Evaluation of Silver Nanoparticle Size by Anodic Particle Coulometry and Optical Methods

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Abstract. Silver nanoparticles (Ag NPs) with diameters in the range between 10 and 100 nm were synthesized in aqueous solution with the stepwise seed growth method. The average size and size distribution of the as-grown nanoparticles were measured in situ with Anodic Particle Coulometry (APC, also called faradaic nano-impact), an electrochemical method developed in recent years. In essence, in APC, the nanoparticles are oxidized at a constant potential for a few seconds. The oxidation and disintegration of the Ag nanoparticles on the electrode produce a series of distinctive current spikes on the curve of current versus time. The comparison of the particle sizes measured with APC and with dynamic light scattering (DLS) and UV-VIS spectroscopy shows that, under our experimental conditions, APC tends to overestimate the sizes of the smaller particles and underestimate the largest particles. The divergences can be explained in terms of the uncertainties in the charge measurements, in addition to possible lateral chemical oxidation reactions and fragmentation of the nanoparticles on the electrode.

1. Introduction
Metallic nanoparticles find now many applications in catalysis, optical devices, cosmetics, environmental remediation, and medicine, to name a few. To understand and control the properties and the applications of metal NPs, the size, the size distribution, the shape of the nanoparticles and the distribution of electrical charges must be characterized with great precision. Dynamic light scattering (DLS), transmission electron microscopy (TEM) and UV-VIS spectroscopy are commonly used for the characterization of sizes and the size distribution of metallic nanoparticles [1, 2].

In the past few years, a new family of methods for the in situ electrochemical analysis of metal NP sizes has emerged [3]. Among these methods, the most common is called “faradaic nanoimpact” or anodic particle coulometry, APC, which is based on the oxidation of NPs on working electrodes at a sufficiently high potential to ensure the complete oxidation of the metallic NPs [4]. The current through the cell is recorded as a function of time. Oxidation of NPs on the electrode gives rise to a series of current peaks. The area under each current peak is the charge, Q, which is proportional to the number of atoms in each particle (Figure 1), N, through Faraday’s first law.

\[ Q = neN \] (1)
Figure 1. Schematic representation of the oxidation and disintegration of an Ag NP at an electrode surface held at a sufficiently high potential to produce an oxidation current spike. The area under this current spike yields $Q$, which is proportional to the particle size.

Assuming that the NPs have spherical geometry and that they undergo complete oxidation, the diameter $D$ of the nanoparticle is a function of $Q$ and the density of the NPs, through (2):

$$Q = \frac{4nF\pi r^3\rho}{3M}$$

where $n$ is the number of electrons transferred per atom, $F$ the Faraday constant, $M$ is the atomic mass of the metal, and $\rho$ is the NP density, which is different from that of the bulk material. Recent measurements show that Ag NP, with nominal diameters in the range between 30 and 100 nm, have an average density of $7900 \pm 675$ kg m$^{-3}$, approximately 20% lower than the nominal density of bulk metallic Ag, $10490$ kg m$^{-3}$ [5]. The APC method, introduced by R. Compton et al. [6], has been extended to characterize Ag, Au [7, 8], Ni [9, 10], and Cu NPS [11]. The method has also been used for core-shell particle size analysis, formed by layers of two metals [12].

In the present work, we synthesized Ag NPs in the range size (10 to 100 nm) [13]. These NPs were analyzed by UV-VIS, DLS and APC. The differences in particle size found with the three methods are discussed.

2. Experimental Section

2.1. Reagents
Silver nitrate (AgNO$_3$), sodium borohydride (NaBH$_4$), sodium citrate dihydrate (C$_6$H$_5$Na$_3$O$_7$.2H$_2$O), and potassium chloride (KCl), all analytical grade reagents, were used as received. Solutions were prepared with type 1, ultrapure, 18.2 MΩ water. All glassware was treated with $aqua$ $regia$ and acetone to eliminate traces of metals and organic compounds that promote nucleation.

