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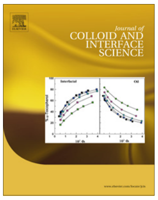

Precipitation of spherical and ‘fiber-like’ silver particles

Lu Lu, Dan V. Goia *

Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699-5814, USA

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ABSTRACT

Silver nanoparticles with various sizes and shapes were prepared by adding silver nitrate to ascorbic acid solutions containing nitric acid and a dispersant (Daxad 11G). It is shown that the reaction environment significantly affects the nature of the interactions between silver ions and dispersant molecules. The stability of the Ag$^+$/Daxad 11G intermediate species formed, which determines the reduction rate and, implicitly, the particle size and shape, is strongly affected by the dispersant/Ag$^+$ ratio and the concentration of nitric acid. Uniform highly dispersed Ag nanoparticles were obtained at high concentrations of HNO$_3$, while lower acid concentrations favored the formation of ‘fiber-like’ metallic structures. The propensity for forming anisotropic silver structures is attributed to the planar structure and chromonic properties of dispersant molecules.

1. Introduction

Bulk metallic silver is extensively used in metallurgy [1–3] and electronics [4–6] due to its excellent electrical conductivity and chemical stability. In dispersed form, particularly at nanosize dimensions, the metal also displays unique properties widely exploited in Surface Enhanced Roman Scattering (SERS) [7–11], catalysis [12–15], optoelectronics [16–18], biosensors [19,20] and for anti-microbial purposes [21–23]. All these exciting applications rely on particles with tightly controlled properties. Chemical precipitation from homogenous solutions remains the most effective synthetic route for tailoring the size, shape, and internal structure of uniform metallic nanoparticles [24]. Although dispersed uniform Ag nanoparticles were prepared in the absence of stabilizers more than a century ago [25], most synthesis protocols include dispersants/capping agents to improve particle uniformity and dispersion stability. Molecules with affinity for the silver surface, such as polyvinylpyrrolidone (PVP) and cetyltrimethylammonium bromide (CTAB), are well suited for such purposes [26–29]. Moreover, capping agents can also control particle shape as a result of their selective absorption on specific crystal facets [30–32]. Despite the presence of dispersion stabilizers, most reported methods yield highly dispersed silver only at very low metal concentrations (typically less than 10 m mol dm^{-3}). While such conditions yield particles with well controlled intriguing properties, they are not suitable for cost effective manufacturing of Ag nanoparticles on a large scale. As a result, the development of practical applications based on such materials are often put on hold. To address this shortcoming, Goia et al [33] have shown that concentrated dispersions of silver nanoparticles can be obtained by reducing silver nitrate with ascorbic acid in the presence of sodium naphthalene sulfonate–formaldehyde copolymer (Daxad 19). Several studies of this system have followed [34–36], triggered primarily by its propensity to yield particles with non-spherical morphologies. Still, the Ag$^+$/naphthalene sulfonate-formaldehyde co-polymer interactions and their impact on particle size and morphology of silver have not been sufficiently investigated. This study reveals that the stability of the intermediate Ag$^+$/dispersant species, which affects the reduction kinetics and thus the properties of the precipitated silver, is strongly affected by experimental conditions. It is also shown that the structure of dispersant molecules not only plays a role in the formation and stability of the intermediate silver complex but also, in specific experimental conditions, alters the growth mechanism favoring the precipitation of anisotropic silver particles.

2. Experimental

2.1. Materials and characterization

Silver nitrate crystals (AgNO$_3$, Ames Goldsmith, Glens Falls/NY), ascorbic acid (C$_6$H$_8$O$_6$, KIC Chemicals, New Paltz/NY), nitric acid solution 70% w/v (Fisher Scientific Co., Fair Lawn/NJ), and Daxad 11G (GEO Specialty Chemicals, Deer Park/TX) were used as received. The particle size and morphology of Ag particles were assessed by field emission electron microscopy (FESEM, JEOL – JSM-7400F). For observation at low magnification the particles were simply deposited as a thin film on an aluminum stub. For examination at high magnification, the specimens were sputtered for 15 s

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* Corresponding author.
E-mail address: goiadanv@clarkson.edu (D.V. Goia).

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Table 1
Experimental conditions used in the synthesis of silver particles.

Exp.	Daxad 11G added (g)	Ag/Daxad weight ratio	Conc. HNO_3 volume added (cm^3)	Final HNO_3 conc. ($mol\ dm^{-3}$)	Reaction time (min)	Particle size (nm)	Characteristics of Ag particles
1[a]	0.0	–	10.0	0.5	15	–	Irregular large aggregates
2	1.4	5/1	10.0	0.5	180	63+/−12	Dispersed spherical nanoparticles
3	3.5	2/1	10.0	0.5	300	41+/−9	Dispersed spherical nanoparticles
4	14.0	1/1	10.0	0.5	600	24+/−5	Dispersed spherical nanoparticles
5	1.4	5/1	2.0	0.1	15	–	'Fiber-like' particles
6	1.4	5/1	0.0	0	15	–	'Platy' particles

[a] Reference experiment.

for better image clarity. The images were taken using an SEI detector at 15 kV and a working distance of 3.2 mm. The average particle diameter and the standard deviation were obtained by measuring ~100 particles. The crystalline structure of the precipitated solids was assessed by X-ray diffraction (XRD) with a Bruker D8 Diffractometer (Madison, WI) using a Cu Kα, $\lambda = 1.5406$ Å line. For the XRD pattern acquisition, the step width and period were 0.02° and 1.5 s respectively, while the source, sample, and detector slits were 2, 0.6, and 1 mm. The optical properties of silver dispersions were evaluated by UV–Vis spectrophotometry using a Perkin–Elmer Lambda 35 instrument operating at a scan rate of 480 nm/min.

