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The Electrochemical Detection and Characterization of Silver Nanoparticles in Aqueous Solution

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Nanoparticles (NPs) have become ubiquitous with an estimated 1600 commercial products available,[1] but they are inevitably released into the environment either by intention, manufacture, or disposal.[2] The commonest metal NPs are Ag (26 %), Ti, C, Si, Zn, and Au (all $<10\,\%$).[1] Of particular interest are AgNPs, which have powerful antibacterial properties, used in many commercial products ranging from clothing (ca. 50 % of AgNPs leach out per washing cycle[4]) to medical dressings. Their biocidal activity is due to the high affinity of Ag^+ for thiols, leading to disruption of enzyme function responsible for nutrient uptake and cellular energy production/storage processes.[5] AgNPs cause endocrine disruption in amphibians[6] and are toxic to many mammalian organs.[7] An estimated 65 t of AgNPs per year are released into global river systems alone.[8] To characterize the risk posed to ecosystems by increased exposure to AgNPs and their environmental fate, the development of detection techniques is urgently required.[9]

Here, we outline a new detection strategy, based on the Faradaic charge transfer when AgNPs strike an electrode. The direct detection of particle collisions at electrodes is a recent field[10–17] with early work concerned with the adhesion of colloidal particles on Hg.[10–12] Of most relevance are studies into the collisions of micron-sized droplets or particles at potentiostatted electrodes.[13–16] For electroinactive oil droplets and particles driven by ultrasound onto an electrode surface, non-Faradaic current transients of microsecond duration occur, the polarity of which inverts at the potential of zero charge of the electrode–electrolyte system.[14] The transients can also be used for measuring the particle size.[15] However, Faradaic charge transfer between an electrode and phenylenediamine-modified graphite powder was not observed during collisions under sonication.[16] Recently, Bard and co-workers have applied these concepts to observe electrochemical reactions on the surface of impacting NPs.[17,18]

Herein, we show for the first time that the direct electro-oxidation of AgNPs colliding with an electrode is both viable and quantitative, and can be used for characterization and NP identification.

Initial experiments on AgNP–electrode collisions were conducted by observing the hydrogen evolution reaction (HER) in citrate solution (see the Experimental Section). HER kinetics on bare glassy carbon (GC) are slow, with no significant currents before the onset of solvent breakdown in aqueous solutions (see the Supporting Information). Any spikes observed were due to the HER at the surface of AgNPs during contact with the electrode (compare the electrocatalytic amplification observed for PtNPs[18]).

First, cyclic voltammetry was performed by using a AgNP-modified GC electrode (diameter 3 mm) to observe the reduction potential for the HER (see the Supporting Information). Next, a 11 μm radius bare GC electrode was potentiostatted in the solution, and no current spikes were observed. The experiment was repeated with dispersed AgNPs, and reductive current spikes were observed in the current–time trace (see the Supporting Information). Repeat experiments at different potentials yielded current spikes which are analyzed in Figure 1. The charge passed during each spike (Q) varies with the potential for both NP size ranges: the onset potential of spikes is in excellent agreement with the formal potential of the HER on AgNPs (see the Supporting Information). The collision frequency was found to vary linearly with the number concentration of AgNPs up to 40 pM (see Figure 1 b) according to $3.9\times10^4\,s^{-1}\,cm^{-2}\,pM^{-1}$; this is in good agreement with the collision rates for PtNPs of 0.012–$0.02\,s^{-1}\,pM^{-1}$ (10 and 25 μm diameter electrodes) reported by Bard and co-workers.[18] Q was also found to increase linearly with the concentration of citrate (see Figure 1 c).

