Supporting Information

Hydrogen Peroxide Reduction on Single Platinum Nanoparticles

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Section 1: Cyclic voltammograms of oxygen reduction and hydrogen peroxide reduction on a gold electrode

Figure S1 presents the voltammetric response of a gold microelectrode in alkaline solution (20 mM KOH) saturated with oxygen (1.24 mM).[1] An oxygen reduction reaction signal is observed at potentials negative of ca. -0.25 V vs Ag/AgCl, corresponding to the formation of hydrogen peroxide. The dash line indicates a half-wave potential of -0.147 V vs Ag/AgCl for the oxygen/peroxide redox couple, which is close to the formal potential (-0.137 V vs Ag/AgCl; calculation described in detail below) at pH 12.3. The gold microelectrode was also immersed into an alkaline solution (20 mM KOH) containing 1.25 mM hydrogen peroxide (red line) and without hydrogen peroxide (blue line) saturated nitrogen. As can be seen in Figure S1 (red curve), hydrogen peroxide oxidation signal can be observed at potentials higher than ca. 0.1 V, while no significant peroxide reduction occurs on the gold electrode surface over the voltammetric range of study. The difference in current responses between the solution containing hydrogen peroxide (red line) and without hydrogen peroxide (blue line) at the potentials lower than -0.2 V is ca. 1 nA. Hence the concentration of the hydrogen peroxide will be altered by no more than 10% due to direct reduction at the gold electrode surface.
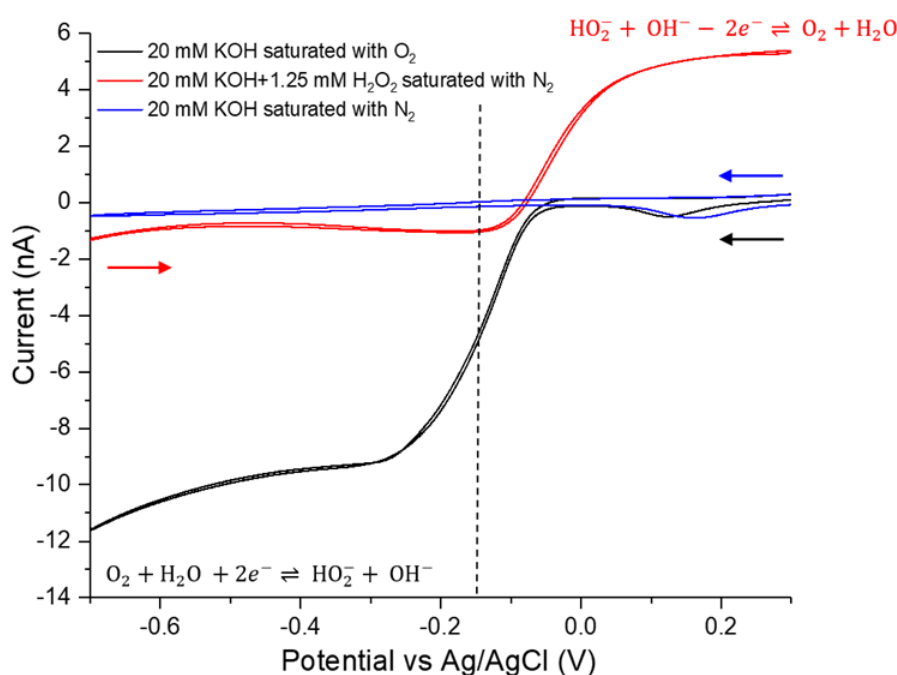

Figure S1: Cyclic voltammograms for oxygen reduction (black) and hydrogen peroxide oxidation (red) on a gold microelctrode. (CE: graphite, scan rate: 100 mV/s)

Calculation of formal potential for the oxygen/hydrogen peroxide redox couple

Under alkali conditions (unit activity of hydroxide) the standard potential ($E_B^{\ominus}$) for the oxygen/hydrogen peroxide redox couple is -0.0649 V (vs SHE).[2]

$$O_2 + H_2O + 2e^- \rightleftharpoons OH^- + HO_2^-$$
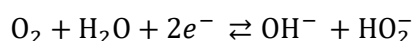
Hence the corresponding Nernst equation for the electrode potential (E) for this reaction is:

$$E = E^{\ominus} - \frac{RT}{2F} ln \frac{a_{^-OH} a_{HO_2^-} p^{\ominus}}{p_{O_2}}$$

