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Nanoparticle–electrode collision processes: The electroplating of bulk cadmium on impacting silver nanoparticles

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ABSTRACT

We report, for the first time, the bulk deposition (electroplating) of a metal onto nanoparticles during collisions with an inert electrode surface. Experiments show that for silver nanoparticles, multiple layers of Cd atoms can be electroplated onto the AgNPs from aqueous Cd^{2+} during collisions with a glassy carbon electrode held at a suitably reducing potential, and an average of 19 atomic layers of cadmium are found to be deposited in the few milliseconds that the NP is in contact with the electrode. For comparison, results are also presented for the underpotential deposition of Cd onto AgNPs under similar conditions.

1. Introduction

The electrochemical signatures of impacts between particles and wet electrode surfaces were first reported in 1995 [1–5]. Since then several studies have investigated the non-faradaic [6–13] and faradaic charge transfer transients [14–21] that can arise during such impacts. Faradaic processes have been identified relatively recently; Bard et al. have identified electrocatalytic processes occurring on the surface of NPs during collisions [14–17]. Very recently, the present authors have reported the exhaustive electro-oxidation of silver NPs (AgNPs) [18–20] during collisions enabling a sample of AgNPs to be sized and identified. Use of this anodic particle coulometry (APC) method has also enabled measurement of NP aggregation effects and sticking coefficients of AgNPs with wet electrode surfaces [19,20]. In addition, the underpotential deposition (UPD) of thallium onto AgNPs has been observed [21].

In this communication, we extend our metal deposition investigations to report the first confirmed bulk deposition of multilayers of metal atoms onto a metal NP during NP–electrode impacts, by electroplating cadmium onto AgNPs. Comparison is made with UPD of Cd on the same AgNPs. The deposition has synthetic application in the facile formation of metal NPs with different core and shell metallic compositions.

2. Experimental section

AgNPs were synthesised according to the method of Pyatenko et al. [22–24] and characterised via SEM imaging to have a mean radius of 45 ± 3 nm. AgNPs were dispersed by ultrasound prior to adding to the solution. An aliquot of AgNPs was determined to give a particle density of 9×10^{12} particles dm^{-3} in the volume of electrolyte used in the reaction cell. Cadmium chloride and sodium chloride (Aldrich, >99%) were used as received. Deposition solutions were made of 1 mM $CdCl_2$ and 0.10 NaCl, using ultrapure water of resistivity $\geqslant 18.2$ MΩ cm (Millipore) and degassed thoroughly with N_2 (oxygen free, BOC Gases plc) and an atmosphere of N_2 maintained during the experiment. Experiments were conducted within a faraday cage using a μAutolab III potentiostat with a time resolution shorter than 0.1 ms (Metrohm-Autolab BV, Utrecht, Netherlands) and three-electrode arrangement: a 11 μm radius glassy carbon (GC) working electrode (BASi Inc.), a graphite counter electrode, and a Ag/AgCl reference electrode (Radiometer, Copenhagen). Impact spikes were analysed using Origin v.8.1 (www.OriginLab.com) for spike identification and integration, and electrical noise reduction [18].

3. Results and discussion

First, the voltammetry of cadmium was recorded at a scan rate of 50 mV s^{-1} on a bare glassy carbon (GC) electrode (diameter of 3 mm) and the same GC electrode covered with immobilised AgNPs [25–28] immersed in a 1 mM solution of $CdCl_2$ (aq) and 0.10 M NaCl, as shown in Figure 1. On bare GC a single cathodic deposition peak was observed at −0.82 V (vs Ag/AgCl), whereas on the AgNP-modified GC electrode the same peak was observed at −0.75 V, along with a cathodic UPD feature at −0.46 V in good agreement with the literature [29] We note that the significant reductive features reported for the desorption and discharge of chloride ions on Ag(1 1 1) [30] are not apparent under our experimental conditions and do not present interference with the UPD peak.

Second, a GC microelectrode (radius 11 μm) was placed in a degassed solution of 1 mM $CdCl_2$ and 0.1 M KCl and the potential held

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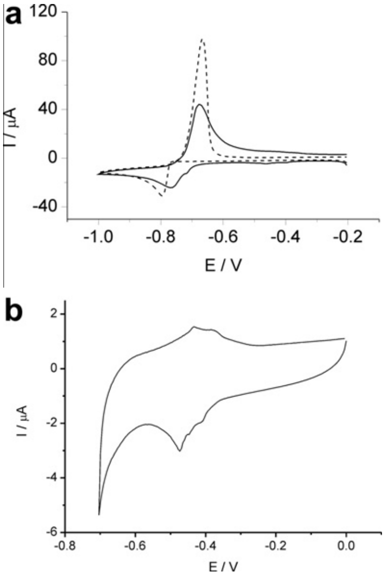

Figure 1. Cadmium deposition on deposition on bare GC (- - -) and AgNP-modified GC (—) electrodes: (a) full voltammograms, and (b) underpotential deposition region. Experimental details are given in the text.