We next investigated the direct characterization of AgNPs through instantaneous oxidation during collisions [Eq. (1)].

$$\mathrm{Ag(nanoparticle)} - e^- \rightarrow \mathrm{Ag^+(aq)} \qquad (1)$$

First, a AgNP-modified GC electrode was scanned anodically in the citrate solution to observe the stripping voltammogram (see Figure 2 a). Next, the GC microelectrode was placed in the citrate solution and dispersed AgNPs (diameter 20–50 nm) were added. Under potentiostatted conditions (from 50–500 mV vs. Ag/AgCl), oxidative (Faradaic) current spikes were observed (see Figure 2 a), showing for the first time that direct oxidation of metal NPs during collision events is both observable and quantitative. The onset of these Faradaic spikes was found to vary with the potential (see Figure 2 b), and the collision frequency is in good agreement with the HER results above confirming that NP collisions are the source of the oxidative transients. Assuming that the NPs are spherical (radius r_{np}), the maximum charge passed as a result of complete oxidation of the AgNP is given by Equation (2),

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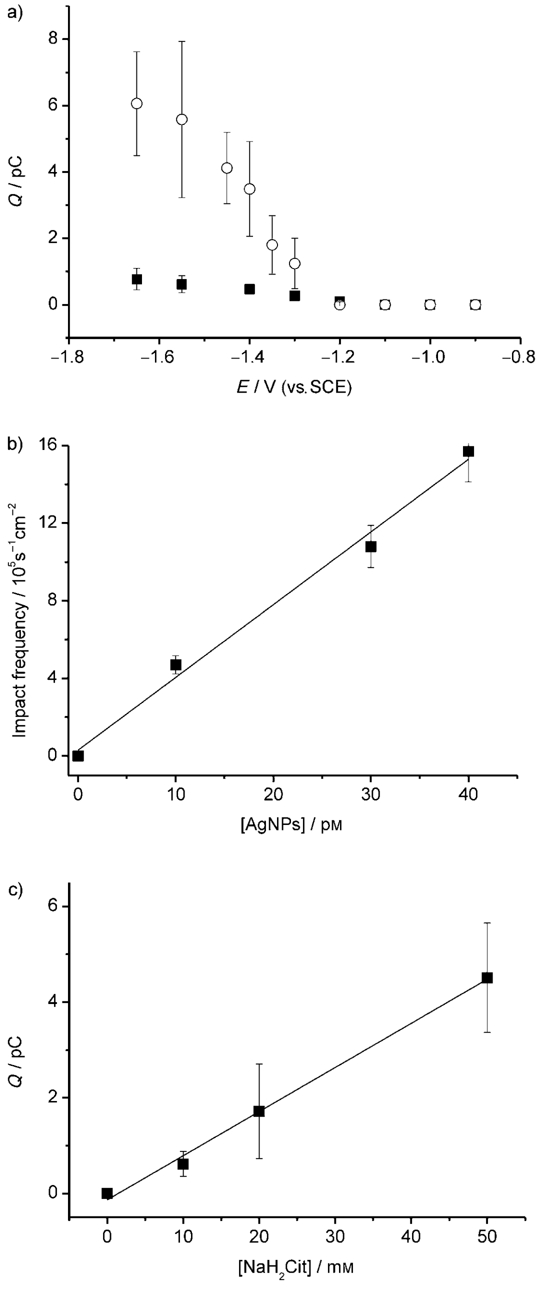

Figure 1. Plots of the variation of: a) the charge passed, Q, during each spike with a potential for 20–50 nm (■) and 80–120 nm (○) AgNPs; b) the frequency of spikes as a function of the number concentration of AgNPs, and c) Q as a function of citrate concentration.

