On-chip in situ Monitoring of Competitive Interfacial Anionic Chemisorption as a Descriptor for Oxygen Reduction Kinetics

Mengning Ding[1], Guangyan Zhong[2], Zipeng Zhao[1], Zhihong Huang[1], Mufan Li[2], Hui-Ying Shiu[1], Yuan Liu[1,3], Imran Shakir[4], Xiangfeng Duan[2,3*] and Yu Huang[1,3*]

[1]Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095, USA; [2]Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095, USA; [3]California Nanosystems Institute, University of California, Los Angeles, CA 90095, USA, [4]Sustainable Energy Technologies Centre, College of Engineering, King Saud University, Riyadh 11421, Kingdom of Saudi Arabia.

*Corresponding email: yhuang@seas.ucla.edu, xduan@chem.ucla.edu

Supplementary Information

1. **Figure S1|** Schematic illustration of device fabrication.

2. **Figure S2|** ETS measurement configuration.

3. **Figure S3|** Quantitative ETS analysis of chloride adsorption on Pt surface.

4. **Figure S4|** ETS characterization of cyanide adsorption (formation of a cyanide adlayer) on Pt surface.

5. **Figure S5|** ETS measurements of chloride adsorption at different concentrations on clean and cyanide modified PtNW surface.

6. **Figure S6|** Electrical transport spectroscopy (ETS) of perchloride adsorption and competition with chloride on Pt surface.

7. **Figure S7|** Equivalent circuit model of the ETS measurement.

1. Materials and Methods

Synthesis of PtNWs. PtNWs were synthesized following a previous procedure[1] with slight modification. Typically, a mixture of KOH (0.6 g) and ethylene glycol (4 mL) was dissolved in DMF (6 mL). Aqueous solution of K_2PtCl_6 (8 wt%, 0.1 mL) was then added into the mixture. After stirring for 20 min, the reaction mixture was transferred into a Teflon-lined autoclave, which was maintained at 150 °C for 15 h and then cooled to room temperature. The black powders were collected after the reaction and washed with ethanol and DI water repeatedly for several times before use.

Preparation of PtNWs films. A free standing film was assembled from as-prepared PtNWs suspension by a co-solvent evaporation method. Typically, PtNWs suspensions in ethanol (400 ul, 0.4 mg/mL) was mixed with DI water (miliQ filtered, 600 uL) and n-Butanol (250 uL). The suspension of PtNWs in mixed solvents was added drop by drop into a flask (about 9 cm in diameter) filled with DI water. A film of PtNWs was then formed on the water surface which was later transferred onto the device.

Fabrication of the PtNWs electrochemical device. PtNWs device is fabricated using a previously described approach[2,3]. Typically, a poly(methyl methacrylate) (PMMA, A8, MicroChem Corp.) film was prepared by spin-coating on the substrate (p++ silicon wafer with 300 nm thermal oxide) surface with pre-patterned Au electrodes (Ti/Au, 50nm/50nm). E-beam lithography was then used to open windows on PMMA, which created desired patterns on the substrate. The pre-prepared (by co-solvent evaporation) free standing film of PtNWs was then deposited onto the substrate surface (LB film). For a fine-controlled deposit, the substrate was made hydrophilic by Oxygen plasma treatment before LB deposition. After the removal of PMMA template, PtNWs was then patterned on the device substrate with desired designs. To eliminate the influence of electrolyte and to avoid electrochemical reactions on the metal electrodes, another layer of PMMA (~500nm thick, electrochemically inert) was then deposited on the PtNWs device with spin-coating. A smaller window that only exposes PtNWs was opened by e-beam lithography. The final device, with exposed PtNWs and PMMA protected electrodes was used for in-device electrochemistry and in situ electrical spectroscopy.

Instead of an open chamber configuration[2], a microfluidic set-up was used in this work to achieve an efficient control of the electrolytes exposed to the PtNW device. A PDMS microfluidic channel was mounted on the Si chip with the channel aligned with the central region where the PtNW device are located. Polyethylene tubing was attached to the inlet and the outlet holes on the PDMS channel, and $HClO_4$ solutions or mixed electrolytes containing $HClO_4$ and desired anions (for introducing each anion, the corresponding sodium salt is used) were drawn through the channel using a syringe pump. Typical flow rate was 1 $mL \cdot h^{-1}$ during ETS tests and 10 $mL \cdot h^{-1}$ for the electrolyte switching. All electrolytes were degassed with ultrahigh purity nitrogen before use. The surface cyanide modification of PtNW device was also performed within the microfluidic system. The electrochemically cleaned PtNW devices were exposed to 0.1 M KCN solution for 30 min under open circuit to allow the formation of irreversibly adsorbed surface cyanide, followed by extensive rinsing with the flow of DI water and then the 0.1 M $HClO_4$ electrolyte.

