Particle-electrode impacts: Evidencing partial versus complete oxidation via variable temperature studies

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ABSTRACT

The partial electro-oxidation of large silver nanoparticles is evidenced by comparing the charges passed in nanoparticle-electrode impacts at a range of temperatures. For larger silver nanoparticles (> 100 nm diameter), the variation in the charge passed per nano-impact event at higher temperatures demonstrates that single nanoparticles undergo multiple oxidations events at the electrode, and these oxidations do not go to completion. In contrast, the relative insensitivity of the charge passed in the electrode impacts of smaller silver nanoparticles (< 50 nm diameter) to the variation of temperature is consistent with their complete oxidation.

1. Introduction

The dynamics of a particle differ markedly when it is situated near or at an interface. This interaction between the particle and a surface is influenced by a range of chemical and physical phenomena. First, when close to a boundary wall a particle's hydrodynamic mobility is decreased leading to its diffusion being 'hindered' [1, 2]. Furthermore, at very short distances the structure of the solvent leads to an oscillatory force varying on the length scale of the solvent [3]. Second, many surfaces when submerged in an aqueous solution have an associated surface charge; this charge may lead to electrostatic interactions – repulsive or attractive – of the particle with the interface [4]. Third, chemical binding, including hydrogen bonding, of the particle to the surface can significantly influence its behaviour [5, 6]. Fourth, van der Waals forces between the surface and the particle are ever present and predominantly lead to an attractive interaction between the particle and surface [4, 7]. These interactions can become even more complex when considering the dynamics of agglomeration near surfaces, where long range attractive forces between particles may arise during the course of such many-body interactions [8]. The particle-surface interaction dynamics will be sensitive to the local temperature. Moreover, apart from being of fundamental interest, these particle-surface interactions are important for a range of both biological and technological processes.

The area of single particle detection has expanded significantly over the previous decade [9, 10], here an electrode is submerged into a solution containing nanoparticles and upon random collision with an electrified interface, a reaction of or at the nanoparticle can be induced to occur. The rate of this reaction is extremely sensitive to the particle-surface separation distance. Assuming the electrons are transferred between the electrode and the nanoparticle by tunnelling and that this transfer is the rate determining step for the reaction then the resulting current will be proportional to $e^{-\beta r}$ [11, 12], for water the magnitude of β is $\sim 1.6\,\text{Å}^{-1}$ [13], where r is the tunnelling distance. In a destructive nano-impact [14], a redox active nanoparticle is used and the direct oxidation or reduction of the individual particle is driven by the applied electrode potential. In the case of silver nanoparticle (AgNP) oxidation and for small particles of ca. 20 nm diameter, in most experimental cases the oxidation of the particle likely goes to completion and the resulting shape of the spike in current commonly predominantly reflects the bandwidth of the used measurement electronics [15]. However, as first experimentally demonstrated in 2015, for larger particles (ca. 100 nm diameter) the individual nano-reactions do not necessarily lead to complete oxidation of the particle without the presence of high concentrations of electrolyte, particularly in the presence of chloride [16]. In more recent work in the literature this was demonstrated to be, as theoretically predicted in 2012 [17], likely due to the nano-motion of the particle adjacent to the interface such that for larger particles there is an increased probability of material being 'lost' from the interface prior to the reaction going to completion [18, 19]. The shape and magnitude of the individual spike maxima are found to be experimentally sensitive to both the electrolyte concentration and the applied electrode potential [20, 21]. The charge passed during a single nano-impact event gives a *direct* measure of the amount of material oxidised

during the course of a single event. However, challengingly, unambiguously determining if such an oxidation event corresponds to a complete or partial oxidation (or reduction) of a nanoparticle can presently only be evidenced by comparison, on a statistical basis, of the experimental electrochemical data with other sizing information such as that obtained from electron microscopy. This issue is further compounded by the fact that in order for a quantitative comparison to be made between the different techniques a number of important factors, including the nanoparticle population's morphology, the measurement electronics' signal-to-noise ratio and the influence of the particle's diffusion coefficient have to be fully accounted for [22]. If a single nanoparticle event does not go to completion then, assuming that the extent to which the reaction proceeds is determined by a balance of kinetic factors, such as the dynamic movement of the particle adjacent to the interface and the electrochemical oxidation kinetics, the charge passed per event will be anticipated to be temperature sensitive.

This work evidences the partial oxidation of large (~100 nm diameter) silver nanoparticles using a variable temperature nano-impacts study and subsequent comparison of this data with TEM imaging. The study yields insights into the processes occurring during the nanoparticle oxidation reaction. An analogous study is carried out on smaller 50 nm silver nanoparticles to demonstrate the value of varying the temperature in establishing the extent of oxidation of nanoparticles.

2. Experimental

2.1. Chemical reagents

Spherical citrate-AgNPs of ca. 50 nm and 100 nm (Nanoxact, $0.02 \, mg \, mL^{-1}$ silver, 2 mM sodium citrate) were purchased from Nanocomposix, USA. Potassium Chloride ($\geq 99.0\%$) was obtained from Sigma-Aldrich and was used as received without further purification. Solutions were prepared using deionised water (Millipore) with a resistivity of no < 18.2 MΩ cm at 25 °C.

2.2. Nanoparticle characterisation

UV–Vis studies were carried out using a Shimadzu UV-1800 spectrophotometer in disposable cuvettes (Eppendorf UVette, Sigma-Aldrich) using a 10 mm optical path length at wavelengths of $\lambda = 300–1100$ nm for the 100 nm AgNPs and $\lambda = 300–700$ nm for the 50 nm AgNPs.