where $a_{^-OH}$ and $a_{HO_2^-}$ are the activities of the hydroxide and peroxide anions respectively. $p^{\ominus}$ is the standard pressure (1 bar) and p_{O_2} is the oxygen partial pressure. First, as water is an almost pure liquid its activity is by definition unity. Second, the pK_a at 25 °C for hydrogen peroxide is 11.7,[2] consequently under alkaline conditions the peroxide is deprotonated and present in the anion form. However, in this work the solution phase pH is 12.3. Hence when considering the thermodynamics of this reaction we need to not only account for the decreased hydroxide concertation but we also need to account for the fact that the peroxide will be partially protonated at pH 12.3. Below pH 11.7 the oxygen/peroxide redox couple will shift with ~59.1 mV pH^{-1}, whereas above this threshold the equilibrium potential will only shift with ~29.5 mV pH^{-1}. This variation in the electrode potential with the systems pH will be returned to below.

The formal potential for a redox couple is defined as the potential under standard concentrations. Consequently, the above Nernst equation needs to be expressed on a concentration basis (and not activity and partial pressure). The aqueous oxygen concentration, C_{O_2}(mol dm^{-3}) is well described by Henry's law:

$$p_{O_2} = K_{O_2} C_{O_2}$$

where for oxygen Henry's Constant K_{O_2} has a value of 783.3 bar dm^3 mol^{-1} at 25 °C.[3] Furthermore, if we express the activity of the anions in terms of their activity coefficients:

$$a_i = \gamma_{\pm} \frac{C_i}{C^{\ominus}}$$

where $C^{\ominus}$ is the standard concentration (1 mol dm^{-3}), then the Nernst equation for the reaction can be written as:

$$E = E^{\ominus} - \frac{RT}{2F} ln \frac{\gamma_{^-OH} \gamma_{HO_2^-} p^{\ominus}}{K_{O_2} C^{\ominus}} - \frac{RT}{2F} ln \frac{C_{^-OH} C_{HO_2^-}}{C_{O_2} C^{\ominus}}$$

As a simplification we will assume that the activity coefficients are unity, hence:

$$E_f^{\ominus} = E^{\ominus} - \frac{RT}{2F} ln \frac{\gamma_{^-OH} \gamma_{HO_2^-} p^{\ominus}}{K_{O_2} C^{\ominus}}$$

$$E_f^{\ominus} = -0.0649 + 0.0855 = +0.0207 \, V \, vs \, SHE$$

The above formal potential is essentially correct at 1 M hydroxide if $\gamma_{^-OH}$ = 1, however the experiment is performed in the presence of 20 mM KOH and hence we wish to know the formal potential for this reaction at pH 12.3.

The total peroxide concentration (C_{perox}) can be expressed as:

$$C_{perox} = C_{HO_2^-} + C_{H_2O_2}$$

and the acid dissociation constant (K_a) for hydrogen peroxide is:

$$K_a = 10^{-pK_a} = \frac{C_{H^+}C_{HO_2^-}}{C_{H_2O_2}}$$

Hence:

$$C_{perox} = C_{HO_2^-}\left(1 + \frac{C_{H^+}}{K_a}\right)$$

From this we can define the electrode potential for the redox reaction to be:

$$E = E_f^{\ominus} - \frac{RT}{2F}ln\frac{K_wK_a}{C_{H^+}(K_a + C_{H^+})C^{\ominus}} - \frac{RT}{2F}ln\frac{C_{perox}}{C_{O_2}}$$

where K_w is the water self-ionisation constant. Consequently, at pH 12.3 the formal potential for the oxygen/peroxide redox couple is +0.0677 V vs SHE. The silver chloride (3.5M KCl) reference electrode is 0.205 V vs SHE. Hence the formal potential for the oxygen/peroxide redox couple at pH 12.3 is -0.137 V vs Ag/AgCl.

