas of nanoscience and technology for biomedical applications or for the fabrication of highly conductive elements for printed electronics [17].

In this paper, we demonstrate a way to prevent particle growth and the generation of new nuclei using ammonia to trap all the free Ag^+ in the system after the nucleation step, resulting in stable aqueous colloidal suspensions of spherical silver nanoparticles of 2 nm on average and a sharp size distribution.

2. Materials and methods

Solutions were prepared with deionized water obtained from a commercial Millipore Elix 3 system. All the chemicals used in this work were of analytical grade and were used as received, with no further purification. Silver nanoparticles were prepared by the reduction of silver nitrate (98.8% Merck, Germany) solutions with sodium citrate (99% Synth, Brazil) by the standard method described by Turkevich [15]. A volume of 100 mL of an aqueous solution of silver nitrate (1.0 mmol L^{-1}) was heated and stirred gently with a magnetic Teflon-coated bar. When the silver nitrate solution reached 90 °C, 1.0 mL of a 0.3 mol L^{-1} solution of sodium citrate preheated to 90 °C was added to the solution. During the reaction, aliquots of 10 mL were removed from the flask, cooled to room temperature, and subjected to UV-Vis characterization to monitor the reduction of silver ions based on the characteristic plasmon absorbance band at approximately 425 nm. A second experiment was performed in the same conditions, but immediately after the system became yellow, indicating the formation of silver nanopar-

* Corresponding author. Address: LIEC – Interdisciplinary Laboratory of Electrochemistry and Ceramics, Department of Chemistry, UFSCar – Federal University of São Carlos, Rod. Washington Luis, km 235-CP 676, São Carlos-SP 13565-905, Brazil. Fax: +55 16 3351 8414.

E-mail addresses: lfgorup@gmail.com (L.F. Gorup), elson@iq.unesp.br (E. Longo), derl@power.ufscar.br (E.R. Leite), camargo@ufscar.br (E.R. Camargo).

ticles, which normally occurred after 12 min of reaction, 1.0 mL of a previously prepared 1.4 mol L⁻¹ aqueous solution of ammonia was added.

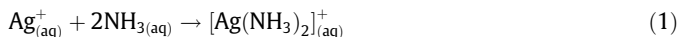
Silver nanoparticles were characterized in the 2θ range from 20° to 110° by X-ray diffraction (XRD) using a Rigaku Dmax 2500PC diffractometer with Cu Kα radiation operating at 40 kV and 40 mA. To collect the patterns, nanoparticles were deposited on silicon substrate by dripping the aqueous colloidal dispersion onto the substrate at room temperature and waiting for the solvent to evaporate. The UV-Vis spectra of silver nanoparticles aqueous dispersions were obtained with a UV-Vis spectrophotometer (Shimadzu Multispec 1501) in the region of 190–800 nm, using a commercial quartz cuvette. Scanning transmission electron microscopy (STEM) images were recorded at 20 kV using a FEG Zeiss Supra 35-VP, and scanning electron microscopy (SEM) images were recorded with a Zeiss DSM 940A. Histograms were constructed using the public domain ImageJ image processing software. To estimate the reaction yield, conductometric titrations were performed at room temperature.

3. Results and discussion

The key point in obtaining small metallic colloidal nanoparticles is the formation of a high density of nuclei at the beginning of the process. Therefore, the rapid addition of the reducing agent into a salt solution is necessary to form a large number of nanoparticles simultaneously, decreasing the total available ion concentration. However, unlike other noble metals such as gold or platinum, only a fraction of silver ions are reduced to metal, even when using an excess of reducing reagent. Due to this inevitable presence of silver ions in the medium, new nuclei will still be formed while the particles formed initially will continue to grow at the same time, fed by silver ions that remain in the medium. This process will result in particles with a broad size distribution, consisting of large particles formed initially and small particles formed subsequently.

To overcome this intrinsic characteristic of the silver system and obtain stable aqueous colloidal suspensions of spherical silver nanoparticles of 2 nm on average and a sharp size distribution, in this paper we demonstrate a way to prevent particle growth and the generation of new nuclei using ammonia to trap all the free Ag⁺ in the system after the nucleation step. When an excess of ammonia is added in the presence of silver ions, soluble diamine silver (I) complexes should be formed immediately (Eq. (1)), removing the silver ions that have not yet been reduced, and thus

preventing the formation of new nuclei and the growth of already formed nanoparticles. Without ionic silver available in the medium, the system will be frozen in the initial stage, resulting in virtually monodisperse silver nanoparticles.



