Supporting Information:

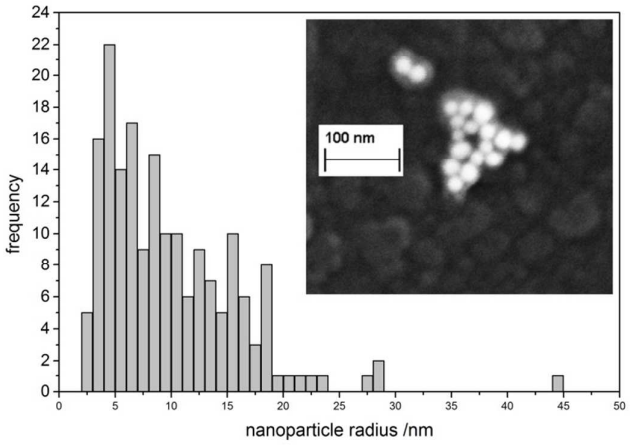
A Critical Evaluation of the Interpretation of Electrocatalytic Nano-Impacts

*Loretta S.Y. Ly, Christopher Batchelor-McAuley, Kristina Tschulik, Enno Kätelhön and Richard G. Compton**

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom

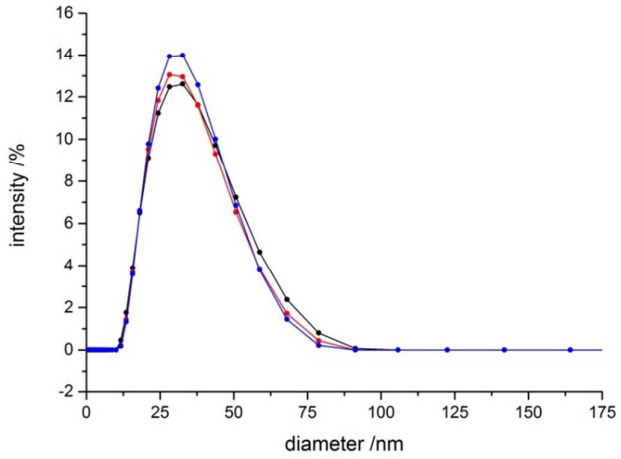
Section 1: Nanoparticle characterisation

This section provides the characterisation data for the Mintek (Randburg, South Africa) supplied citrate capped gold nanoparticles. SI Figure 1 depicts a representative SEM image recorded on a LEO Gemini II 1530 (Zeiss, Oberkochen, Germany). The SEM images were analysed using image-J (National Institutes of Health). 181 particles were analysed and the resulting size distribution is also shown in the figure. The mean radius was determined to be 9.6±6 nm and this value was for the radius was used throughout the main text.



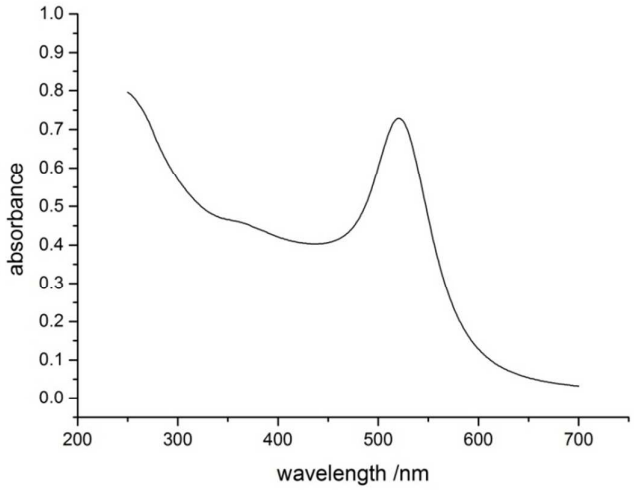
SI Figure 1: SEM image and particle size distribution for the gold nanoparticles showing them to be 9.6±6nm in radius

