

**Cathodically Dissolved Platinum Resulting from the O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> Reduction Reactions on Platinum  
Ultramicroelectrodes**

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**Chemicals and Materials.** All aqueous solutions were prepared using deionized water (>18 M $\Omega$  cm, Milli-Q) and all chemicals and materials were used as received from the manufacturers. Potassium chloride (KCl, Fisher Scientific), potassium hydroxide (KOH, Fisher Scientific), Hydrochloric acid (HCl, concentrated Fisher Scientific), Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, concentrated Fisher Scientific), Nitric acid (HNO<sub>3</sub>, concentrated, Fisher Scientific), Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>, 30% Fisher Scientific), 4-aminothiophenol (Acros Organics 97%). Ferrocene methanol (FcMeOH, Aldrich 97%) was used without further purification. Aqua Regia (1:3 concentrated HNO<sub>3</sub>: HCl) was made and used to clean the carbon fiber electrodes after platinum detection experiments to be sure the platinum was completely removed.

**Electrode Fabrication.** The electrodes used in this study were constructed by sealing either a 25 or 100  $\mu$ m Pt wire (Alfa Aesar, 99.95% purity) or a 10  $\mu$ m carbon fiber into a borosilicate glass capillary (0.75 mm inner diameter and 1.5 mm outer diameter, Sutter Instrument) under vacuum. After sealing, the electrode was electrically contacted with silver conductive epoxy (Epo-tek H20E, Epoxy Technology, Ted Pella) and NiCr wire. Surface modification of a 25  $\mu$ m Pt electrode for the cleaning experiment was done by placing the polished electrode in a solution of 30 mM 4-aminothiophenol in EtOH for 12 hours followed by rinsing with copious amounts of EtOH followed by water. The procedure to prepare the platinum disk nanoelectrodes is described in detail elsewhere.<sup>1-3</sup> To briefly summarize, a 25  $\mu$ m diameter platinum wire was placed in a fused silica capillary tube (O. D.: 1 mm, I. D.: 0.3 mm, Sutter Instrument Co.) and one end sealed closed using an oxygen/hydrogen flame. The fused silica capillary was then placed in a P-2000 laser pipette puller (Sutter Instrument Co.) and vacuum applied to the unsealed end of the capillary. The laser was used to heat and seal the fused silica around the platinum without pulling the capillary. Then the platinum/fused silica assembly was pulled (Pull parameters: Heat = 750 Filament = 2, Velocity = 60, Delay = 140, Pull = 250) resulting in two ultra-sharp tips with the platinum nanowires sealed inside. The Pt wire in the tips was then electrically contacted and carefully polished to expose the disk electrode.

**Electrochemical Measurements.** Electrochemical measurements were recorded using a 920C potentiostat (CH Instruments) operating with a three electrode setup using a carbon counter electrode with a single compartment electrochemical cell in an earth grounded faraday cage. A commercial Ag/AgCl reference electrode (CH Instruments) or Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode (CH Instruments) were used for all experiments. All potentials are referenced to NHE unless otherwise noted. All solutions were purged with Ar before use except when performing the ORR experiments. Solutions involving the dissolution of platinum metal were first acidified to a concentration of 1 M H<sub>2</sub>SO<sub>4</sub> and typically diluted by 10x into 1 M H<sub>2</sub>SO<sub>4</sub>.

### Further Discussion.

The diffusion limited steady-state currents of the CVs obtained from the nanoelectrodes before hydrogen peroxide reduction (shown in Figure 5 of the main text) were used to calculate the radii of the electrodes using the diffusion-limited steady-state current equation for a planar disk electrode<sup>1-4</sup>;

$$i_{DL} = 4nFDCr \quad (1)$$

where  $n$  is the number of electrons transferred per redox molecule,  $F$  is Faraday constant,  $D$  is the diffusion coefficient of the redox molecule (for FcMeOH  $D = 6.7 \times 10^{-6} \text{ cm}^2/\text{s}$ ),<sup>5</sup>  $C$  is the bulk concentration of the redox molecule and  $r$  is the radius of the electrode. The CVs were not only used to determine the sizes of the electrodes but are also used to determine any general changes to the electrodes because a decrease in the diffusion-limited current indicates recess of the electrode into the glass surrounding it. The depth of the recess can be estimated using equation 2 below<sup>6,7</sup>;

$$i_{DL} = \frac{4\pi nFDCr^2}{4L + \pi r} \quad (2)$$

where the constants are the same as previously defined for equation 1 and L representing the depth of the electrode recess. This equation was used to estimate the depth of recession for the platinum electrode shown in Figure 5 of the main text.

