

## Supporting Information

### Electrocatalytic Hydrogen Redox Chemistry on Gold Nanoparticles

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#### SI 1: Gold nanoparticles

##### Materials

All chemicals and solvents were of highest available purity standard and were used as received. Hydrogen tetrachloroaurate trihydrate and sodium borohydride were purchased from Aldrich (UK), tetraoctylammonium bromide from Fluka (CH), sodium citrate from Mallinckrodt (USA) and 1-mercapto-undecane-11-tetra(ethyleneglycol) from Prochimia (Poland).

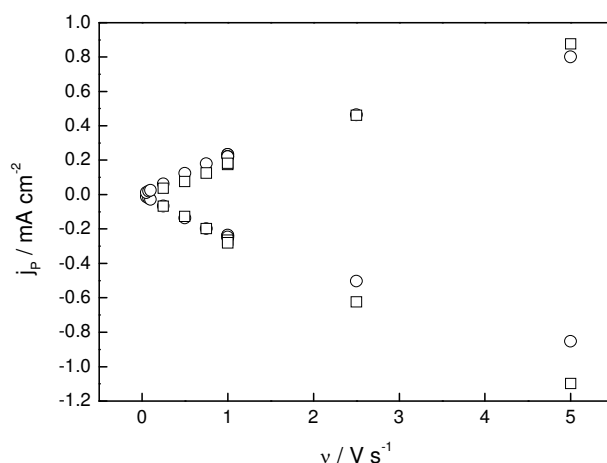
##### Preparation of 2-3 nm gold nanoparticles.

Monolayer protected clusters in the 2-3 nm range were prepared by a modification of a well-established literature method.<sup>S1</sup> Briefly, hydrogen tetrachloroaurate trihydrate ( $\text{HAuCl}_4 \times 3 \text{H}_2\text{O}$ , 50mg, 0.12mMol) was first dissolved in 30 ml deionised water and then quantitatively extracted as tetraoctylammonium tetrabromoaurate into 70ml toluene in a vigorously stirred two-phase liquid/liquid system after addition of solid tetraoctylammonium bromide (500mg, 0.9mMol), which rapidly dissolves. After extraction, the deeply orange organic phase was separated from the colourless aqueous phase, dried with anhydrous magnesium sulphate and filtered. The same protocol was repeated, but, instead of hydrogen tetrachloroaurate, sodium borohydride (50mg, 1.3mMol) was extracted from the aqueous to the organic phase for about 10 minutes under vigorous stirring to yield a concentration of borohydride in the organic phase that is sufficient to quantitatively reduce the gold in the other organic phase prepared before. Once the two dried organic solutions were ready, 1-mercapto-undecane-11-tetra(ethyleneglycol) (13mg, 33 $\mu$ Mol) dissolved in 1ml of methanol was added under stirring to the gold precursor solution, followed by rapid addition of the organic borohydride solution also under stirring. An immediate reaction took place leading to the formation of a deep, reddish brown dispersion, typical of nanoparticles in the desired size range. The particles precipitated quantitatively within a few hours and formed a greasy film at the bottom of the beaker, which was washed copiously first with toluene and then with pentane to yield a dry odourless product that readily dispersed in water, acetone and short chain alcohols. The size of the particles has previously been established by TEM<sup>S1</sup> and is routinely confirmed by the near absence of the characteristic plasmon band that emerges in the UV-vis spectrum when the particle size reaches around 3 nm.

### Preparation of 14-16 nm gold nanoparticles.

Citrate stabilised gold nanoparticles of a narrow size distribution centred at 15 nm diameter were prepared by an established in-house variant of the Turkevich-Frens method.<sup>S2</sup> Briefly, hydrogentetrachloroaurate trihydrate (HAuCl<sub>4</sub> x 3 H<sub>2</sub>O, 86mg, 0.2mMol) was dissolved in 140ml deionised water and brought to reflux. Trisodium citrate dihydrate (0.2565g, 0.9mM) was dissolved in 20 ml deionised water, brought to boil on a hot plate and quickly added to the refluxing solution of tetrachloroaurate under rapid magnetic stirring (caution! danger of scalding). The mixture turned colourless immediately, then deep blue for less than a second, and finally ruby red. It was refluxed for 30 min and then allowed to cool to room temperature. 1-mercapto-undecane-11-tetra(ethyleneglycol) (6.6mg, 17µMol) was dissolved in 1ml methanol, added to 40 ml of the as prepared sol of citrate stabilised gold nanoparticles in a plastic vial with screw top, and shaken vigorously. The mixture was left overnight to reach maximal surface coverage by the protecting ligand, and excess ligand was removed by repeated precipitation and re-dispersion of the gold by ultracentrifugation, once with methanol and three times with water. The size of these particles has previously been established by TEM and analytical centrifugation<sup>S2c</sup> and is routinely checked by UV-vis spectroscopy applying the method of Haiss *et al.*<sup>S3</sup>

**SI 2:** Lineal dependence of anodic and cathodic peak currents on potential sweep rate for gold particles of 1 to 3 nm (squares) and 14 to 16 nm (circles) indicating in both cases that the electroactive species is adsorbed on the electrode surface. Gold content 0.1 g/L.

