Supporting Information for

Highly efficient hydrogen evolution of platinum via tuning the interfacial dissolved-gas concentration

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Experimental Section

Chemicals and materials. Perchloric acid (HClO₄, 70%), sodium perchlorate (NaClO₄, 98%) and calcium chloride (CaCl₂, 99%) were purchased from Sigma-Aldrich. Potassium perfluorooctanesulfonate (PFOS) was received from Matrix Scientific. Platinum wires (Pt, 25 and 50 μm diameter, 99.95%) were obtained from Alfa Aesar. Glass capillaries were received from Dagan Corporation. Ultrapure water (Milli-Q, 18.2 MΩ) was used in all experiments.

Fabrication of Pt nanoelectrode. The Pt nanoelectrodes were fabricated through two steps based on a previous method.¹ First, the Pt tips were prepared by electrochemically etching of Pt wire in 15 wt% CaCl₂ solution using a 100 Hz sinusoidal wave with an amplitude of 4.0 V. After sharpening, the Pt tips were washed by water. Second, the as-prepared Pt tips were thermal sealed in a glass capillary. Then the sealed tip was polished on a silicon carbide polishing sandpaper until a Pt nanodisk was exposed, which was monitored by using an electronic feedback circuit. The radius (a) of obtained nanoelectrode was calculated through testing the steady-state diffusion-limited current (i_d) associated with the reduction of proton in 0.1 M HClO₄ solution. i_d = 4nFDC* a, where n is the number of electrons transferred per molecule, F is Faraday constant, D is the diffusion coefficient of proton (7.8 × 10⁻⁵ cm²/s),² and C* is the bulk concentration of proton.

Electrochemical measurements. The electrochemical measurements were performed on a CHI 760E electrochemical workstation. For the measurements of Pt nanoelectrode, an Ag/AgCl was used as the counter/reference electrodes. The radius test was carried out via voltammetry in 0.1 M HClO₄ solution at a sweep rate of 100 mV/s with 0.1 M NaClO₄ added as supporting electrolyte. The nanobubble tests were performed by the voltammograms in 0.5 M HClO₄ solution at a sweep rate of 100 mV/s. For HER measurements, a typical three-electrode system was used. A Pt rotating disk electrode (Pine Instruments, diameter of 5 mm) was used as the working electrode with a graphite rod as the counter electrode and an Ag/AgCl as the reference electrode. All the potentials were calibrated with respect to the reversible hydrogen electrode (RHE),³ and in 0.5 M HClO₄ solution with all the PFOS concentrations, E_RHE = E_Ag/AgCl + 0.205 V. The cyclic voltammetry (CV) measurements were recorded in 0.5 M HClO₄ solution at a sweep rate of 50 mV/s under a flow of N₂. The polarization curves were obtained in N₂-saturated 0.5 M HClO₄ electrolyte at a rotation rate of 1,600 rpm and a scan rate of 2 mV/s. The galvanostatic measurements were carried out in an N₂-saturated 0.5 M HClO₄ solution under a current density of 10 mA cm⁻².

Characterizations. SEM images were taken using a JSM-7600 field-emission scanning electron microscope operated at 15 kV. Digital images were collected on an optical microscope with a high-speed charge coupled device (OMAX). Electrical continuity during nanoelectrode polishing was measured using a high-input impedance (MOSFET)-based circuit.

References

Figure S1. (A) SEM image of a Pt tip fabricated by electrochemical etching. (B) Corresponding SEM image of Pt tip with high magnification.
Figure S2. Steady-state voltammetric response of Pt nanoelectrode recorded at a sweep rate of 100 mV/s.
Figure S3. The blow-ups of $H_{upd}$ desorption peaks for (A) pure Pt and (B) PFOS-Pt at different galvanostatic test time.
Figure S4. Normalized ECSA for PFOS-Pt and pure Pt before and after long-term galvanostatic test.
Figure S5. Bubble generation on the electrode (A) before and (B) after HER test without applying a rotating speed.
Figure S6. iR-corrected polarization curves of (A) Pt mesh and (B) Au disk electrode with PFOS modulation.
Figure S7. Chronopotentiometric measurements for PFOS-Pt and pure Pt at the cathodic current density of 10 mA cm$^{-2}$. 
Figure S8. (A) IR-corrected polarization curves of PFOS-Pt with different PFOS concentrations in N$_2$-saturated 0.5 M HClO$_4$ solution. (B) Tafel plots of PFOS-Pt with different PFOS concentrations.
Figure S9. (A) IR-corrected polarization curves of PFOS-Pt with high PFOS concentrations. (B) Comparison of current densities of PFOS-Pt with high PFOS concentrations.
Figure S10. Comparison of the blow-ups of $H_{upd}$ desorption peaks for $10^5$ PFOS-Pt before and after HER test.