Figure S-1A shows the amperometric response of a 10  $\mu\text{m}$  carbon fiber electrode in 1 M  $\text{H}_2\text{SO}_4$  when there is no dissolved platinum present in the solution. The amperometric trace is flat and devoid of any current spikes that would be typical of the deposition of platinum species. Figure S-1B shows an amperometric trace from a control experiment where a 25  $\mu\text{m}$  Pt electrode was pulsed 150 times in de-aerated 100 mM KCl. This shows that without oxygen present there is essentially no platinum dissolved into solution.

In addition, we were concerned that the presence of HCl and  $\text{H}_2\text{O}_2$  (present in solutions from the test if chemically produced hydroxyl radicals would oxidize and etch platinum) in the solution could give false positive detection events that may have looked like platinum cluster detection. To test this we made a solution that had the same final concentrations of HCl and  $\text{H}_2\text{O}_2$  as what was used in the detection of platinum in Figure 6 of the main text. An example amperometric trace in this blank (Pt free) HCl and  $\text{H}_2\text{O}_2$  solution is shown in Figure S-2 of a 10  $\mu\text{m}$  carbon fiber held at negative 150 mV vs NHE. Again, similar to the trace seen in Figure S-1, the curve is smooth and there is no response that is similar to what is observed when dissolved platinum is present, i.e. no spikes or blips.

Figure S-3 shows SEM images of a polished platinum electrode. Figure S-3A and S-3B show an electrode that was biased to negative 400 mV (vs AgCl) for ~18 hours in 100 mM KCl and Figure S-3C and S-3D is an electrode that was not biased to perform the ORR for any length of time. The constant potential of negative 400 mV is more positive than what was used for the pulses but was sufficient to drive the ORR in the diffusion limited region over the course of the experiment. The images show the biased electrode is clearly etched and shows pitting of the surface and the edges are severely etched away from the glass sheath surrounding the electrode (where mass transport to the UME would be highest due to radial diffusion dominating at the edges). In contrast the unbiased electrode surface is smooth and is not etched or pitted and the edges are flush with the glass sheath

surrounding the electrode. This further supports that the platinum electrode was etched as a result of the ORR.

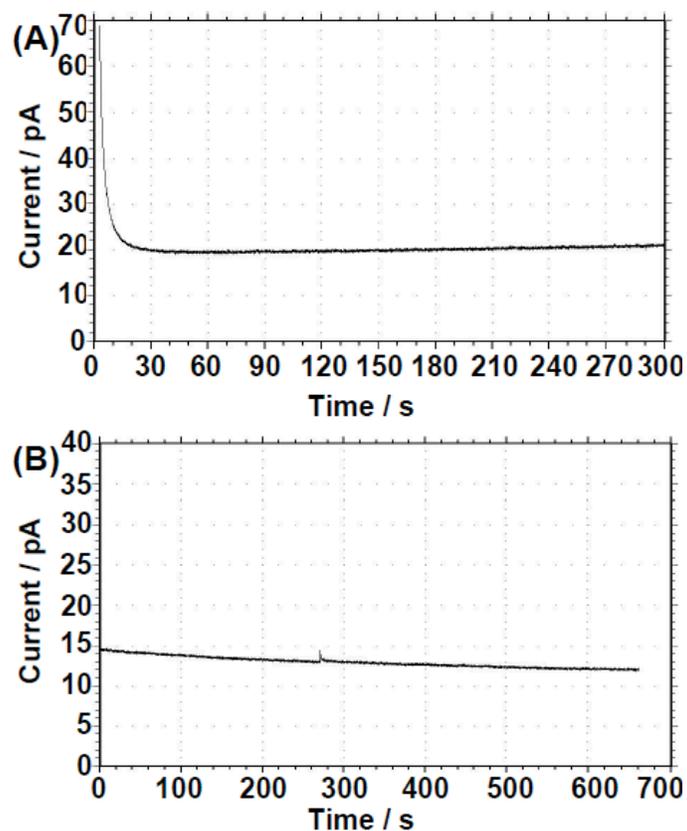
Figure S-4 shows CVs from a 25  $\mu\text{m}$  platinum electrode in 100 mM KCl without added  $\text{H}_2\text{O}_2$  and with added 10 mM  $\text{H}_2\text{O}_2$ . When hydrogen peroxide is not in the solution there is no large reduction wave and the main feature is the onset of water reduction near the end of the forward scan starting at approximately negative 900 mV. The CV with  $\text{H}_2\text{O}_2$  displays a very large reduction wave, which is due to the hydrogen peroxide being reduced on the platinum electrode. This wave starts at approximately negative 50 mV and is seen to rise quickly and plateau to a diffusion controlled current. On the reverse scan the current trace is observed to cross over the forward scan trace, presumably due to hydrogen peroxide that is still adsorbed/dissociated on the platinum surface. Also there could be hydroxyl radicals in the solution formed from the reduction of  $\text{H}_2\text{O}_2$  that are diffusing to the electrode and being reduced as the probability is low that of all the radicals produced will etch the metal. On the forward scan either these radicals are not yet present in solution or the hydrogen peroxide is not adsorbed/dissociated.