On-chip electrochemical and electrical transport spectroscopy (ETS) measurements. A two-channel source-measure unit (SMU, Keysight B2902a) was used for ETS measurements. A first SMU channel was used as a potentiostat to perform the on-chip CV by applying the potential (V_G) of source/drain electrode (acting as working electrode) as to the reference electrode (leak-free Ag/AgCl), while collecting the current (I_G) through the counter electrode (Pt wire). In a typical CV measurement, the scan rate is 28 mV s^{-1}. A second SMU channel was used to record ETS signals by supplying a small bias potential (50 mV) between source and drain electrodes and collecting the electrical conductive current (I_{SD}).

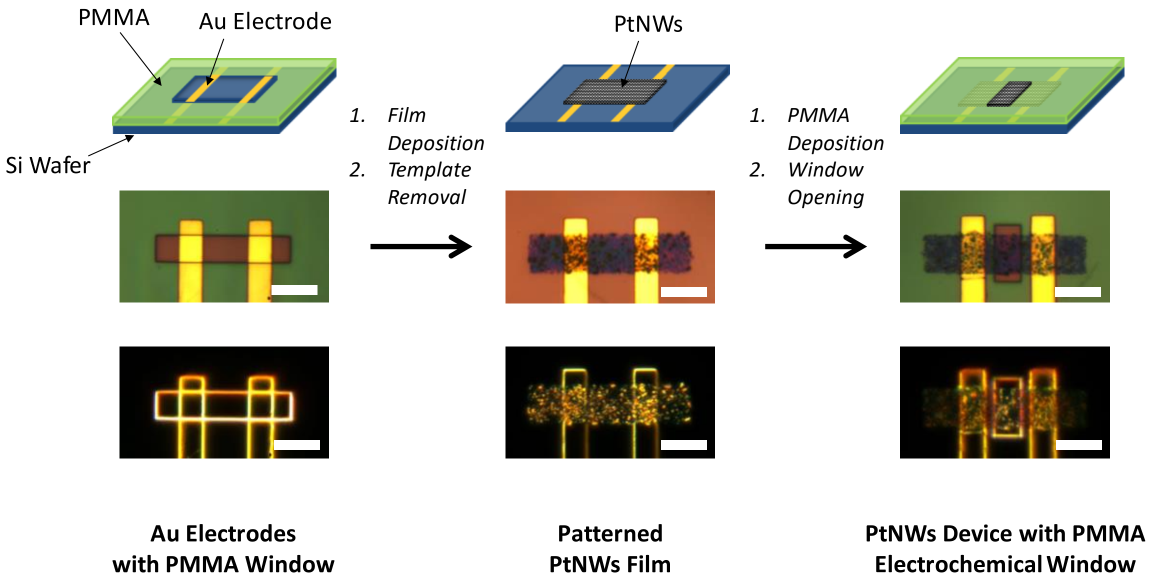
For a typical measurement in this study, the Gate (Faradaic) current is generally several orders of magnitude smaller than the ETS current (I_G ~1 nA and I_{SD} ~50 μA). Therefore, the in-device CV current does not affect the ETS current and no additional background subtraction or other mathematical treatment is needed before the data analysis. In case the electrochemical I_G is significant enough to affect the accuracy of I_{SD}, an equivalent circuit[4] can be used to subtract the I_G background from the ETS (I_{SD}) channel, as shown in supplementary Fig. S7.

Normalization of the I_{SD}-V_G results. In an aqueous environment under open circuit, the conduction electrons were at least scattered by surface adsorbed water molecules, and the conductance of PtNWs at this stage is considered as “baseline” conductive current (I_{SD}^0). This baseline value can be determined before each electrical spectroscopic scan by measuring the I-V characteristics of PtNWs with no V_G applied. With I_{SD}^0 measured, the I_{SD} of each test could also be normalized to relative conductance change ($\Delta I_{SD}/I_{SD}^0$). This normalization does not change the characteristic of each I_{SD}-V_G curve, and makes the comparison between different scans and different devices more reasonable, as the baseline conductance of each device are different and each could drift during measurements, due to the reasons such as Pt atom dissolution. The shape of I_{SD}, G_{SD} and ΔG_{SD} are the same, and in the paper this characteristic is all referred as ETS result. In the presence of strongly adsorbed anions such as halide, the "baseline" conductive current is also affected by the specially adsorbed anions under open circuit. Note that in such case the "baseline" surface condition is changing from clean $HClO_4$ to the that containing halide anions. Therefore, the comparison of absolute ETS current is more appropriate and more accurate in the study of halide adsorption and is thus adapted in this work.