Section 2: Underpotential hydrogen deposition (H_{upd}) reduction and hydrogen peroxide reduction on platinum nanoparticles
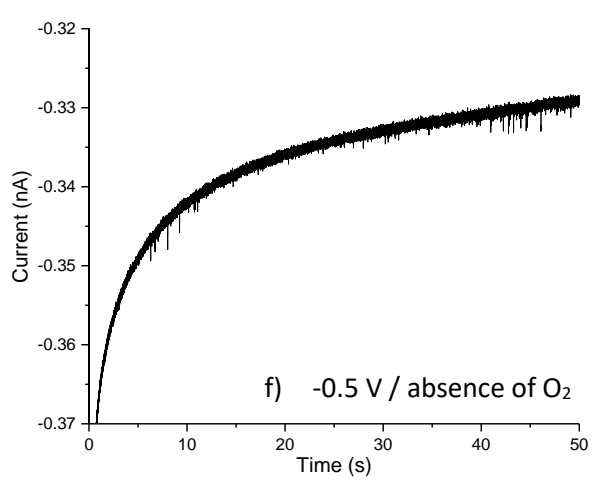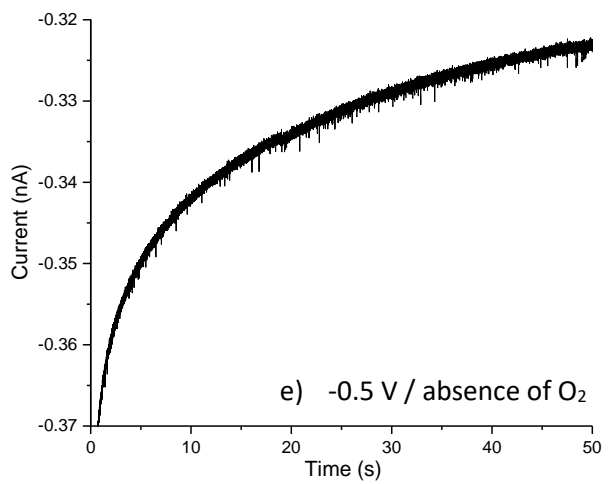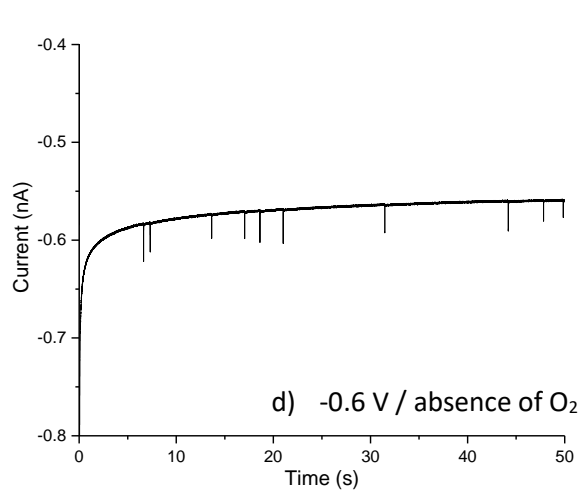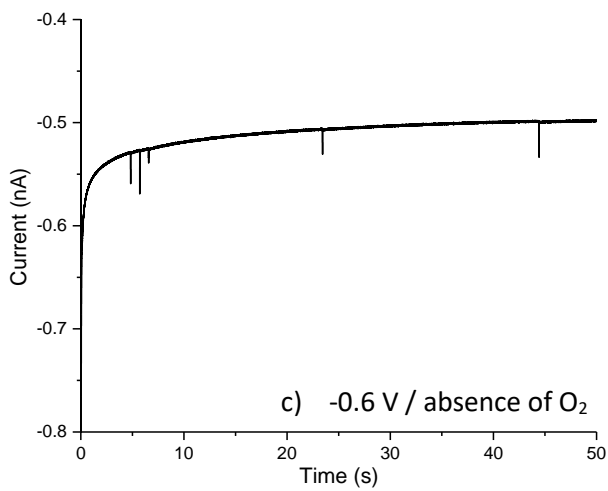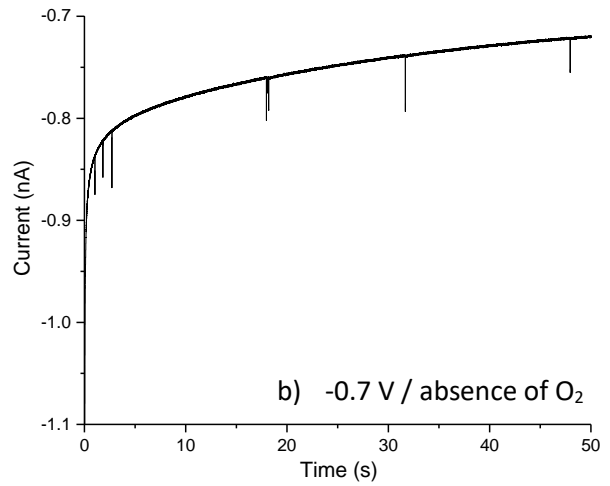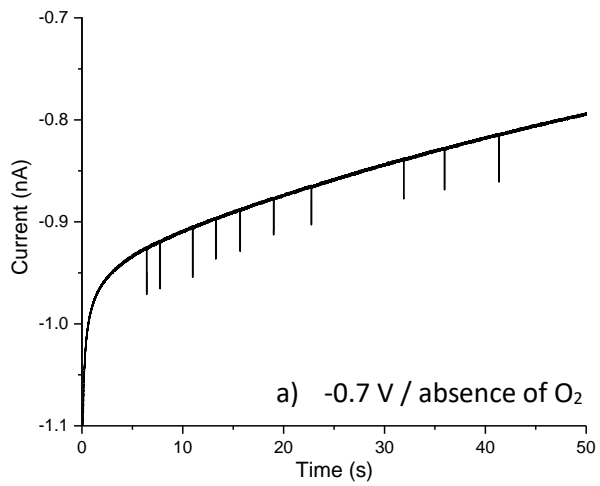
To investigate the nano-impact events on single platinum nanoparticle, a gold microelectrode was submerged into a suspension of 6 pM platinum nanoparticle containing 20 mM KOH under