SI Figure 2 depicts the results of a *dynamic light scattering* (DLS) measurement recorded on a Zetasizer Nano ZS (Malvern, UK). The modal radius was determined to be 14.2 nm. This value is slightly larger than that attained from the SEM image analysis, however DLS measures the the hydrodynamic radius associated with the nanoparticles and is also volume weighted.[1]



SI Figure 2: DLS data recorded for the nanoparticles showing the modal size to be 28.43 nm in diameter

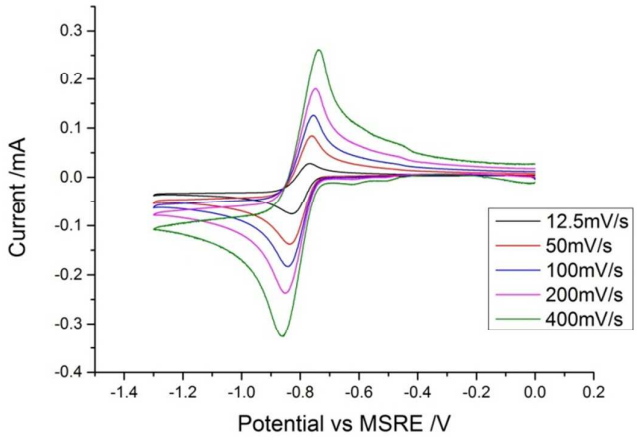
SI Figure 3 shows representative UV-Vis spectrum recorded on a Hitachi-2001 (Tokyo, Japan) for a 500 pM solution of the citrate capped gold nanoparticles. The characteristic plasmon peak is observed at 520 nm and in accordance with the literature this evidences the particles to be <15 nm in radius (note below this threshold the UV-Vis spectrum is relatively insensitive to the particle size).[2]



SI Figure 3: UV-Vis spectrum of the gold nanoparticles (concentration = 500 pM), showing the characteristic plasmon peak at 520 nm.

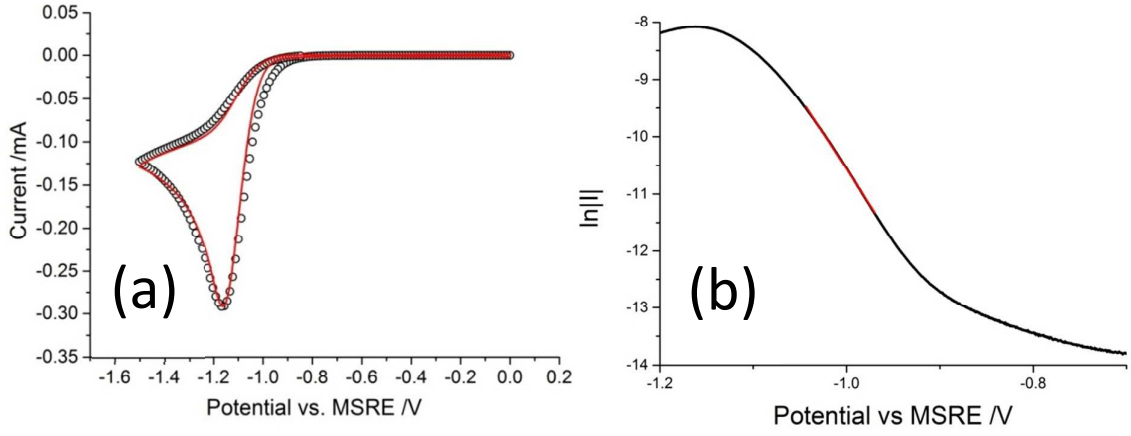
Section 2: The kinetics of proton reduction on macro and micro gold

This section serves to characterises the kinetics and thermodynamics of proton reduction (HER) in 0.6 M $NaClO_4$ and 10 mM $HClO_4$. Initially the voltammetric response of platinum macroelectrode was studied at a range of scan rates (12.5-400 mV s^{-1}). A quasi-reversible wave was observed corresponding to proton reduction on the forward scan and hydrogen oxidation on the reverse. The mid-point potential was determined to be -0.799 V (vs MSRE). This value for the mid-point potential was taken to accurately reflect the formal potential for the redox couple in this experimental setup.



