## **Supporting Information**

## Analysis of Diffusion Controlled Stochastic Events of Iridium Oxide (IrO<sub>x</sub>) Single Nanoparticle Collisions by Scanning Electrochemical Microscopy

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**Figure S1**. Cyclic voltammograms of water oxidation at NaBH<sub>4</sub>-treated Pt UME (radius 5  $\mu$ m) in pH 13 solution (0.1 M NaOH) first (black) and second (red) scan at 4 pM IrO<sub>x</sub> NP after immersion of about 3 min. Scan rate is 50 mV/s.



**Figure S2**. (a) Schematic illustration of pre-adsorption experiments (NaBH<sub>4</sub> treatment for 3 min  $\rightarrow$  rinsing  $\rightarrow$  immersing in IrO<sub>x</sub> NP containing solution (1, 3, or 5 min)  $\rightarrow$  washing in 0.1 M NaOH  $\rightarrow$  electrochemical measurement in NP free solution) and (b) peak current (at ~ 0.7 V vs Ag/AgCl) for water oxidation with different immersion times before a voltammetric scan at Pt UME (radius 5 µm) in pH 13 solution (0.1 M NaOH) containing different concentrations of IrO<sub>x</sub> NPs. (diameter 28 ± 4.8 nm) Scan rate, 50 mV/s.



**Figure S3**. Chronoamperometric curves for single  $IrO_x$  NP collisions at the NaBH<sub>4</sub> treated Pt UME (radius 5  $\mu$ m) in a PBS (pH 7-8) and tris (pH 9-10) buffer solution containing  $IrO_x$  NPs.



**Figure 4**. Peak height difference in chronoamperometric curves for single  $IrO_x$  NP collisions at the NaBH<sub>4</sub> treated Pt UME (radius 5  $\mu$ m) using different size of  $IrO_x$  NP.



**Figure S5**. Peak height distribution in chronoamperometric curves for single  $IrO_x$  NP collisions at the NaBH<sub>4</sub> treated Pt UME (radius 5  $\mu$ m) in a solution containing 4 pM  $IrO_x$  NPs of various applied potential from 0.8 V to 1.0 V (vs. Ag/AgCl). Data acquisition time is 50 ms.



**Figure S6**. Chronoamperometric curves for single  $IrO_x$  NP collisions at the NaBH<sub>4</sub> treated Pt UME (radius 5  $\mu$ m) in a solution containing 2 pM  $IrO_x$  NPs and PB (pH 7) of various concentration of phosphate from 10 to 200 mM. Applied potential is 1.1 V (vs. Ag/AgCl). Data acquisition time is 50 ms.



**Figure S7.** Chronoamperometric curves for single  $IrO_x$  NP collisions on the NaBH<sub>4</sub> treated Pt UME (radius 5  $\mu$ m) in a solution containing 4 pM (black), 8 pM (red), or 16 pM (green)  $IrO_x$  NPs, PB (pH 7, 75 mM), and 1.5 mM sulfite ion. Applied potential is 1.1 V (vs. Ag/AgCl). Data acquisition time is 50 ms.



**Figure S8.** TEM image of an  $IrO_x$  nanoparticle. The  $IrO_x$  NP (average diameter  $28 \pm 4.8$  nm) consisted of small (diameter ~1 nm) NPs.



**Figure S9.** Experimentally obtained (blue triangle) normalized collision frequency in the presence of 0.5 mM sulfite ion containing solution as a function of distance between a tip and insulating surface. The red line is theoretical negative feedback approach curve. The radius of tip is 5  $\mu$ m and RG is ~10. Total data collecting time is 300 s (for 5 replicate measurements).