potentiostatic control. When the solution was saturated with nitrogen (Figure S2 a) - f)), reductive spikes can be observed at various applied potentials, corresponding to the reduction of water to underpotential hydrogen deposition (H_{upd}):
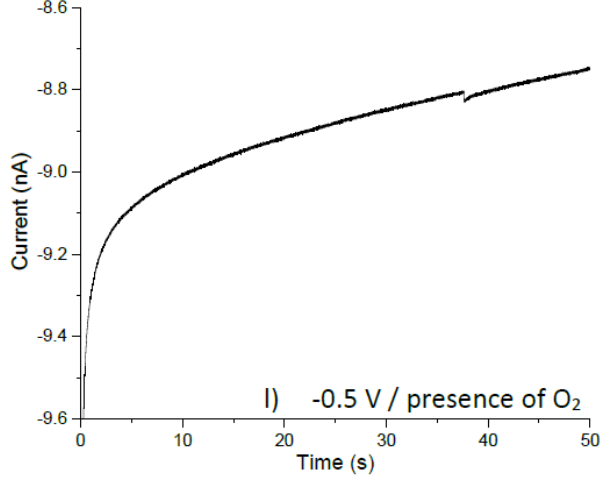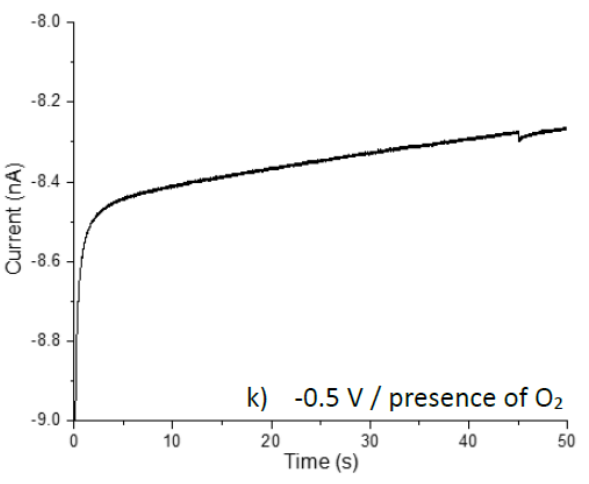
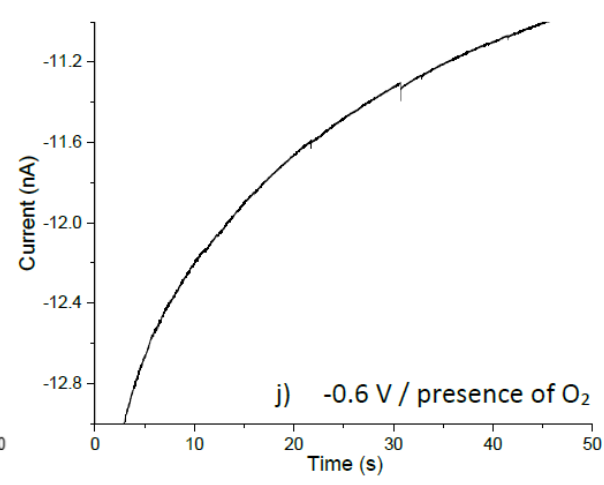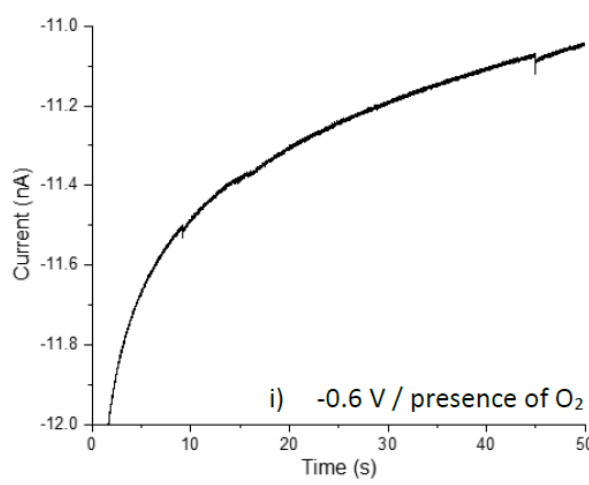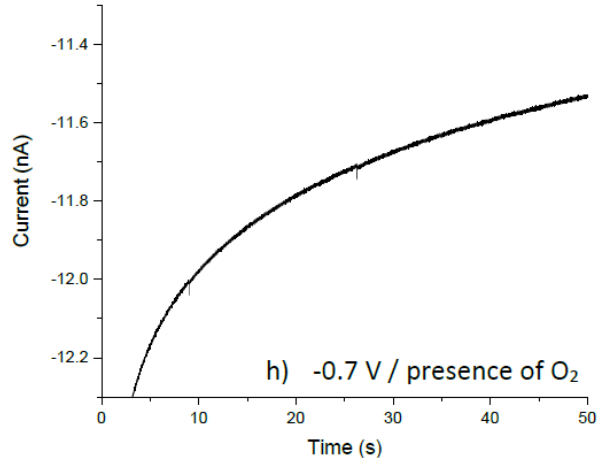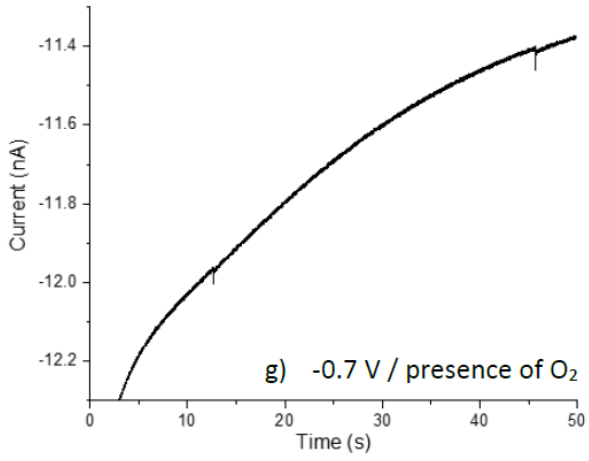$$H_2O + e^- + M \rightleftharpoons Pt-H + OH^- \tag{1}$$