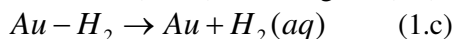


**SI 3:** Mechanistic analysis and simulation. For a reversible reaction of adsorbed species the peak current density ( $j_p$ ) is related to the charge transferred,  $Q$ , by the following equation<sup>S4</sup>:

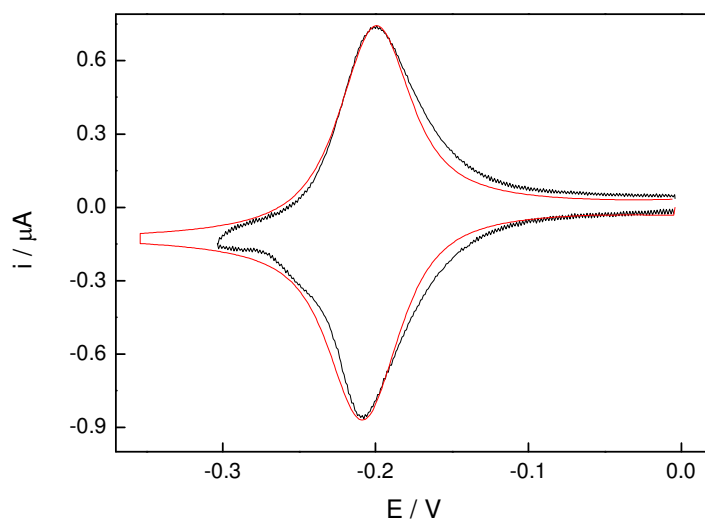
$$\frac{j_p}{Qv} = \frac{F}{4RT} = n \cdot 9.73 V^{-1} \quad \text{at } 25^\circ\text{C}$$

where  $n$  is the number of electrons involved in the process. The half peak width,  $\Delta E_{p/2}$ , is expected to be  $90.6/n$  mV. Analyzing the anodic peak at low  $v$ , values of  $j_p/Qv$  and  $\Delta E_{p/2}$  close to  $16.3 V^{-1}$  and 56 mV are obtained, respectively. This indicates that two electrons are involved in the electrochemical reaction.

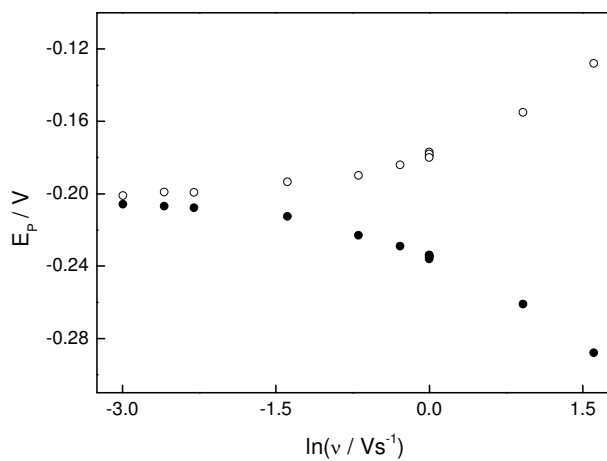
Although here only the reduced species is adsorbed, the same results for  $j_p/Qv$  and  $\Delta E_{p/2}$  are obtained by numerical simulation. The following figure shows the cyclic voltammogram experimentally obtained for  $v = 0.1 V s^{-1}$  (red) together with the simulated one under reversible conditions (black) assuming the (1.a), (1.b) sequence, i.e. the two electron process followed by:



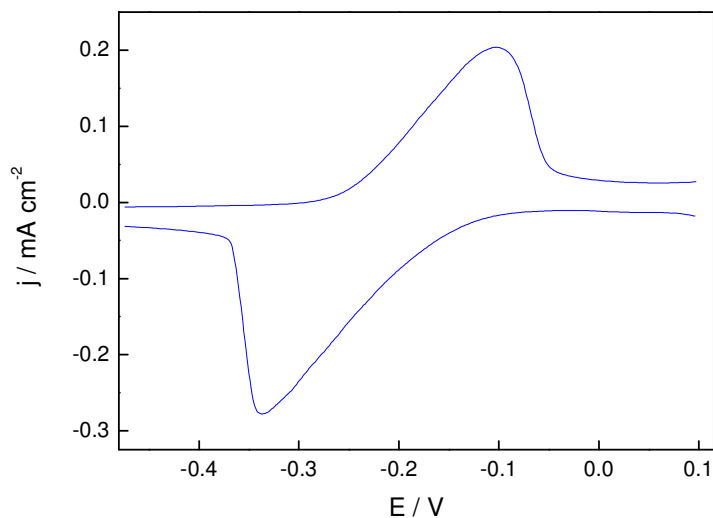
The simulation of the one electron process also yields the correspondingly expected results for  $j_p/Qv$  and  $\Delta E_{p/2}$ .