Rotating Disk Electrode Test. A typical catalyst ink was prepared by mixing 1.5 mg of Pt/C (20% Pt, Alfa Aesar) catalyst powder with 2 mL of ethanol solution containing 20 μL of Nafion (5 wt%) with 5 min ultrasonication time. Then, 10 μL of catalyst ink was dropped onto a 5 mm diameter glassy-carbon electrode (Pine Research Instrumentation). Estimation of Pt loading is based on overall Pt ratio within catalyst, and Pt loading is about 1.5 μg for all tested Pt based alloy samples. The ink was dried under an infrared lamp, then the electrode was ready for electrochemical test.

A three-electrode cell was used to carry out the electrochemical measurements. The working electrode was a catalyst coated glassy carbon electrode. One Ag/AgCl electrode was used as the reference electrode. A Pt wire was used as the counter electrode. Cyclic Voltammetry (CV) measurements was conducted in a N_2 saturated 0.1 M $HClO_4$ solution between 0.05 to 1.1 V vs. reverse hydrogen electrode (RHE) at a sweep rate of 100 mV/s.

Oxygen reduction reaction (ORR) measurements were conducted in an O_2 saturated 0.1 M $HClO_4$ (Sigma Aldrich) solution between 0.05 to 1.1 V vs. RHE at a sweep rate of 20 mV/s. iR compensation and background subtraction are applied for ORR curves following the protocol in previous literature.



Au Electrodes with PMMA Window

Patterned PtNWs Film

PtNWs Device with PMMA Electrochemical Window

Figure S1. Schematic illustration platinum nanowires (PtNWs) device fabrication (top) for on-chip electrochemical and ETS measurements and corresponding optical images (bright field, middle; dark field, bottom). Scale bars in the optical images are 10 μm.

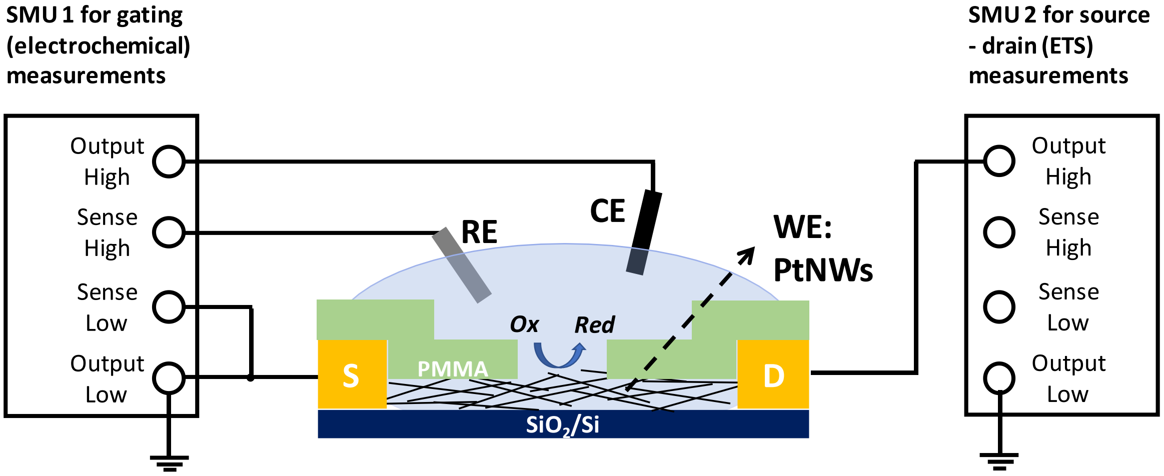


Figure S2. Schematic illustration of on-chip electrochemical and ETS measurements configuration.