Figure S-5 shows two CVs of a 25  $\mu\text{m}$  diameter platinum UME in 0.5 M  $\text{H}_2\text{SO}_4$ . These CVs show the typical platinum oxidation (onset is at  $\sim 700$  mV) and reduction waves (centered at  $\sim 550$  mV) that are due to the formation of a layer of platinum oxide followed by its reduction. The CVs also show the characteristic hydrogen under potential deposition region (UPD) showing the typical adsorption and desorption waves in the potential range of -230 mV to +100 mV. The amount of charged passed under the hydrogen UPD adsorption/desorption waves are directly related to the electroactive surface area (EASA) of the platinum electrode. The freshly polished platinum electrode CV had a measured EASA of  $1.09 \times 10^{-5} \text{ cm}^2$ . This electrode was then placed in a solution of 10 mM  $\text{H}_2\text{O}_2$  with 100 mM KCl and had a -1 V (vs Ag/AgCl) potential applied to it for 1 hour. Which would drive the reduction of the hydrogen peroxide. After this  $\text{H}_2\text{O}_2$  reduction step the electrode was again evaluated by CV scanning in 0.5 M  $\text{H}_2\text{SO}_4$  and was found to have increased in EASA to  $1.88 \times 10^{-5} \text{ cm}^2$ , which is 1.72 times larger than before the  $\text{H}_2\text{O}_2$  reduction step.

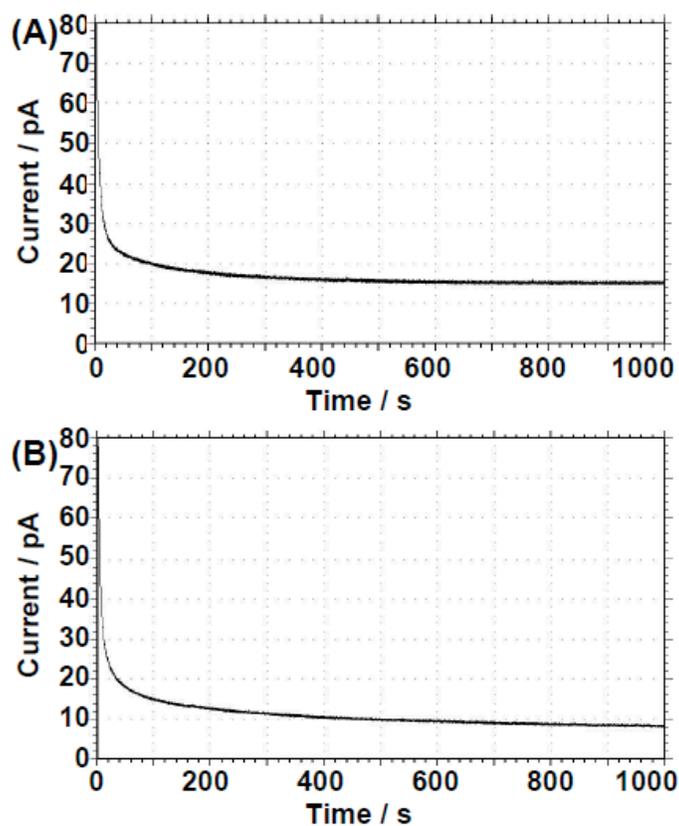
**Table S-1:** Table showing the conditions and determined platinum dissolution. All trials shown in this table were pulsed 150 times using the square wave pulse discussed earlier. Platinum concentration (fM) is the concentration from the detection experiment after dilution, listed with dilution factor (DF). Moles of Pt calculated from the concentration before dilution with total volume of 5 ml, and is the total amount dissolved from the experimental results. The chloride ion concentration was kept at 100 mM for all solutions except for the KOH test. EASA stands for the Electro-Active Surface Area.