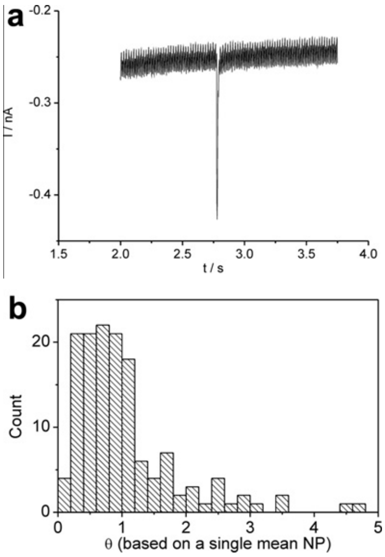

Figure 2. (a) A typical impact transient at −0.55 V, and (b) a histogram showing the number of impacts in terms of layer coverage of an average AgNP, see text for comments on the effect of aggregation.

at −0.55 V (the potential where underpotential deposition is found to occur). An aliquot of dispersed AgNPs were then added to the solution which was then agitated by bubbling with N_2. Impact transients were recorded as shown in Figure 2. The impact transients were observed as sharp, reductive spikes of duration 1–10 ms and peak heights of several nA, similar to those reported previously for NP impact events [18–21]. Over one hundred impact spikes were recorded and analysed according to a previously published procedure [18]. The frequency of collisions is consistent with previous measurements of ca. 1.8 collisions s^{-1} at this size electrode with the same concentration of NPs (9×10^{12} particles dm^{-3}). No spikes were found to occur when the electrode was potentiostatted at potentials more positive than the UPD feature (e.g. at −0.30 V), confirming that the reductive transients were due to the deposition cadmium on the AgNPs during the collisions with the GC electrode surface:

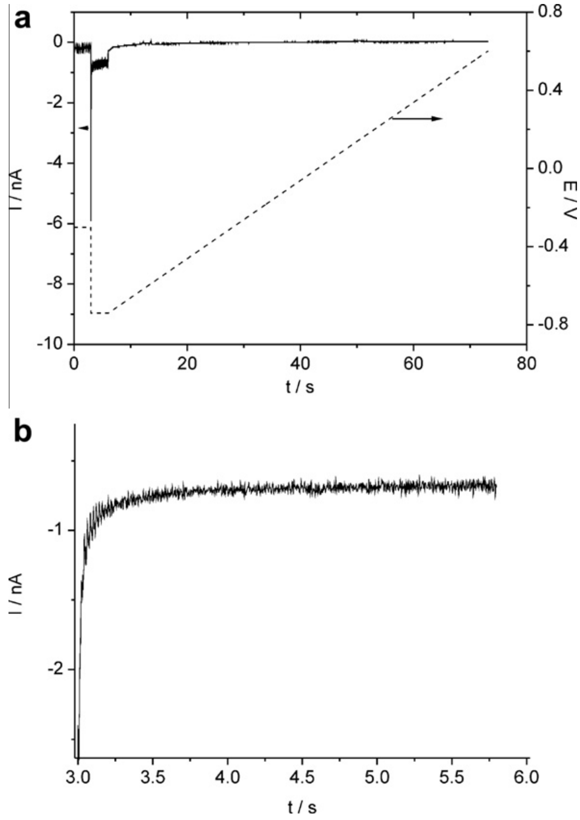

Figure 3. (a) Potential step-sweep experiment of GC electrode (r = 11 μm) in 1 mM $CdCl_2$ in 0.10 M NaCl. Potential held at −0.74 V (vs Ag/AgCl) and scanned positive at 20 mV s^{-1}. (b) Shows an enlargement of the 'transient' region after noise reduction to confirm no spikes.

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(np)$$

Analysis of the spikes according to a previously described method [21], enables the charge passed per impact spike to be converted into an approximate coverage of an average single nanoparticle, since the charge passed per impact transient, Q, is related to the number of electrons passed, N, via the electronic charge according to

$$Q = eN \tag{1}$$

and a surface area (S) can be calculated for a single, fcc geometry AgNP with knowledge of the Ag atomic radius, r_A.

$$S = 24 r_A^2 N^{2/3} \tag{2}$$

This therefore allows monolayer coverage of Cd atoms (θ = 1) to be calculated to be 9.1×10^5 atoms for a mean AgNP. Figure 2 shows that in the case of Cd UPD, the agreement of the experimental data to approximately monolayer coverage is very good: at these ionic strengths, agglomeration of AgNPs is rapid to the point where after 20 min less than 20% of the AgNP species present are in the form of single dispersed NPs, the remainder being larger cluster species [19]. The most common clusters observed in Ref. [19] were of 4 and 8 NPs, which have surface areas of 3 and 4 times greater than the single NP used as the basis for the scale in Figure 2.

Next, the bulk deposition of cadmium onto AgNPs was investigated by first verifying the deposition of Cd onto bare GC. The GC microelectrode was placed in a degassed solution of 1 mM $CdCl_2$