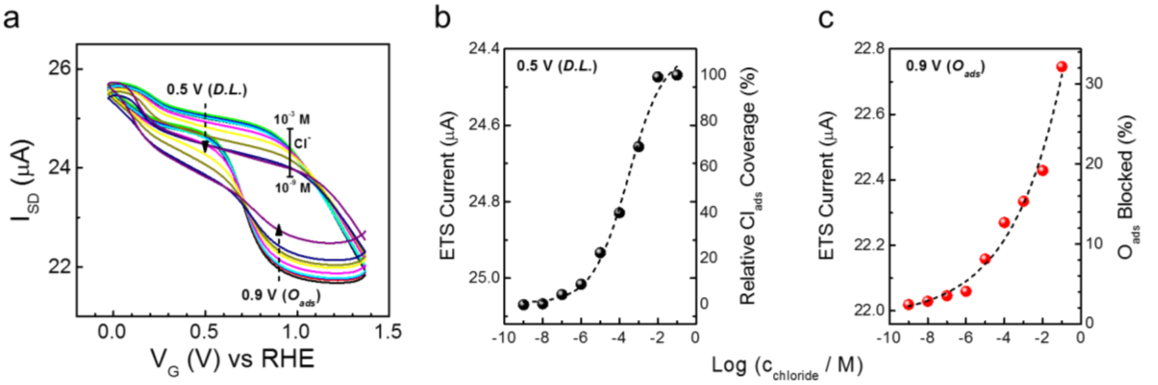


Figure S3. Quantitative ETS analysis of chloride adsorption on Pt surface. a, ETS characteristics of a typical PtNWs device in 0.1M $HClO_4$ and in presence of chloride anions with increasing concentrations from 10^{-9} to 10^{-3} M (indicated by solid line mark). Dashed arrows indicate the reading position of ETS currents in response to the effect of chloride specific adsorption in double layer (at 0.5 V) and oxide regions (at 0.9 V) that are plotted in **b** and **c**, respectively. Quantitatively derived surface coverage of Cl_{ads} at the D.L. region and percentage of blocked O_{ads} by Cl_{ads} in oxide region are given at the corresponding right axis in **b** and **c**, respectively.