To validate this idea, two experiments were performed, one traditional without ammonia and a second with the addition of ammonia (Fig. 1), in order to demonstrate that the size and size distribution of silver nanoparticles can be efficiently stabilized by controlling the amount of silver ions available after the nucleation step. The diluted aqueous solution of silver nitrate was heated and stirred gently, followed by the addition of sodium citrate solution. During the reaction, small aliquots were removed from the reaction flask, cooled to room temperature, and characterized by UV-Vis spectroscopy. Immediately after the system became yellow, aqueous ammonia solution was added to the reaction flask. Conductometric titrations were performed to estimate the reaction yield, which indicated that only about 50% of the Ag⁺ was reduced to metallic nanoparticles.

Silver colloids nanoparticles were dripped onto silicon and characterized by XRD (shown in the supporting information), allowing for the identification of the typical cubic structure of metallic silver in all the samples. These samples were also characterized by STEM and histograms of size distribution obtained by processing the images with the public domain software [18]. As expected, during the synthesis of silver nanoparticles without ammonia (route A), the yellow color appeared after approximately 12 min of reaction. After this point, the absorbance increased exponentially and the colloids rapidly lost their stability. Although the dependence of the light scattering on the particle size, the increase in absorbance intensity over time was an indication that new particles were still being formed as the reaction proceeded. In addition, the shift of the plasmon band to a lower wave number indicated that particles continued to grow as a function of the reaction time. These findings were confirmed by the STEM images obtained from aliquots removed in an interval of 8–60 min. Images of samples removed after 20 min (Fig. 1a) showed spherical particles with an average diameter of 34 nm and a wide particle size distribution (Fig. 1b). It was found that the longer the reaction time the larger the particle size, with some particles showing sizes as large as 70 nm. Particle growth was also found to occur in samples kept at room temperature. For instance, aliquots removed from the reaction flask after 15 min and left to rest at room temperature be-

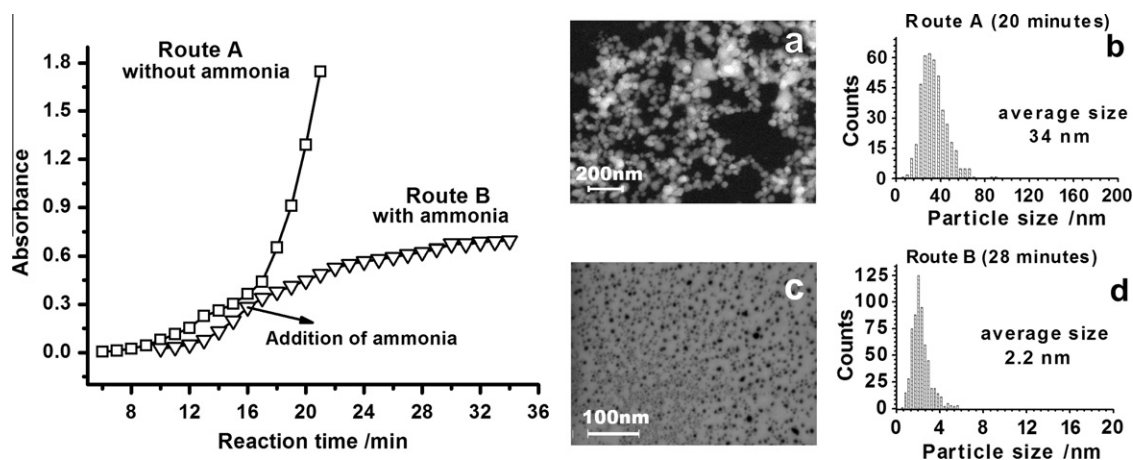


Fig. 1. Absorbance intensity of the plasmon band as a function of reaction time for two synthesis routes, (A) without ammonia and (B) with the addition of ammonia after the system became yellow. (a) STEM image of the sample without ammonia after 20 min and (b) histogram showing an average size of 34 nm with a wide size distribution. (c) STEM image of the sample with ammonia added after 12 min and histogram showing nanoparticles with an average size of 2.2 nm and (d) a narrow size distribution.

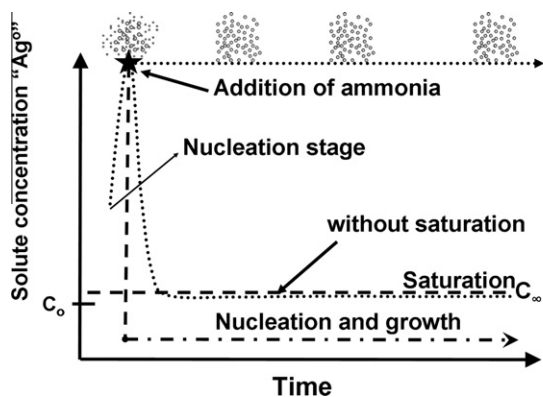


Fig. 2. Reduction in the metallic silver concentration as a function of reaction time, showing the initial nucleation stage after the addition of citrate ion and the addition of ammonia immediately after the system turned yellow, reducing the amount of metallic silver to a quantity below the saturation limit.

came dark and lost their stability after one week, indicating that silver particles continued to grow because of the continuous reduction of silver by the citrate ion, even in the absence of heating. Of course, this process is faster at higher temperatures, which allow particles to grow rapidly and precipitate in a matter of hours.