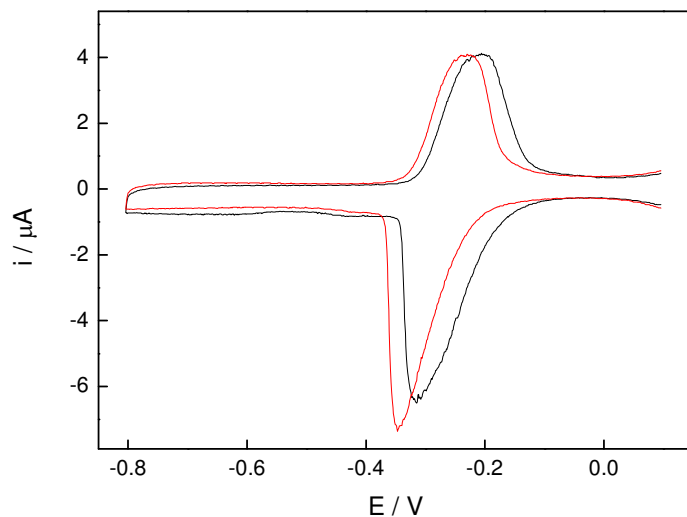
**SI 4:** Dependence of peak potentials on the log of the sweep rate for gold particles of 14 to 16 nm. The separation between anodic and cathodic peak potentials,  $\Delta E_p$ , increases with increasing  $v$ . At low sweep rates,  $\Delta E_p$  approaches zero and the voltammetric peaks are nearly symmetric. This is characteristic of an electrochemically reversible reaction of adsorbed species. All potentials were measured against a Ag|AgCl 3.5M reference electrode. Gold content 0.1 g/L.



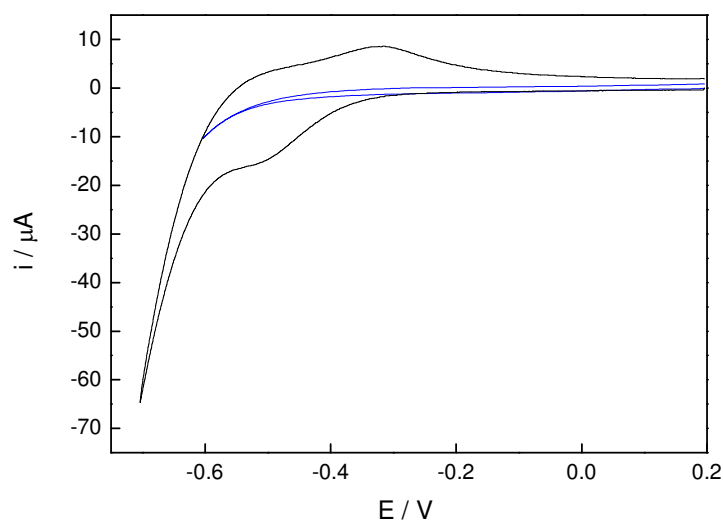
**SI 5:** Cyclic voltammogram obtained with pre-adsorbed multilayer of 1 to 3 nm gold particles at pH 4.5. Gold content of dispersion for multilayer adsorption was 1g/L. Note increased peak separation and distortion of peak shape in comparison to monolayer coverage. All potentials were measured against a Ag|AgCl 3.5M reference electrode.



**SI 6:** Two successive cyclic voltammograms (first black, then red) obtained with pre-adsorbed multilayer of 14 to 16 nm gold particles after changing the buffer from pH 4.5 to 5.9. The black curve was obtained approximately 30 s after change of buffer, while the red one, obtained five minutes later, represents the final profile. This result indicates slow equilibration of pH between the electrode surface and the bulks solution due to the presence of a dense nanometric network surrounding the electroactive area. All potentials were measured against a Ag|AgCl 3.5M reference electrode. Gold content 0.1 g/L.



**SI 7:** Cyclic voltammograms of clean gold electrode (black) and gold electrode that has been modified with five successively attached layers of citrate-stabilized 14 to 16 nm gold particles (blue) in acetic-acetate buffer of pH 4.5. (All potentials were measured against a Ag|AgCl 3.5M reference electrode)



## References

**S1 (a)** Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D.J.; Whyman, R. *J. Chem. Soc. Chem. Commun.* **1994**, 7, 801-802. **(b)** Kanaras, A.G.; Kamounah, F.S.; Schaumburg, K.; Kiely, C.J.; Brust, M. *Chem. Comm.* **2002**, 20, 2294-2295.

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**S3** Haiss, W.; Thanh, N.T.K.; Aveyard, J.; Fernig, D.G. *Anal Chem.* **2007**, 79, 4215-4221.

**S4** A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, second ed., Wiley, New York, 2001