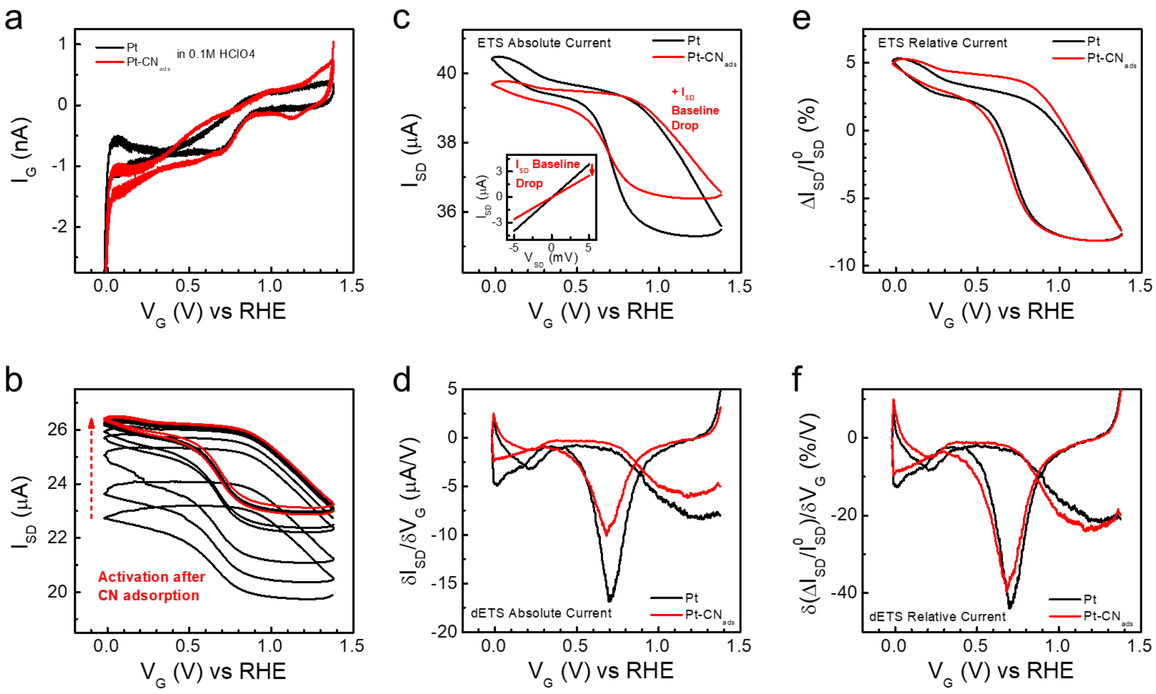


Figure S4. ETS of cyanide adsorption (formation of a cyanide adlayer) on Pt surface. **a,** On-chip CV characteristics of ETS characteristics of clean PtNWs (black) and PtNWs modified by a surface cyanide adlayer (blue) in 0.1 M HClO$_4$. **b,** ETS evolution of a cyanide treated PtNWs device in 0.1 M HClO$_4$ that eventually reached a stable Pt-CN$_{ads}$ characteristic. Dashed arrows indicate the change of ETS. **c,** ETS characteristics (absolute current value) of clean PtNWs (black) and PtNWs modified by a surface cyanide adlayer (blue) in 0.1 M HClO$_4$. Due to the scattering of CN$_{ads}$, the baseline conductivity of PtNWs-CN$_{ads}$ is smaller compared to the PtNWs with clean surface. Inset depicts the I-V measurements of PtNWs before and after cyanide adsorption. For better comparison between ETS characteristics of PtNWs and PTNWs-CN$_{ads}$, the ETS curve of PtNWs-CN$_{ads}$ (blue) is corrected by adding such current drop back to the ETS result. **d,** Differentiated ETS (dETS) results (absolute current value) of clean PtNWs (black) and PtNWs modified by a surface cyanide adlayer (blue) in 0.1 M HClO$_4$. **e,** ETS characteristics (relative current change) of clean PtNWs (black) and PtNWs modified by a surface cyanide adlayer (blue) in 0.1 M HClO$_4$, no correction is required for comparison. **f,** Differentiated ETS (dETS) results (relative current change) of clean PtNWs (black) and PtNWs modified by a surface cyanide adlayer (blue) in 0.1 M HClO$_4$. From these results (the difference observed in absolute current value and in relative current change, as well as the highly consistent ETS results of PtNWs and PtNWs-CN$_{ads}$ expressed in relative current change), it can be concluded that surface adsorbed cyanide adlayer blocks the general electrochemical surface reactions of bonded Pt sites, but does not alter the redox behavior of unbounded Pt sites.

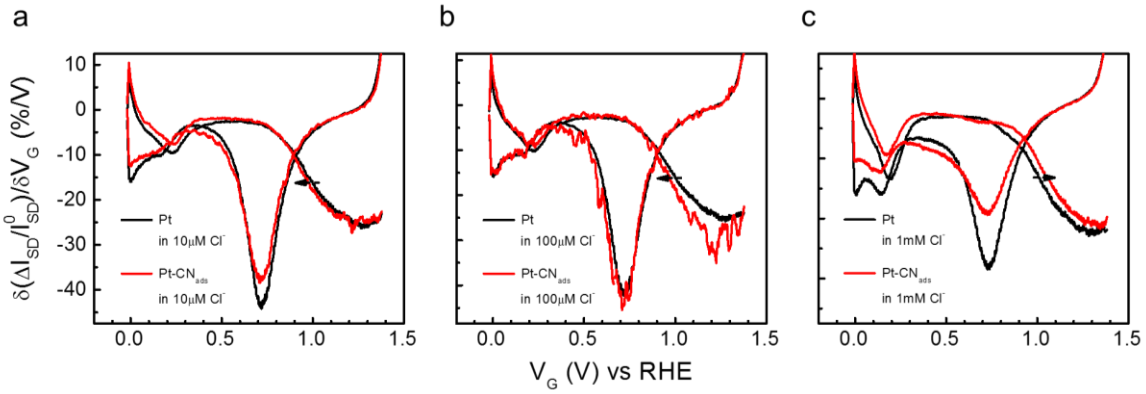


Figure S5. ETS measurements of chloride adsorption at different concentrations on clean and cyanide modified PtNW surface. a-c, ETS characteristics of clean PtNWs (green) and PtNWs modified by a surface cyanide adlayer (blue) in 0.1 M $HClO_4$ and 10 µM (**a**), 100 µM (**b**) and 1 mM (**c**) Cl^-. Dashed arrows indicate the effect of CN_{ads} on the Cl_{ads} ETS indicator (O_{ads} peak potential shift). For lower Cl^- concentrations at 10 and 100 µM, the potential shifts can be partially reversed by CN_{ads}; for higher Cl^- concentrations at 1 mM, the potential shift cannot be reversed.