SI Figure 4: The voltammetric response of a platinum macroelectrode (r_0 = 0.85 mm) at variable scan rates in a solution containing 0.6 M $NaClO_4$ and 10 mM $HClO_4$.

Having ascertained the thermodynamics for the redox process the kinetics of the proton reduction were studied at a gold macro-electrode (r_0 = 1 mm) as shown in SI figure 5. From Tafel analysis the transfer coefficient was determined to be 0.63±0.03. Simulation of the voltammetric response allowed the standard electrochemical rate constant to be measured as $7.1\pm0.3x10^{-8}$ m s^{-1}.



SI Figure 5: a) The voltammetric response of a gold macroelectrode (r_0 = 1 mm) in a solution containing 0.6 M $NaClO_4$ and 10 mM $HClO_4$ (red line), also depicted is the DigiSim® simulated voltammetric response (black circles). B) shows the experimental tafel plot for the proton reduction on the macroelectrode, where the transfer coefficient (α) has been determined to be 0.63±0.03.

Finally for this section of the SI the electrochemical proton reduction process was recorded at a gold microelectrode. Si Figure 6 depicts the corresponding voltammogram and Tafel plot and simulated response.

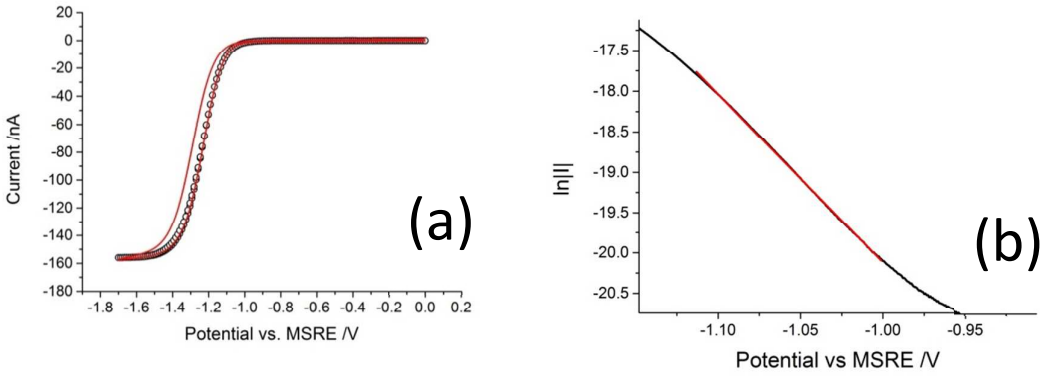


Figure 6: a) The voltammetric response of a gold microelectrode (r0 = 4.6 μm) in a solution containing 0.6 M NaClO4 and 10 mM HClO4 (red line), also depicted simulated voltammetric response using an in house developed program (black circles). B) shows the experimental Tafel plot for the proton reduction process, where the transfer coefficient (α) has been determined as 0.5±0.03.

Section 3: Tafel plot for proton reduction on the AuNP modified carbon macroelectrode

SI Figure 7 depicts the Tafel plot for proton reduction on AuNP-modified carbon electrode. Tafel analysis gave a transfer coefficient of 0.47±0.02 and simulation of the voltammetric response (see main text) gave a standard electrochemical rate constant of 6.6±2.1 $x10^{-8}$m s^{-1}.

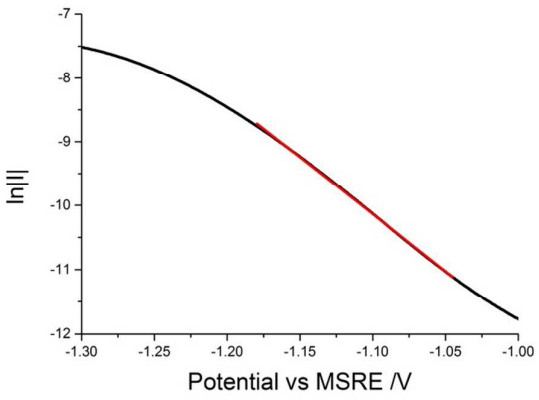


Figure 7 Tafel plot for proton reduction on AuNP modified carbon macroelectrode (r0 = 1.5mm), where the transfer coefficient (α) has been determined to be 0.47±0.02.