2.2. Synthesis of Ag NPs
Quasi-spherical Ag NPs of different sizes were obtained by the reduction of AgNO$_3$ with sodium borohydride and sodium citrate in a boiling solution, following the method reported by Wan et al., in which the smallest Ag NPs were used as seeds in a multi-step growth process [13, 14].

2.3. Characterization
Dynamic light scattering (DLS) measurements were performed with a Malvern Nano S90 Zetasizer, equipped with a 633 nm He-Ne laser, operating at an angle of 90° at 25 °C. The Ag NP solutions were dispersed in 10 mM KCl. UV-VIS spectra were recorded by using a Shimadzu UV-1700 spectrophotometer.
All electrochemical experiments were performed on a CHI760B electrochemical analyzer coupled to a Faraday box, using a cell in a three-electrode configuration with a Pt disk (diameter =10 μm, CHI 107) working electrode, a Ag/AgCl reference electrode, and a Pt wire auxiliary electrode. Test solutions were placed in an ultrasound bath for 5 min and purged with nitrogen for 2 min prior experiments. The working electrodes were polished with 0.05 μm alumina and then washed with type-1 deionized water. For APC measurements, one-min potential steps from the open circuit potential to +1.0 V vs Ag/AgCl were applied to the working electrode. Current sampling rate: 1/ms. Peak identification and integration was performed with Origin 8.5.

3. Results and Discussion

3.1. Dynamic Light Scattering

Figure 2 shows the hydrodynamic size distribution of Ag NPs at different growth stages, from the “seed” stage, through growth stage 4, covering the approximate size range from 10 to 100 nm. The solid curves are for the NPs in deionized water. The dotted curves show the effect of adding KCl, which is used as supporting electrolyte for electrochemical measurements. In the "seed" stage, NPs show an average hydrodynamic diameter of 10.0 nm. Addition of the electrolyte increases the mean diameter by 1.7 nm. For bigger particles (growth stages 1, 2, 3 and 4), the presence of KCl causes the hydrodynamic diameter to increase by a few nanometers. Notice, however, that the size distribution is not significantly affected, suggesting that the presence of 10 mM KCl mainly affects the size of the solvation layer.

![Figure 2. DLS measurements of Ag NP size distribution at different growth stages. Size distribution in deionized water (solid lines) and in 10 mM KCl solutions (dotted lines).](image)

3.2. UV-VIS Spectroscopy

Figure 3 shows the spectra associated with the NPs surface plasmon resonance (SPR) at different stages of NP growth. Spectra were normalized to the height at the maximum absorption wavelength of the seed solution.
The wavelength of maximum absorption, $\lambda_{\text{max}}$, shifts towards longer wavelengths as the NP diameter increases. In the 10 mM KCl solutions, the spectra indicate again an increase in Ag NP size with respect to those in water [15].

The UV-Vis spectra of spherical or quasi-spherical metal NPs were simulated with an open access simulation software from Nanocomposix. In general, there is a very good correlation between the experimental spectra and the simulations and the little differences may be related to differences in the sphericity of the Ag NPs and the degree of dispersion of the samples.

3.3. Anodic Particle Coulometry

Figure 4 is a square wave voltammogram of Ag NP solutions in 10 mM KCl. It shows an oxidation peak at ca 0.63 V vs Ag/AgCl. As a result, for the following chronoamperometry experiments used for the APC analysis, the working electrode potential was stepped to 1.0 V vs Ag/AgCl.

Figure 5 shows a typical chronoamperogram for an Ag NP seed solution in 10 mM KCl.

Figure 4. Square wave voltammetry of the oxidation of Ag NP “seeds” on a Pt microdisk (diameter = 10 µm). Electrolyte sln. 10 mM KCl (dotted line); blank solution (dashed line); Ag NPs seed solution (solid line). Pulse amplitude: 25 mV, Frequency: 20 Hz, Increment: 10 mV.