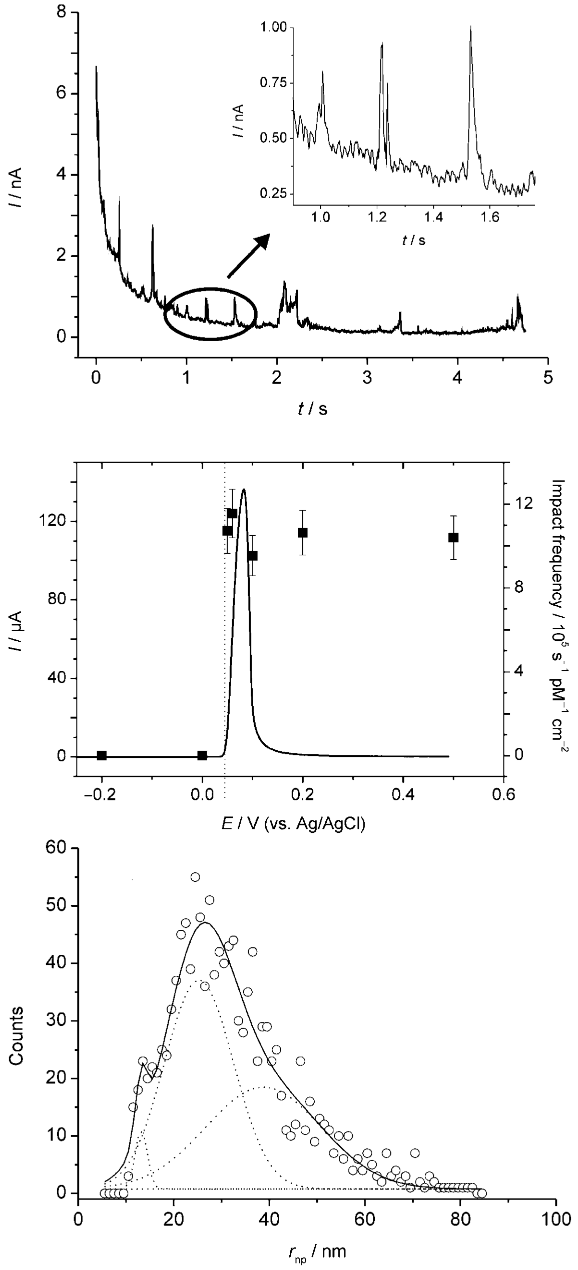

Figure 2. a) Chronoamperometric profiles showing oxidative Faradaic collisions of AgNPs in citrate solution. The inset shows detailed impact spikes. b) Overlay plot of a stripping voltammogram for a AgNP-modified GC electrode (left axis) and the impact frequency (right axis) showing the onset potential of the spikes; and c) distribution of NP radii inferred from Q by Equation (2) with deconvolution.

$$Q_{\max} = \frac{4F\pi\rho r_{\mathrm{np}}^3}{3A_{\mathrm{r}}} \qquad (2)$$

where ρ is the bulk density, and A_{r} is the relative atomic mass. Figure 2c shows the distribution of radii obtained from the analysis of over 1500 impacts, which can be deconvoluted into subdistributions of radii 13, 26, and 39 nm, corresponding to single NPs and agglomerates.

These results demonstrate that this method can be used as a means to identify AgNPs (by comparison of the onset potential of spikes and the known anodic stripping voltammetry of AgNPs) as well as simultaneously determining their size range by analysis of the charge passed per current spike. Research is already underway to extend this phenomenon to the quantitative characterization of other metal NPs as well as mixed NP systems for direct application in public health and environmental monitoring.

Experimental Section

AgNPs of diameter ranges from 20 to 50 nm and 80 to 120 nm were synthesized according to the literature.[19,20] Sodium dihydrogen citrate ($NaC_6O_7H_7$, Aldrich, > 99.5 %) and KCl (Riedel-de-Haan, > 99.5 %) were used as received. All solutions (10 mM $NaC_6O_7H_7$ and 90 mM KCl unless stated) were made by using ultrapure water of resistivity ≥ 18.2 MΩ cm (Millipore) and degassed thoroughly with N_2 (oxygen-free, BOC Gases plc), and an atmosphere of N_2 was maintained during the experiment. Experiments were conducted at (293 ± 2) K within a Faraday cage by using GC working electrodes (BASI), a Ag/AgCl, or a calomel reference electrode (Radiometer, Copenhagen), and a graphite rod counter electrode. An μAutolab III potentiostat (Metrohm-Autolab BV, Utrecht, Netherlands) was used. Impact spikes were analyzed by using the program Origin v.8.1 (www.OriginLab.com) for spike identification and integration, and Gaussian deconvolution of radius distribution. Electrical noise was removed by applying Fourier transform filtering (within Origin software) at 50 Hz and multiples up to 200 Hz. Spikes were automatically identified by the same software at a threshold of 15 % of the highest spike.

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