Section 4: The variation of the pulse height as a function of the solution phase proton concentration

This section seeks to confirm that current pulses are due to single AuNP impacts by varying concentration of protons. When the concentration of perchloric acid was changed, the average pulse height changed proportionally, confirming that observed current pulses corresponded to the catalytic reduction of protons.

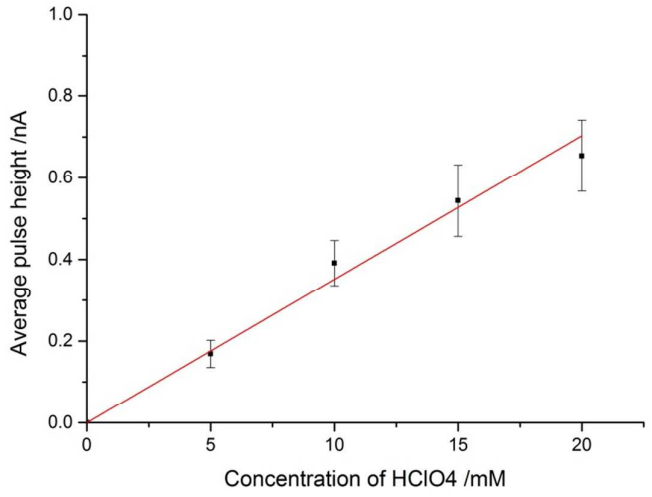


Figure 8 Plot of average pulse height versus HClO4 concentration, where the error bars represent the uncertainty in the mean. Line of best fit shown in red.

Section 5: Impact experiments at high concentrations of AuNPs

Finally, impact experiments were done using 60pM of AuNPs. As discussed in the main body of the text, a higher background signal was observed, which is indicative of multiple nanoparticles residing at the electrode surface. The observed current pulses are of a comparable magnitude to values that are consistent with a fully diffusional response, which provides good agreement with previous work.

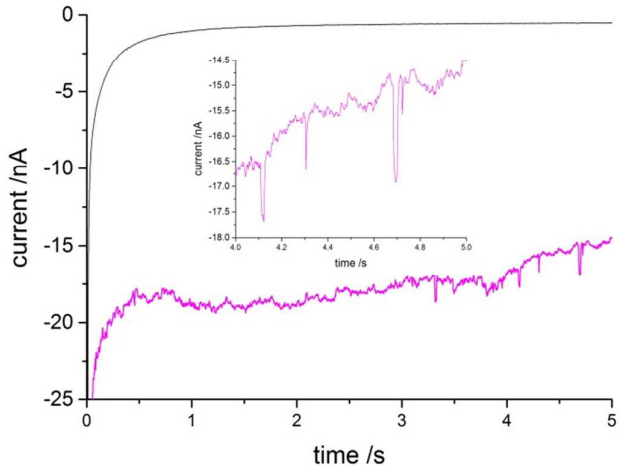


Figure 9 Current transient recorded before (black) and after (pink) a 0.6M $NaClO_4$ and 10mM $HClO_4$ solution was injected with 60pM AuNP. The carbon microelectrode (r0 = 4.6 μm) was held at a potential of -1.9V (vs MSRE).

REFERENCES

(1) Hackley, V. A.; Clogston, J. D. Measuring the Hydrodynamic Size of Nanoparticles in Aqueous Media Using Batch-Mode Dynamic Light Scattering. *Methods Mol. Biol. (N. Y., NY, U. S.)* **2011**, *697*, 35-52.

(2) Martinez, J. C.; Chequer, N. A.; Gonzalez, J. L.; Cordova, T. Alternative Metodology for Gold Nanoparticles Diameter Characterization Using Pca Technique and Uv-Vis Spectrophotometry. *Nanosci. Nanotechnol. (Rosemead, CA, U. S.)* **2012**, *2*, 184-189.