where M is an unoccupied platinum surface site. In the presence of oxygen (Figure S2 g) - l)), small catalytic current steps can be seen, due to the platinum nanoparticle catalysed reduction of hydrogen peroxide formed locally at the gold interface electrochemically via the following reaction:

$$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^- \tag{2}$$

The magnitude of both spikes and steps is sensitive to the applied potential. Figure S2 (m) and (n) present the background current of consecutive chronoamperograms of 20 mM KOH containing 6 pM 50 nm platinum nanoparticles overlaid with catalytic current (reduction of hydrogen peroxide) and spike charge (reductive formation of H_{upd}) of single nano-impact events as a function of experimental time. The Au microelectrode was potentiostated at -0.7 V and the solution was saturated with oxygen before the experiment. The background current (ca. 10 nA) decreases by approximately 10% over the course of 6.2 minutes due to loss of oxygen from the system. Moreover, the measured step size and spike charge are not correlated with the experimental time. Hence, each nanoparticle is viewed as arriving independently and the measured change in the current reflects the reaction occurring at the individual nanoparticle. The average collision frequency of nano-impact events in the absence and presence of oxygen were found to be 0.145±0.042 s^{-1} and 0.040±0.029 s^{-1}, respectively. However, the physical origin of this difference in rates is as of yet undetermined. Note the formation of underpotential deposited hydrogen on Pt nanoparticles has been studied first by Jiao et al[4] in alkaline solution and also in acid by Zhang et al[5]; the latter measurements are challenging since the Pt NPs are more prone to agglomeration and aggregation in acid, and the values reported In Table 1 of reference 5 [Analytical Chemistry 2019, 91 (6), 40235] are open to question in the light of previous results[4], recent tomography[6] and the data presented within the present paper.

