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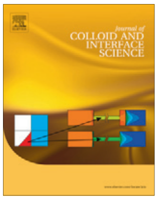

Precipitation of silver/palladium alloy platelets from homogeneous solutions

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ABSTRACT

Dispersed silver/palladium (Ag/Pd) nanoplatelets were prepared by delivering in parallel solutions of mixed metal nitrates and L-ascorbic acid into a nitric acid solution containing Arabic gum. The shape and size of bimetallic nanoparticles varied with the silver/palladium weight ratio and the concentration of nitric acid. The optimum conditions for platelets formation were a palladium content of ~2.0 wt.% and nitric acid concentrations above 1.0 mol dm^{-3}. The data presented show that both parameters play a critical role in the nucleation and growth of AgPd particles. A mechanism explaining the formation of the bimetallic nanoplatelets is proposed.

1. Introduction

The unique optical [1–8] and catalytic [9–13] properties of anisometric metallic nanoparticles have for long time fascinated scientists from both academic and industrial settings. Particularly, metal platelets have been the subject of many investigations and their preparation via liquid phase reductions has been widely reported [14–28]. Ascorbic acid has been often the reductant of choice in the precipitation of noble metals. In the case of silver, it was used either to generate the seeds needed for the nucleation of less electropositive metals [11,21,22] or to precipitate anisometric particles in homogeneous solutions [29]. Although it is widely agreed that nucleation and the ensuing rapid diffusional growth play essential roles in dictating particle morphology, the investigation of these early stages is fraught with major difficulties. Consequently, the mechanisms responsible for the formation of anisometric particles are still not well understood and we are rarely able to predict in previously unexplored systems, which experimental conditions would yield a particular shape [30]. It is thus not surprising that most attempts to interpret experimental results have relied on theoretical considerations. One common approach is to explain the formation of metal platelets based on process kinetics [31–34]. The proponents of this methodology have suggested that lattice defects formed during nucleation and subsequent growth promote the formation of anisotropic structures. Other investigations [35] have shown that the incorporation of foreign atoms in the crystal lattice of the host metal can be also an important source of structural inhomogeneity. The evidence of such defects was reported by Germain et al. [36] who identified {1 1 1} stacking faults in silver nano-disks by electron diffraction and high-resolution TEM analysis. The authors proposed [37] that the stacking faults are responsible for the 2.5 Å lattice spacing corresponding to the forbidden 1/3{4 2 2} reflections seen in electron diffraction patterns and suggested a link between these and anisotropic growth. Starting from a well-known model used to explain the formation of anisometric silver halide crystals, Lofton and Sigmund [38] proposed that lamellar twin planes are responsible for the formation of precious metal platelets. In their view, the twin planes form reentrant grooves on the crystal edges and create high energy facets that grow more rapidly. In a separate work, Rocha and Zanchet [39] showed that both stacking faults and twin planes are present in their nanoplatelets and have a role in anisotropic growth. More recently, Aherne et al. [26] showed that regions containing multiple lamellar stacking faults are present in metal platelets.

Although widely accepted, these theories often overlook or offer only anecdotal evidence of the role played by chemical factors in the formation of defects. For this reason, several theoretical models for anisotropic growth in the absence of defects have been also recently proposed [40–44]. The present study attempts to close this gap by providing experimental evidence of direct correlations between specific precipitation parameters and the shape of the resulting metallic particles. The system consists in generating dispersed AgPd alloy nanoplatelets by co-reducing silver and palladium ions with ascorbic acid in nitric acid solutions. It is proposed that the incorporation of Pd atoms in the silver lattice and a strongly oxidative reducing environment are the essential ingredients in forming the necessary structural defects and for promoting and sustaining the growth of the metallic platelets.

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2. Experimental

2.1. Reagents

Silver nitrate crystals (Ames Goldsmith, Glens Falls/NY), palladium nitrate solution containing 9.0% Pd (Umicore, South Plainfield/NJ), nitric acid 70% (Fisher Scientific Co., Fair Lawn/NJ), Arabic gum (Frutarom, North Bergen/NJ), L-ascorbic acid (/Roche Vitamins Inc., Parisppany/NJ), sodium hydroxide solution 10N (Fisher Scientific Co., Fair Lawn/NJ), and ethanol (Pharmco Products Inc., Brookfield/CT) were all used as received.

2.2. Synthesis and isolation of nanoplatelets

In a typical experiment, *mixed metal nitrates* and *reducing* solutions were added simultaneously into the *receiving solution* over 7 min (flow rates of 1.7 $cm^3\,min^{-1}$and 2.0 $cm^3\,min^{-1}$, respectively). The *mixed metal nitrates* solution was obtained by adding $Pd(NO_3)_2$ solution and $AgNO_3$ crystals into ~12.0 cm^{-3} deionized (DI) water. The total amount of metals was always 1.24 g but the Ag/Pd weight ratio varied from 100% Ag/0% Pd to 90% Ag/10% Pd (Table 1). Alternatively, a larger volume of *metal nitrates* solution was prepared and 12 cm^3 aliquots were used for individual experiments. The *reducing solution* was prepared by dissolving 0.12 g Arabic gum into 10.0 cm^{-3} DI water. After 1.0 h stirring, 2.5 g of L-ascorbic acid was dissolved in this solution and the volume was adjusted to 14.0 cm^{-3}. The *receiving solution* was prepared in a 1000 cm^{-3} glass beaker by dissolving 2.3 g of Arabic gum in 300 cm^3 DI water for 1 h. Five minutes before the start of the precipitation, 21.0 cm^3 of concentrated nitric acid solution (70.0% HNO_3, 15.5 mol dm^{-3}) was added to obtain a solution of 1.0 mol dm^{-3} HNO_3. Receiving solutions without nitric acid and with higher concentration (3.5 mol dm^{-3}) of nitric acid were also tested.