Figure 5. Chronoamperogram of Ag NP seeds in 10 mM KCl (solid line). Dotted and dashed lines are for 10 mM KCl and blank solutions, respectively. Potential step from open circuit potential to 1.0 V vs Ag/AgCl. The insert shows one of the current spikes related to the Ag NPs nano-impact and oxidation at a Pt microdisk (diameter = 10 µm).
The current spikes result from the oxidation of the Ag NPs impacting on the electrode. The sharp increase of the current during the first few ms of each spike is consistent with a rapid adsorption of the Ag NP on the electrode. Figure 6 shows the size distribution of Ag NPs in the 10-100 nm size range.

Figure 6. Size distribution of Ag NP measured by electrochemical nanoimpact (APC) at different Growth stages: a) seeds, b) stage 1, c) stage 2, d) stage 3, e) stage 4. All solutions contain 10 mM KCl.

The smallest Ag NPs (seeds and stage 1 of growth) show very asymmetric size distributions with a long tail towards larger sizes. This is likely to be a result of aggregation caused by the presence of the electrolyte. Table 1 compares the Ag NP sizes as measured by DLS and APC and estimated by UV-VIS.

Table 1. Ag NP sizes at different growth stages as measured by DLS, UV-VIS and APC.

| Growth Stage | UV-VIS | DLS | APC |
|--------------|--------|-----|-----|
| Seeds        | 10.7   | 11.8| 23.5|
| 1            | 28.9   | 28.8| 26.8|
| 2            | 56.5   | 50.1| 60.4|
| 3            | 80.0   | 75.7| 69.1|
| 4            | 99.6   | 104.5| 81.1|

Particle sizes estimated by DLS are within a few nm of those estimated by UV-VIS for all particle sizes. In contrast, the APC method overestimates the size of the smallest nanoparticles (seeds) and underestimates the size of the larger particles. Assuming that the particles have spherical shape, APC calculates the particle diameter via equation (2) which depends on the experimentally measured charge under the current spike, Q, and the NP density.

For Ag NPs with sizes below 100 nm, the NP density becomes lower than that of the bulk metal. In this work, we use Ag NP density = 7.9 g/cm³, an average value that has been recently estimated for Ag NPs in the range between 30 and 100 nm [14]. The density may be even lower for smaller particles as recently suggested by the work of Broßell et al. [16]. The accuracy of measuring the charge under the current spike is compromised by several factors. Electrochemical analyzers use a low bandwidth low-pass filter to improve the signal-to-noise ratio but this filter can degrade short current signals, such as those observed in APC, where the current transient height is typically of a few nA and the width is a few ms.
Another uncertainty in the measurement of charge that may affect specially the smallest peaks is the superimposition of capacitive current on the faradaic current (associated with the oxidation of Ag). In other words, part of the measured charge does not correspond to the oxidation of Ag but to capacitive charging, resulting in an overestimation of the size of the seed Ag NPs.

The dynamics of NP disintegration upon adsorption and oxidation on the electrode surface is not completely understood and it is far more complex than it shows in the simple electrochemical reaction scheme in Figure 1. In addition, alternative NP oxidation chemical routes may occur, for instance by the presence of residual oxygen or Cl\textsuperscript{-} oxidation to form Cl\textsubscript{2} which may, in turn, partly oxidize the Ag NPs. The fragmentation of the NPs on the surface and competitive NP oxidation routes may lead to an underestimation of the size of the larger nanoparticles in our experimental series.

4. Conclusions

The sizes of Ag NPs, in the approximate size range between 10 and 100 nm, were measured with the APC electrochemical method and compared to DLS and UV-VIS measurements. Under our experimental conditions, the electrochemical method overestimates the sizes of the smallest particles (about 10 nm) and underestimates the sizes of the larger particles (about 100 nm). Both the uncertainties in the density of the NPs, the measurement of charge, and possible competition between electro-oxidation with chemical oxidation routes influence the accuracy of the APC method.

5. References

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