a)   -0.7 V / absence of O₂

b)   -0.7 V / absence of O₂

c)   -0.6 V / absence of O₂

d)   -0.6 V / absence of O₂

e)   -0.5 V / absence of O₂

f)   -0.5 V / absence of O₂

g)   -0.7 V / presence of O$_2$

h)   -0.7 V / presence of O$_2$

i)   -0.6 V / presence of O$_2$

j)   -0.6 V / presence of O$_2$

k)   -0.5 V / presence of O$_2$
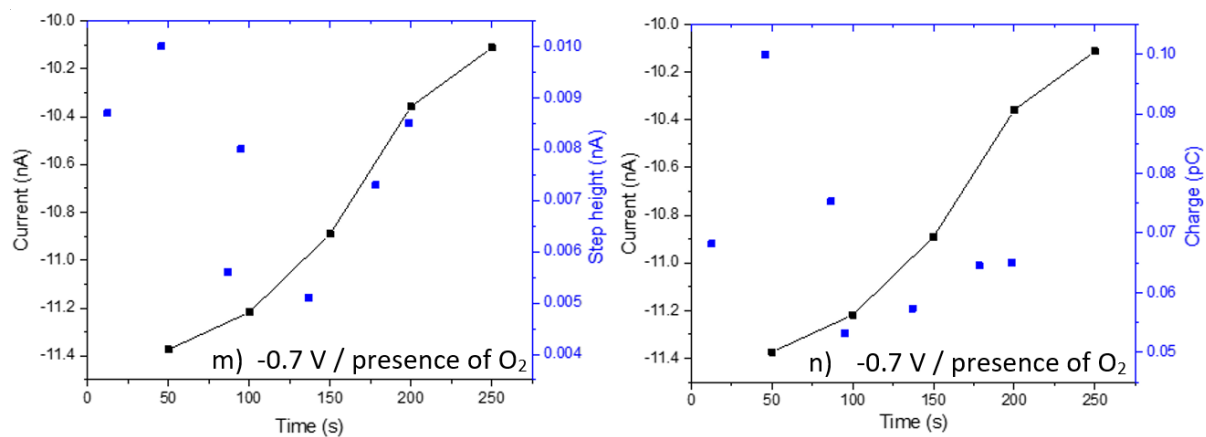
l)   -0.5 V / presence of O$_2$

Figure S2: Chronoamperogram of 6 pM 50 nm platinum nanoparticles in 20 mM KOH at a gold microelectrode with various applied potentials, in the absence (a-f) and presence (g-l) of oxygen. The background current of consecutive chronoamperograms of 6 pM 50 nm platinum nanoparticles in 20 mM KOH overlaid with (m) catalytic current (reduction of hydrogen peroxide) and (n) spike charge (reductive formation of H_{upd}) of single nano-impact events as a function of experimental time in the presence of oxygen.