<b>Electrolyte</b>	<b>Electrode Diameter</b>	<b>EASA (cm<sup>2</sup>)</b>	<b>Collision Frequency (Hz)</b>	<b>Pt conc. (fM)</b>	<b>Moles of Pt</b>	<b>Dissolved Pt (ng/cm<sup>2</sup>)</b>
100 mM KCl	25 μm	1.1x10 <sup>-5</sup>	0.0538	31.2 (10x DF)	1.56x10 <sup>-15</sup>	28.6
100 mM KCl	100 μm	1.3x10 <sup>-4</sup>	0.0867	50.3 (20x DF)	5.03x10 <sup>-15</sup>	7.5
100 mM KOH	25 μm	1.8x10 <sup>-5</sup>	0.0340	19.7 (10x DF)	9.86x10 <sup>-16</sup>	10.6
10 mM HCl + 90 mM KCl	25 μm	1.2x10 <sup>-5</sup>	0.0135	7.8 (10x DF)	3.91x10 <sup>-16</sup>	6.5
1 mM HCl + 99 mM KCl	25 μm	1.0x10 <sup>-5</sup>	0.0423	24.5 (10x DF)	1.23x10 <sup>-15</sup>	23.7
1 mM H <sub>2</sub> O <sub>2</sub> + 100 mM KCl	25 μm	1.0x10 <sup>-5</sup>	0.0871	50.5 (20x DF)	5.05x10 <sup>-15</sup>	98.1

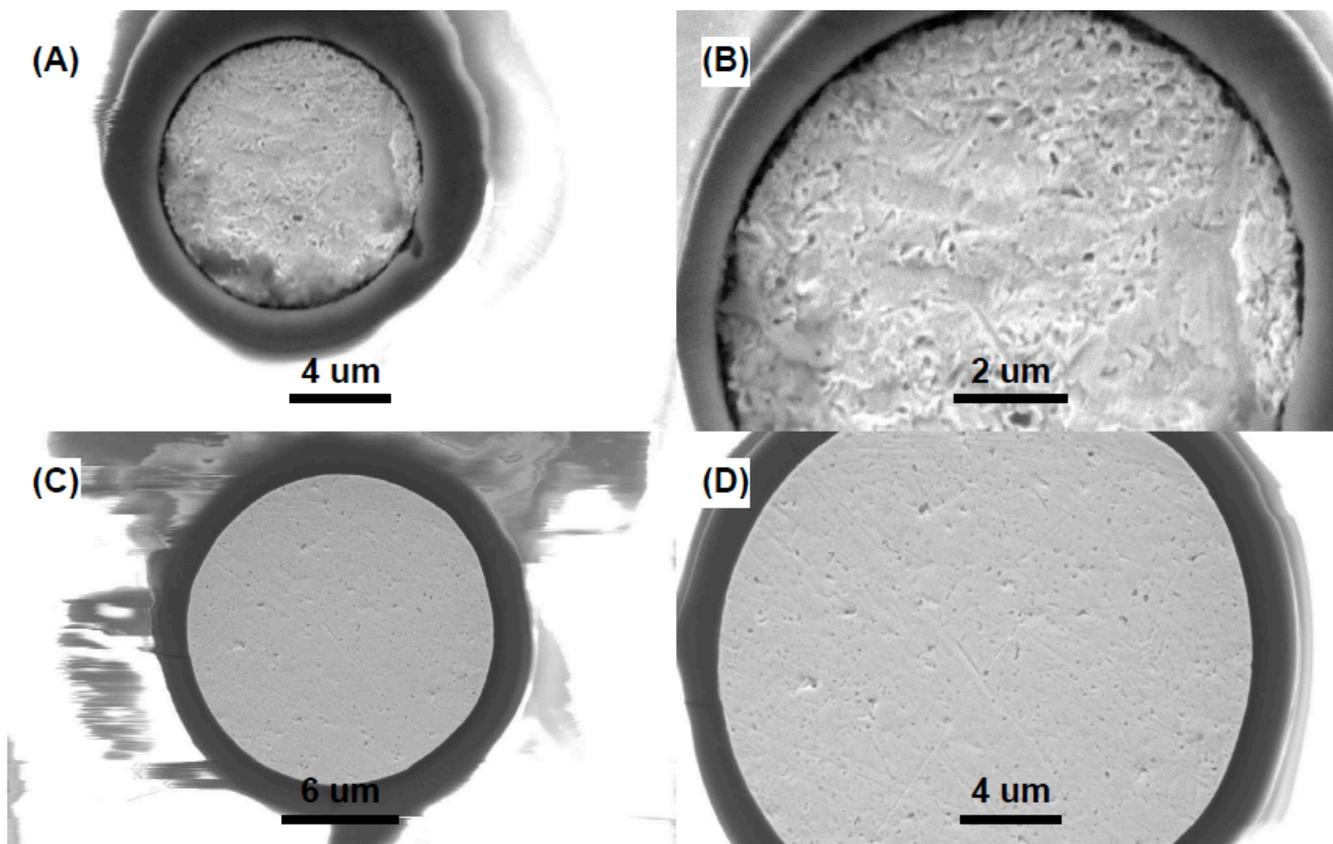
**Figure S-1:** (A) Plot showing the amperometric response of a 10  $\mu\text{m}$  carbon fiber in 1 M  $\text{H}_2\text{SO}_4$  only without the presence of dissolved platinum species. (B) Plot showing the amperometric response of a 10  $\mu\text{m}$  carbon fiber in 1 M  $\text{H}_2\text{SO}_4$  with 10 mM KCl from the de-aerated control experiment. Electrodes were both held at negative 150 mV vs NHE.