On the other hand, the addition of ammonia immediately after the nucleation step (route B) caused the intensity of the plasmon band to change very slowly over time, with no shift in the maximum position. These results are explained by the fact that the particle size of the silver nanoparticles was practically unmodified and only the particle concentration increased slightly over time. Surprisingly, silver nanoparticles obtained after 28 min of reaction in the presence of ammonia were quasi-monodisperse, with an average diameter of 2.2 nm and a narrow particle size distribution (Fig. 1d). Moreover, a significant finding was that the colloidal suspension remained stable for a long time (several months) without the use of different stabilizing agents than citrate, such as alkanethiols or surfactants.

At this point, it is difficult to propose a simple kinetic model for the growth of silver nanoparticles since there are many variables to consider. However, the interdependence of density of nuclei and reaction time may serve to shed light on the formation of these monodisperse nanoparticles with such small sizes and of how ammonia acts as a moderator of nanoparticle growth in the colloidal medium (Fig. 2).

This apparently simple idea effectively results in stable colloidal aqueous suspensions of spherical silver nanoparticles with narrow size distributions (Fig. 3a). These results reveal that the addition of ammonia to the system immediately after the nucleation stage is an efficient way to stabilize colloidal suspensions of quasi-monodisperse silver nanoparticles with much smaller average sizes than previously reported, since free silver ions, which are responsible for particle growth and the formation of new nuclei, are trapped by the formation of soluble complexes, preserving the silver nanoparticles for long storage periods without coalescing or precipitating.

This procedure, which involves the use of inexpensive and non-toxic reagents, also allows the particle size to be determined by choosing the right moment at which to add ammonia. The stability of these small silver nanoparticles in water would be useful in a variety of applications in fields such as antimicrobial agents in medical devices containing silver [3] or for use in highly conductive elements for printed electronics [17], since their surfaces are free of stabilizing agents that are difficult to remove at low annealing temperatures.

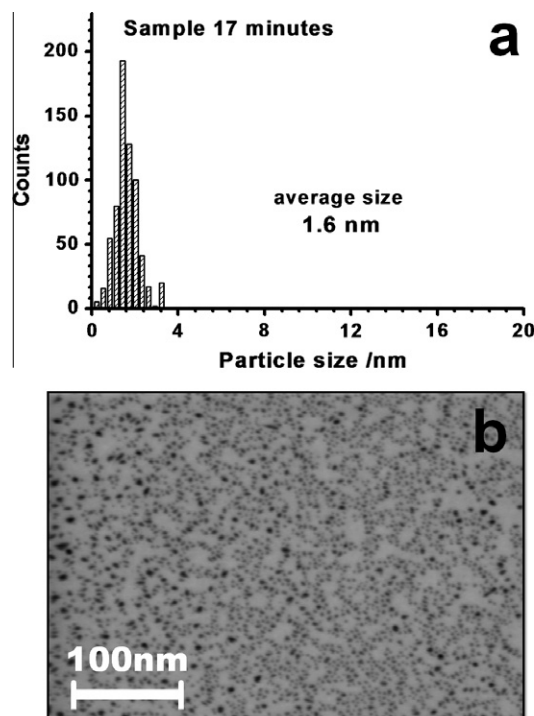


Fig. 3. Sample with ammonia after 17 min of reaction (a) and histogram (b) STEM image showing particles with an average size of 1.6 nm and a narrow size distribution.

4. Conclusions

Addition of diluted ammonia to the system immediately after the nucleation stage to form soluble diamine silver (I) complexes played an important role in the synthesis and stabilization of metallic silver nanoparticles with sizes as small as 1.6 nm, since free silver ions, which are responsible for particle growth and the formation of new nuclei, are trapped by the formation of soluble complexes.

Acknowledgments

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Appendix A. Supplementary materials

Preparation details, XRD patterns, conductometric titration, and supplementary STEM images (PDF). This material is available free of charge via the Internet. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jcis.2011.04.099](https://doi.org/10.1016/j.jcis.2011.04.099).

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