Section 3: TEM characterization and charge distribution of nano-impact events

High-resolution conventional transmission electron microscopy image of 50 nm platinum nanoparticles was recorded on a JEOL-3000F FEGTEM with an accelerating voltage of 300 kV. The image was analysed by ImageJ software developed at the National Institutes of Health.
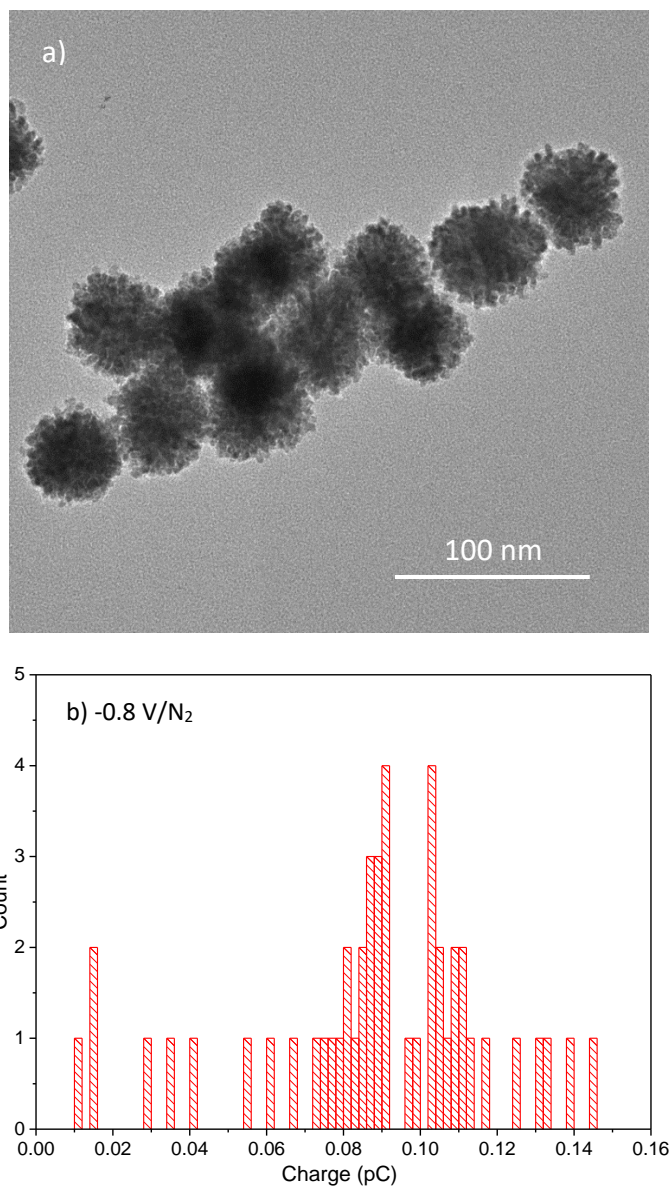

Figure S3: (a) HR-CTEM image of the 50 nm mesoporious platinum nanoparticles showing how the overall particle structure comprises of an aggregate of smaller substituent crystallites, and (b) the charge distribution of nano-impact events for 50 nm platinum nanoparticles at applied potential of -0.8V in the absence of oxygen.

Table S1. Analysis of PtNPs provided by nanoComposix, San Diego, USA.

Diameter (nm)	Particle Concentration (particles/mL)	Mass Concentration (mg/mL)	Platinum Purity
50	3.3×10^{10}	0.051	99.99 %
70	1.2×10^{10}	0.052	99.99 %

Section 4: Comparison of measured impact surface areas distribution via different reactions

Figure S4 shows the cumulative frequency distribution for the 50 nm platinum nanoparticle surface areas measured via hydrogen deposition (red) and hydrogen oxidation (blue) reactions.[7] To characterize the platinum catalysed hydrogen oxidation reaction, a gold microelectrode was immersed into a platinum nanoparticle suspension containing 20 mM NaNO$_3$ saturated with hydrogen, and held at a potential of -0.5 V (vs. MSE). At this potential oxidative spikes corresponding to the solution phase hydrogen oxidation were observed, which can be utilized to generate the surface area of the platinum nanoparticles. The approach used to estimate the surface areas via hydrogen deposition was discussed in the main text. The electroactive surface areas of the 50 nm platinum nanoparticles measured via these two different reactions are comparable, corroborating the assumption that a complete monolayer coverage of deposited hydrogen occurs at a potential of -0.8 V vs Ag/AgCl.
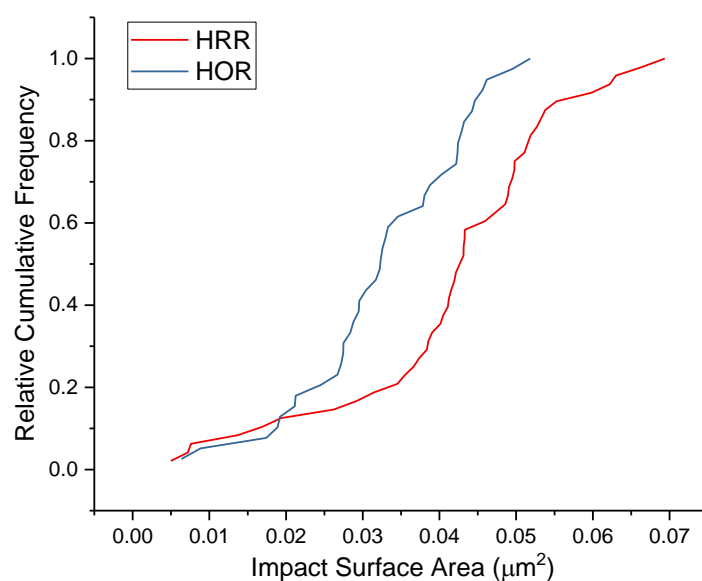