Transmission electron microscopy (TEM) imaging of the 50 nm and 100 nm AgNPs was carried out using a JEOL JEM-3000F instrument with an accelerating voltage of 300 kV. The samples were prepared by drop-casting suspensions of 48 pM 50 nm AgNPs in 2 mM sodium citrate or 6 pM 100 nm AgNPs in 2 mM sodium citrate onto carbon girds (Agar Scientific Ltd., UK) and allowing them to dry. Subsequent image extraction and analysis was performed using ImageJ software.

2.3. Nano-impacts

Nano-impact experiments were carried out using a home-built low noise potentiostat, as described previously [23]. The signal was processed by filtering digitally (4-pole Bessel) to 100 Hz using a script written in Python 3.5. Measurements were carried out at a carbon microdisc (d = 33 μm, IJ Cambria Scientific Ltd., U.K.) working electrode. A saturated calomel electrode (BASi, USA) was used as a reference electrode, and a platinum wire was used as a counter electrode. Cyclic voltammetric measurements were carried out on 12 pM suspensions of 50 nm and 1.5 pM suspensions of 100 nm AgNPs containing 20 mM KCl, initially scanning anodically in the potential range of 0.0 V to 0.8 V (vs. SCE) at a scan rate of $10 \, mV \, s^{-1}$. A 16-bit DAC was used to provide the waveform with a full potentiostat range of ± 2 V, effectively corresponding to staircase voltammetry with a step size of 61 μV. Chronoamperometry was performed on the same solutions, with the

potential stepped to 0.426 V (vs. SCE) for 60 s. These chronoamperometric measurements were repeated with varying immersion times of 10, 30, 90, 120 and 240 s for both nanoparticle sizes. Prior to each experiment, the working electrode was polished on aqueous slurries of 1.0, 0.3 and 0.05 μm alumina in descending order of size, before rinsing with deionised water. Nano-impact spikes were identified and analysed using a script written in Python 3.5. The details of the signal analysis have been described elsewhere [22]. These studies were carried out at 15 °C, 25 °C and 50 °C for both sizes of nanoparticles, and additionally 35 °C for the 100 nm nanoparticles. The thermostating system used in the variable temperature study was fabricated in-house as described elsewhere [21], and has been optimised to minimise the effects of natural convection. It is noted that natural convection can never be completely eliminated; however, its effects are lessened in interfacial experiments such as those studied in this work compared to techniques such as SECM where they can be prohibitive [24]. Here, the effects of natural convection are mitigated not only by the proximity of the nanoparticles to the boundary, but also to their significantly lower diffusion coefficients compared to molecular species.

3. Results and discussion

This work begins with the characterisation of the two sizes of nanoparticles by use of UV–Vis spectroscopy and TEM imaging. Next, artefacts of the electrochemical analysis are accounted for using chronoamperometry. Finally, cyclic voltammetry is employed as a function of temperature to explore the partial oxidation of the larger nanoparticles, and to confirm the complete oxidation of the smaller nanoparticles.

3.1. Nanoparticle characterisation

First, the stabilities of the 50 nm and 100 nm AgNPs suspensions were investigated by means of UV–Vis spectroscopy in varying electrolytes at both 25 °C and 50 °C. AgNPs are strongly plasmonic [25], exhibiting a strong peak in the visible region at ca. 400 nm, a wavelength that is dependent on NP size, shape, environment and NP potential [26]. Here, the magnitude of the peak of maximum absorbance will be used to assess their stabilities. Suspensions of 1.5 pM 100 nm AgNPs were prepared in deionised water, with 20 mM KCl or 20 mM KCl + 1.5 mM citrate. Fig. 1 a) presents the UV–Vis spectrum for the suspension in 20 mM KCl at 25 °C. The two peaks at ca. 495 nm and 410 nm reflect the dipolar and quadrupolar resonance modes observed for larger nanoparticles [27]. The inlay of Fig. 1 a) depicts the relative absorbance at 495 nm as a function of time and electrolyte. It can be seen that the 100 nm AgNPs are extremely stable over a 40 min period in deionised water (noting the 0.5 mM citrate present from the AgNP stock solution), with the absorbance only dropping 1% at 25 °C and 4% at 50 °C. As the ionic strength increases, the stability falls; the presence of 20 mM KCl causes a 45% and 61% decrease in peak absorbance at 25 °C and 50 °C respectively, whilst the presence of 20 mM KCl and an extra 1.5 mM citrate (total 2 mM citrate, including that present from the stock solution) leads to a decrease of 53% and 66%. The decrease in stability with increasing ionic strength can be rationalised on the basis of the DLVO theory of colloidal stability; aggregation is induced by the screening of the nanoparticle surface charge [28, 29]. Notably, the stark increase in the absorbance feature at wavelengths greater than ca. 700 nm over the 40 min is indicative of the agglomeration of the nanoparticles with time [30]. This nanoparticle agglomeration has previously been shown to be reversible [31]. To confirm this reversibility, the suspension of 100 nm AgNPs in 20 mM KCl and 1.5 mM citrate following the 40 min period was sonicated for 10 min. This returned the peak absorbance to within 20% of its initial value; this data is presented in the SI section S1. Moreover, agitating the suspensions by means of bubbling N_2 gas through them for 1 min was found to inhibit this agglomeration. The slightly lower stability of the 100 nm AgNPs at 50 °C