Supplementary Information

Intrinsic electrocatalytic activity of single IrO\textsubscript{x} nanoparticle toward oxygen evolution reaction

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Experimental Details

Reagents

Potassium hexachloroiridium (K\textsubscript{2}IrCl\textsubscript{6}) was obtained from Alfa Aesar (Ward Hill, USA), sodium citrate, sodium hydroxide and sodium borohydride were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All chemicals were used as received. Ultrapure water (> 18 M\Omega) was used in all experiments.

Preparation of iridium oxide nanoparticles (IrO\textsubscript{x} NPs)

K\textsubscript{2}IrCl\textsubscript{6} (6 mg, 1.2 mM) was added to 10 ML of an aqueous solution containing sodium citrate (10 mg, 3.4 mM). The red-brown solution was adjusted to pH 7.5 with a 0.01 M NaOH solution and then heated to 100 °C in an oil bath with constant stirring. After heating for 30 minutes, the solution was cooled to room temperature and the NaOH solution was added to adjust the pH to 7.5. The addition of NaOH solution at room temperature, followed by heating at 100 °C for 30 minutes was repeated until the pH stabilized at 7.5. The solution was kept at 100 °C for 2 hour with oxygen bubbling through the solution. The color of the solution then became deep blue.

Preparation of Pt ultramicroelectrode (UME)
Pt UME was prepared following the general procedure as followed. Briefly, 10 µm diameter Pt wire was sealed in glass after repeated rinsing with methanol and water. Then, the electrode was polished with the alumina powder water suspension to a mirror face. The surface area was checked with standard redox electrochemistry of ferrocene methanol.

**Electrochemical technique**

Three electrode system was used including a Pt UME as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3M) as the reference electrode. Electrochemical experiment was performed using a CHI model 660 E potentiostat (CH Instruments, Austin, TX, USA). The chronoamperometry curves were obtained with data acquisition time of 50 ms, which was the optimal value for high signal to noise ratio. The average peak current of collision spikes $\overline{H}$ was calculated according to equation S1:

$$\overline{H} = \sum_{i=1}^{n} \frac{H_i \times n_i}{N}$$

where the $H_i$ is the peak height (current) of collision signals, $n_i$ was the number of such collision signals with the height of $H_i$, and $N$ is the total number of collision signals as $N = n_1 + n_2 + ... + n_i$.

**The steady-state limiting current expectation**

The steady-state limiting current of 26 nm IrO$_x$ OER collision signal could be expected by (i) the mass transport of OH$^-$ to the nanoparticle or (ii) O$_2$ removal from the particle.

**For (i) in the case of limitation by supply of OH$^-$:**

$$I_{ss} = 4 \cdot \pi \cdot \ln (2) \cdot z \cdot F \cdot \frac{D_{OH^-}}{D_{OH^-}} \cdot \frac{C_{OH^-}}{} \cdot r_{NP}$$

$$= 4 \cdot \pi \cdot \ln (2) \cdot 4 \cdot 96485 \cdot 5.27 \cdot 10^{-9} \cdot 100 \cdot 13 \cdot 10^{-9} = 23.0 \text{ nA}$$

Considering that the experimental collision spike height is about two orders of magnitude lower than this calculated value and the fact that the collision spikes do not significantly change with the change of pH value (as shown in Fig. S3), it is concluded that the mass transport of OH$^-$ is not the limiting factor. So, the steady-state limiting current in our system was estimated by the removal of O$_2$.

**For (ii) in the case of limitation by O$_2$ removal:**

$$I_{ss} = 4 \cdot \pi \cdot \ln (2) \cdot z \cdot F \cdot D_{O_2} \cdot \frac{C_{eff}}{2} \cdot r_{NP}$$
The parameter $C_{O2}^{eff}$ is the effective concentration of oxygen that evolves at a nanoparticle, which is defined as the difference of the oxygen saturation concentration in 0.1 M NaOH under experimental conditions $C_{O2}^{max}$ (about 1.24 mM) and the background concentration $C_{O2}^{bg}$ as:

$$C_{O2}^{eff} = C_{O2}^{max} - C_{O2}^{bg}$$

As $C_{O2}^{bg}$ takes the oxygen evolution at the Pt UME into account, which can be determined from the experimental background current $I_{bg}$ that was measured during NPs collision experiments (about 0.5 nA). The background concentration is estimated by employing the steady-state current relation of UME as:

$$C_{O2}^{bg} = \frac{I_{bg}}{4 \pi n F D \cdot r_{UME}} = \frac{0.5 \cdot 10^{-9}}{4 \cdot 4 \cdot 96485 \cdot 1.9 \cdot 10^{-9} \cdot 5 \cdot 10^{-6}} = 0.048 \text{ mM}$$

Thus, the effective concentration of oxygen $C_{O2}^{eff}$ is:

$$C_{O2}^{eff} = C_{O2}^{max} - C_{O2}^{bg} = 1.24 - 0.048 = 1.192 \text{ mM}$$

The steady-state limiting current is then estimated by:

$$I_{ss} = 4 \pi \cdot \ln(2) \cdot \tau \cdot F \cdot D_{O2} \cdot C_{O2}^{eff} \cdot r_{NP} = 4 \pi \cdot \ln(2) \cdot 4 \cdot 96485 \cdot 1.9 \cdot 10^{-9} \cdot 1.192 \cdot 13 \cdot 10^{-9} = 98.9 \text{ pA}$$

**Supplementary Figures**

Fig. S1 Cyclic voltammograms of the oxygen evolution reaction at bare Pt UME (diameter of 10 μm) (in black) and NaBH$_4$-treated Pt UME without (in red) and with adding 8 pM IrO$_x$ NPs (in blue). The wide peak near 0.65 V on the CV of NaBH$_4$-treated Pt UME...
treated Pt UME with adding of IrO₃ NPs was attributed to electrocatalytic response of IrO₃ NPs adsorbed on Pt.

Fig. S2 Chronoamperometry curves of 0.1 nM IrO₃ NPs when biased at 0.35 V and 0.30 V in 0.1 M NaOH solution.

Fig. S3. Chronoamperometry curves of 8 pM IrO₃ NPs suspended in different NaOH concentrations as: 0.01 M (black), 0.1 M (red), 1 M (blue) when biased it at 0.8 V. The enlarged view showed the typical collision signal.
Fig. S4 The peak height distributions of collision current spikes at each potential as indicated in subfigures of (a) ~ (j). N represents the total number of current spikes for statistic analysis, and H is the average peak current with the standard deviation.
Fig. S5. Small IrO₅ nanoparticles (~ 2 nm in diameter) characterization. (a) TEM bright field image; (b) The comparison of chronoamperometry curves of 8 pM 26 nm IrO₅ NPs and 80 nM 2 nm IrO₅ NPs at the NaBH₄-treated Pt UME (diameter 10 µm) when biased at 0.75 V.

Small 2 nm IrO₅ nanoparticles were prepared according to the procedure reported elsewhere¹. Collision signals of 2 nm NPs are similar to the noise current of the background and exhibit no discernible collision spikes. The observed collision spikes (with dozens of pA current height) for large 26 nm NPs (though consisting of small 2 nm NPs) are attributed to 26 nm IrO₅ NPs, and small 2 nm NPs only contribute to the offset (with several pA current value).

References