Through the entire addition, the dispersion was vigorously stirred using a 1.5″ diameter stainless steel impeller spinning at 1700 rpm. Once the addition of reactants was completed, the pH was increased to 10.6 using 10 N NaOH solution and the temperature was brought to 85 °C. In these conditions, the Arabic gum was hydrolyzed in less than 1 h causing the settling of the nanoplatelets. The supernatant solution was removed by decantation, and the particles were washed four times with DI water and twice with ethanol before they were filtered and dried at 80 °C.

2.3. Particles characterization

The size and shape of the platelets were assessed by field emission electron microcopy (FESEM, JEOL-JSM-7400F) and transmission electron microscopy (TEM, JEOL 2010). In the first case, the samples were prepared by simply placing a drop of dispersion on an aluminum stub and removing the solvent in vacuum. Samples for high resolution transmission electron microscopy were prepared by placing a drop of a dilute dispersion on a carbon coated copper grid and drying the grid overnight. The structure of the nanoplatelets was investigated by powder X-ray diffraction (XRD) analysis with a Bruker D8 Focus analyzer. To obtain 'in-process' samples, 10 cm^3 of dispersion was removed from the reaction vessel and diluted with 90 cm^3 of cold DI water. The nanoplatelets were isolated by either centrifugation or by rapid hydrolysis of Arabic gum using enzymes [45].

3. Results and discussion

The reductions of silver and palladium ions by ascorbic acid are quite straightforward as described by the following equations:

$$2\{Ag^+ + NO_3^-\} + C_6H_8O_6 \rightarrow 2Ag^0 + C_6H_6O_6 + 2\{H^+ + NO_3^-\} \qquad (I)$$

$$\{Pd^{2+} + 2NO_3\} + C_6H_8O_6 \rightarrow Pd^0 + C_6H_6O_6 + 2\{H^+ + NO_3^-\} \qquad (II)$$

Although nitric acid is released from these reactions, the quantity does not significantly change the total concentration of HNO_3 in the system due to the large amount of acid already present.

In the conditions of the reference run (Experiment #3, Table 1), the nucleation of the metallic phase was preceded by an induction period, which lasted ~3 min. Once the nucleation occurred, the color of the dispersion changed over the next ~60 s from yellow, to red, to purple, and blue. The succession of vivid colors reflected the gradual red-shift of the in-plane dipole surface plasmon resonance absorption band of the growing metal platelets [46]. As the reaction progressed, the turbidity of the dispersion increased and the color of the dispersion changed to brown.

The addition of palladium in the system was an essential factor in the formation of platelets. In the absence of palladium (Experiment #1, Table 1), the pure silver particles formed were large and mostly isometric (Fig. 1a). As the content of palladium was gradually increased, the particles started to adopt the platelet morphology (Fig. 1b), the fraction of anisometric particles reaching a maximum at 2.0% Pd (Fig. 1c). In this case (Experiment #3, Table 1), the edge lengths ranged from 200 to 300 nm and the thickness from 20 to 40 nm. At a Pd content of 10% (Experiment #4, Table 1), the fraction of anisometric particles did not change much but the aspect ratio decreased noticeably and so did the average particle size (Fig. 1d). Above 10% Pd an insignificant number of platelets were observed.

The concentration of nitric acid played also a role in promoting the platelet morphology. In the absence of acid, even at a Pd content of 2.0% the particles formed were mostly isometric (Fig. 2a). When the concentration of nitric acid was increased from 1.0 mol dm^{-3} to 3.5 mol dm^{-3}, the aspect ratio of the particles was higher than in the 'reference' experiment. Their edge and shape definition were also improved despite the fact that local etching on the large facets occurred. Above 3.5 mol dm^{-3} nitric acid, the metallic phase did not form as the strong oxidative environment continuously re-dissolved the freshly formed metallic nuclei.

The evaluation of platelets by HRTEM revealed important structural information. The presence of a reflection in the SAED pattern in Fig. 3(right), often noted as 1/3{422}, is associated with a 2.5 Å lattice fringe and has been interpreted generally as being caused by the presence of lamellar defects.[35,36]

The X-ray diffraction analysis supported this interpretation as a small peak was observed at 2.52 $Å^{-1}$ (Fig. 4). The peak, previously attributed to the presence of a *hcp* region containing multiple lamellar stacking faults [26], has a low intensity due to the small volume occupied by the lamellae. The remaining XRD spectrum contains only one set of slightly shifted reflections of the *fcc* silver lattice, an indication that the two metals are alloyed.

This study reveals two factors that are essential in the formation of AgPd platelets. The first is the ability of palladium atoms to promote anisotropic growth by inducing structural defects in the silver lattice. The second is the strongly oxidative environment of the system, which leads to different deposition/dissolution rates for selected crystal facets.

A likely source of structural defects is the difference in the reduction kinetics of the two metals. Since the redox potential (E^0) of Pd^{2+}/Pd^0 system is more electropositive than that of the Ag^+/Ag^0 pair (+1.0 V vs. +0.8 V), the nucleation event is dominated by the former. The decrease in the length of the induction period with increased palladium content in the metal nitrates solution confirmed this thermodynamic prediction. The difference in bond dissociation energy of silver (Ag–Ag = 1.659 eV) and palladium