2.2. Preparation of silver particles

All precipitation experiments were carried out at 40 °C in a 500 cm^3 jacketed cylindrical glass beaker. In all cases a silver nitrate solution (40.0 cm^3, 1.62 $mol\ dm^{-3}$) was first prepared separately in a 100 cm^3 glass beaker by dissolving 11.0 g of $AgNO_3$ crystals (equivalent of 7.0 g metallic silver) in deionized (DI) water. The reducing solution was prepared directly in the reaction vessel by dissolving 10.2 g ascorbic acid and variable amounts of Daxad 11G in 260.0 cm^3 DI water. Next, controlled volumes of HNO_3 solution 70% (15.7 $mol\ dm^{-3}$) were added slowly (1.0 $cm^3\ min^{-1}$) to the vigorously stirred ascorbic acid/dispersant solution to prevent high local acid concentration and uncontrollable oxidation of ascorbic acid. Immediately after the addition of nitric acid, the $AgNO_3$ solution was pumped into the reducing solution over 15 min and the mixing was continued until all silver was reduced. The reaction end point was indicated by the lack of silver precipitation when adding ascorbic acid crystals to the heated supernatant obtained by centrifuging a small dispersion aliquot. The metallic particles were subsequently washed four times by decantation with 300 cm^3 DI water and twice with 100 cm^3 ethyl alcohol. This purification protocol is possible due to the rapid settling of silver nanoparticles at high ionic strength. For this reason, a small volume of electrolyte (ammonium nitrate) solution was added to the aqueous dispersion to aid particles settling and ensure a high yield of metal recovery. Once transferred to alcohol, the silver nanoparticles remained permanently coagulated and could be easily filtered and then dried. The experimental conditions used in the investigations and the characteristics of the resulting silver particles are summarized in Table 1.

3. Results and discussion

The Daxad 11G/silver ratio and the volume of nitric acid added to the ascorbic acid solution were found to have dramatic effects on the kinetics of Ag^+ reduction and the properties of silver particles formed. In the reference precipitation (Experiment 1*), which included the maximum volume of nitric acid (10.0 cm^3) but no dispersant, the precipitation of silver was observed at the first contact between the reacting solutions, and the reduction was complete once the delivery of $AgNO_3$ was finished. As expected, the rapid reduction in the absence of a stabilizer resulted in the formation of large non-uniform and heavily aggregated silver particles (Fig. 1a), which settled quickly once the agitation was stopped. The presence of only a pure crystalline silver phase was confirmed by XRD analysis (Fig. 1b).

In stark contrast, when in otherwise identical conditions 1.4 g Daxad 11G (representing 1/5 of the metal weight) were added to the reductant solution (Experiment 2), the reaction mixture remained clear for the first ~30 s followed by the gradual formation of a white–yellow precipitate. The FESEM analysis of the solids collected at the end of the silver nitrate addition step (Fig. 2a) revealed the presence of few silver nanoparticles (circled features) distributed in an amorphous organic mass (square area). The latter is likely a complex formed between silver and the dispersant molecules, which is only sparingly soluble at the pH where the

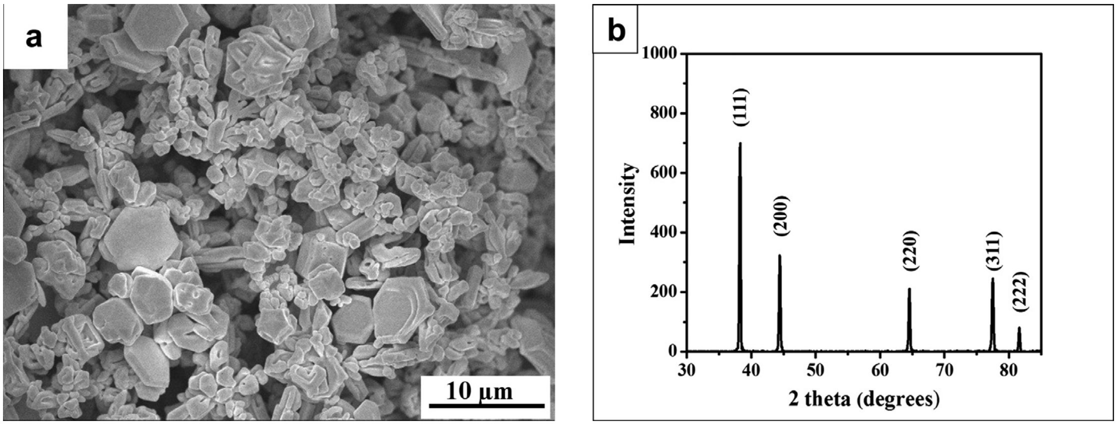

Fig. 1. (a) FESEM image and (b) XRD pattern of silver particles obtained in the reference experiment.