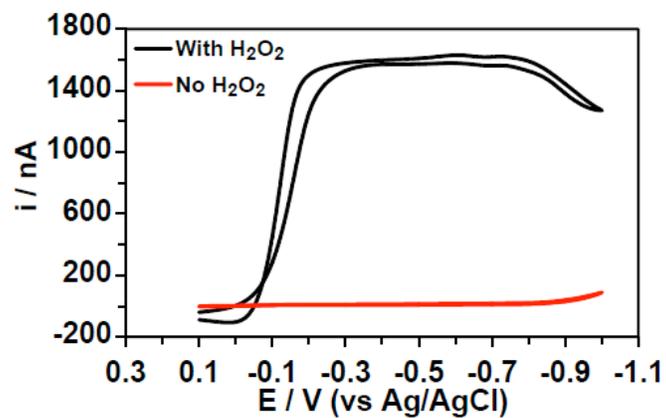
**Figure S-2:** Plots showing results from control experiments. (A) The presence of 10 mM HCl and 600  $\mu\text{M}$   $\text{H}_2\text{O}_2$  and HCl into the 1 M  $\text{H}_2\text{SO}_4$  solution does not by itself generate the blips we would observe when there is dissolved platinum in solution. (B) Control amperometric trace in 1 M  $\text{H}_2\text{SO}_4$  and 10 mM HCl showing no Pt detection events when a platinum wire left in 100 mM HCl for 48 hours does not generate dissolved platinum without  $\text{H}_2\text{O}_2$  being added to the solution. Applied potential was held at negative 150 mV vs. NHE for both.



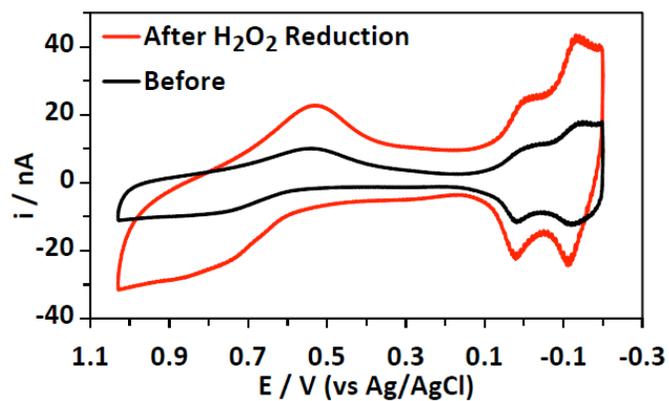
**Figure S-3:** (A) and (B) are SEM images of a Pt electrode that has been polarized to -400 mV vs AgCl for ~18 hours in air saturated 100 mM KCl showing that the electrode appears etched and pitted. (C) and (D) are SEM images of an un-etched electrode showing the platinum surface is much smoother and does not appear pitted or etched.



**Figure S-4:** CVs from a 25  $\mu\text{m}$  Pt UME in 100 mM KCl without and with added 10 mM  $\text{H}_2\text{O}_2$ . CV scan rates were 100 mV/s.



**Figure S-5:** Sulfuric acid CVs from a 25  $\mu\text{m}$  Pt electrode before and after reducing hydrogen peroxide (10 mM  $\text{H}_2\text{O}_2$  and 100 mM KCl, -1 V applied potential for 1 hour) showing the increase in EASA after hydrogen peroxide reduction was performed. Solution was 0.5 M  $\text{H}_2\text{SO}_4$  recorded with 1 V/s scan rate.



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