Figure S4: Relative cumulative frequency distribution for the estimated 50 nm nanoparticle surface areas giving average surface areas of $0.042 \pm 0.015 \, \mu m^2$ (Red, measured via hydrogen deposition reaction) and $0.033 \pm 0.011 \, \mu m^2$ (Blue, measured via hydrogen oxidation reaction).

Section 5: Quantification of the variation in the single platinum particle responses of different sizes

Figure S5 presents the comparison of the measured single nanoparticle data collected from hydrogen peroxide reduction at 50 and 70 nm platinum nanoparticles. All the nano-impact experiments were conducted in 6 pM platinum suspension saturated with oxygen at applied potential of -0.7 V vs. Ag/AgCl. The magnitude of the catalytic hydrogen peroxide reduction scales linearly with the nanoparticle surface area measured via the hydrogen deposition reaction, corroborating the inference that the catalytic reduction is controlled by a surface limited process.
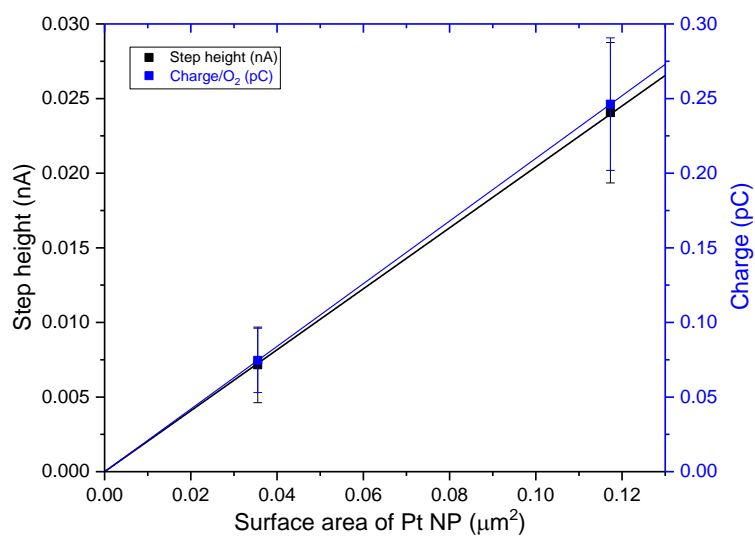

Figure S5: Quantification of the variation in the single platinum particle responses as a function of the surface area of platinum particles. Black, the measured magnitude of the single particle catalytic current associated with the surface reaction limited reduction of hydrogen peroxide. Blue, the magnitude of the spike in current associated with the reductive formation of under potential deposited hydrogen on to the platinum surface, as measured in the presence of oxygen in the bulk solution phase.

Reference

[1]   R. Davis, G. HorvathandC. Tobias, *Electrochimica Acta* **1967**, *12*, 287-297.

[2]   A. Bard, *Standard potentials in aqueous solution*, Routledge, **2017**.

[3]   R. Battino, T. R. RettichandT. Tominaga, *Journal of Physical Chemical Reference Data* **1983**, *12*, 163-178.

[4]   X. Jiao, C. Batchelor-McAuley, N. P. YoungandR. G. Compton, *Physical Chemistry Chemical Physics* **2018**, *20*, 23847-23850.

[5]   P. A. Defnet, C. HanandB. Zhang, *Analytical Chemistry* **2019**, *91*, 4023-4030.

[6]   W. Yu, C. Batchelor-McAuley, Y.-C. Wang, S. Shao, S. M. Fairclough, S. J. Haigh, N. P. YoungandR. G. Compton, *Nanoscale* **2019**, *11*, 17791-17799.

[7]   W. Yu, C. Batchelor-McAuley, X. Chang, N. P. YoungandR. G. Compton, *Physical Chemistry Chemical Physics* **2019**, *21*, 20415-20421.