Electronic Supplementary Information

The Fate of Nano-Silver in Aqueous Media

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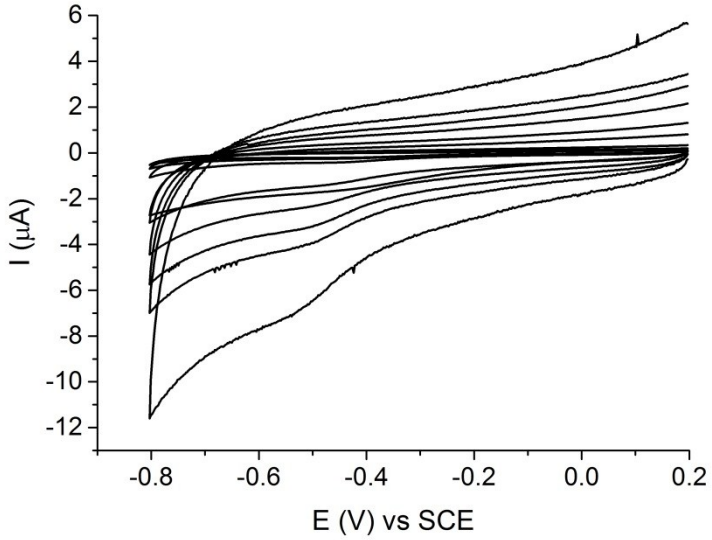

Figure S1. Cyclic voltammetry of 0.1 M HNO_3 recorded using a glassy carbon electrode with variable scan rates (5-800 mV s^{-1}).

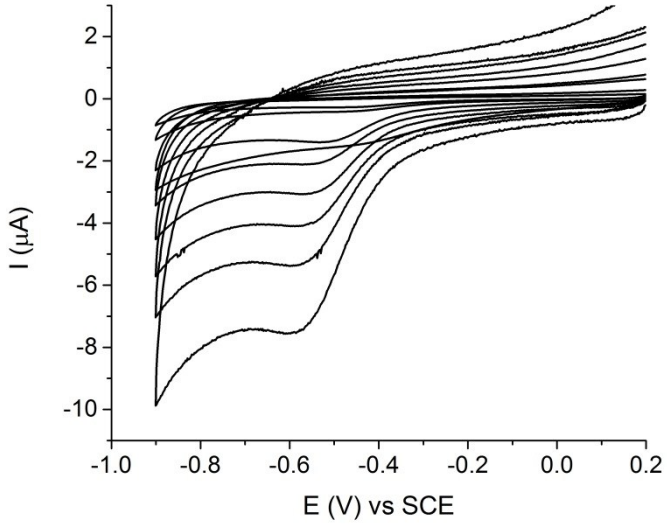

Figure S2. Cyclic voltammetry of 0.1 M HCl recorded using a glassy carbon electrode with variable scan rates (10-800 mV s^{-1}).

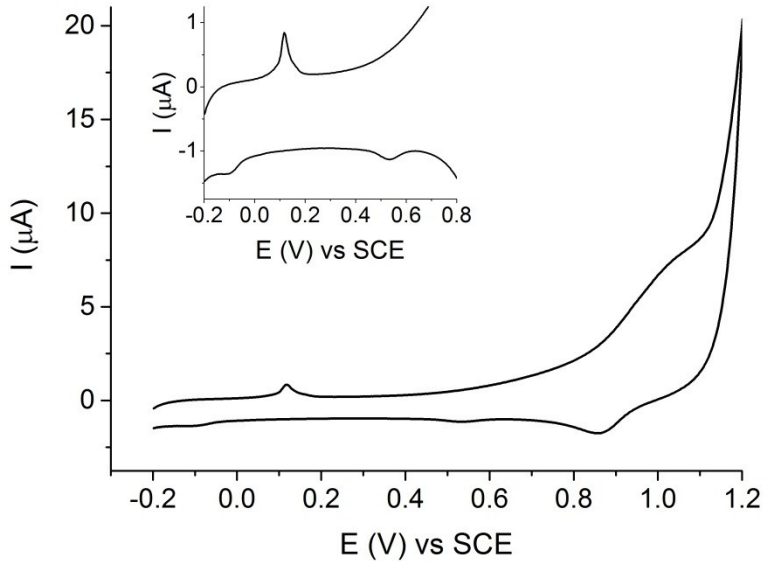

Figure S3. Cyclic voltammetry in 20 mM NaCl of 2 µL of drop cast gold-core silver-shell nanoparticles, recorded at a scan rate of 50 mV s^{-1}.

Determination of O_2 Concentrations

The concentration of O_2 was measured in solutions which had been thoroughly bubbled with N_2. This was performed using cyclic voltammetry with a range of scan rates (5-800 mV s^{-1}) in 0.1 M HNO_3 (Figure S1) and 0.1 M HCl (Figure S2). From this data a line of best fit was obtained for the plot of the peak current versus the square root of the scan rate, and using the irreversible Randles-Ševčik equation:[1]

$$Ip = (2.99 \times 10^5) n(n' + \alpha)^{1/2} v^{1/2} AcD^{1/2}$$

where *Ip* is the peak current (A), *n* is the number of electrons transferred (2), *n'* is the number of electrons transferred prior to the rate determining step (0), *α* is the transfer coefficient (determined from the Tafel slopes to be 0.233 in 0.1 M HNO_3 and 0.226 in 0.1 M HCl), *v* is the scan rate (V s^{-1}), *A* is the area of the electrode (cm^2), *c* is the concentration of O_2 (moles cm^{-3}) and *D* is the diffusion coefficient (1.9 x 10^{-5} cm^2 s^{-1}).[2]

Additional Experimental Details

All solutions were made using Milli-Q water (resistivity of 18.2 MΩ cm at 25 °C), and degassed by bubbling with N_2 for at least 45 min. Chemicals (Analytical Reagent grade) were used as received from Fisher Chemicals (HNO_3, HCl, $NaNO_3$) and BDH (NaCl). A cetyl trimethylammonium bromide (CTAB) capped gold-core (35 nm diameter) silver-shell (thickness of 7.5 nm) nanoparticle suspension (with a free CTAB concentration of ca. 3-5 mM) was purchased from Nanopartz and used as received.

Working electrodes for nano-impact experiments were carbon fibre microcylinder electrodes. These were fabricated by the attachment of a carbon fibre (7 μm diameter, Goodfellow) to a wire using a conductive epoxy (RS) and heating for 15 minutes at 90 °C. This was then sealed within a pipette tip using a cyanoacrylate glue (Permabond 102 Instant Adhesive), and after allowing it to set the carbon fibres were cut to a length of ca. 1 mm. All electrochemical experiments were performed within seconds (ca. 5-10 s) of immersing the electrode into the solutions. The statistical analysis of the cyclic voltammetry results (Table 1) shows the mean and the standard deviation of the mean based on at least five repeated experiments.

Transmission electron microscopy (TEM) was performed using a JEOL JEM-3000F field emission gun (FEG) TEM equipped with an Oxford Instruments energy dispersive X-ray (EDX) spectrometer. Scanning transmission electron microscopy was obtained using a high angle annular dark field detector (HAADF-STEM). Sample preparation was performed by drop casting 2 μL of the core-shell nanoparticle suspension on holey carbon TEM grids (Agar Scientific).

References

1. R. Nissim and R. G. Compton, *ChemElectroChem*, 2014, **1**, 763-771.
2. K. Sundberg, W. Smyrl, L. Atanasoska and R. Atanasoski, *Journal of The Electrochemical Society*, 1989, **136**, 434-439.