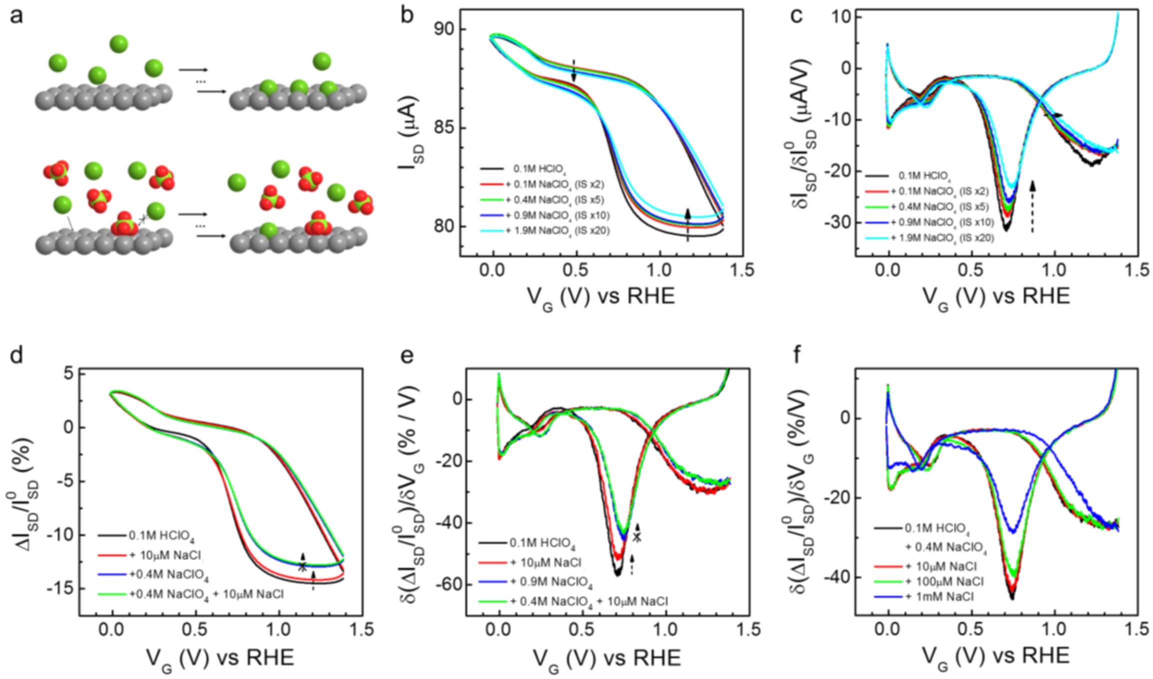
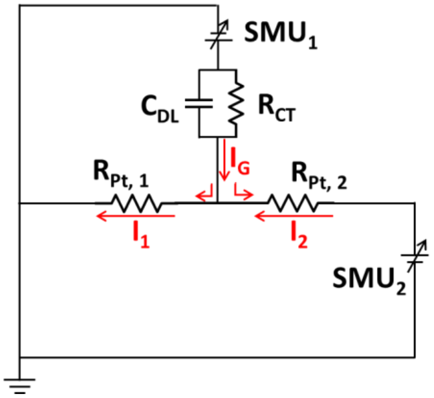


Figure S6. Electrical transport spectroscopy (ETS) of perchloride adsorption and competition with chloride on Pt surface. a, Schematic illustration of enhanced Cl^- resistance through "dynamic" competitive surface adsorption. Cl^- accumulation is suppressed by high concentration of perchloride anions. Pt atoms are grey, O atoms are red, and Cl atoms are dark green. **b-c,** ETS (**b**) and dETS (**c**) characteristics of a typical PtNWs device in 0.1 M $HClO_4$ (black) and with addition of varying concentrations (from 0.1M to 1.9M) of perchloride anions. Dashed arrows indicate the change of ETS or dETS results by the effect of perchloride adsorption. The ETS results reveal that even though it has been identified as a weakly adsorbed anion, high concentrations of ClO_4^- still show adsorption on the Pt surface, causing anionic competition in O_{upd} region. **d-e,** ETS (**d**) and dETS (**e**) characteristics of Cl^- (10 µM) adsorptions on PtNWs in 0.1 M $HClO_4$ (black to red) and 0.1 M $HClO_4$ + 0.4 M $NaClO_4$ (blue to green). Dashed arrows show the lack of Cl_{ads} features in 0.4 M $NaClO_4$ containing electrolyte. **f,** ETS characteristics of PtNWs in 0.1M $HClO_4$ with addition of 0.4M perchloride anions (black) and 10 µM, 100 µM and 1 mM of Cl^-.



$$I_{sd} = I_2 + I_g/2$$

Figure S7. Equivalent circuit model of the ETS measurement. The contributions of I_G to I_{SD} during the measurement can be properly deducted by the equations on the right. For a typical measurement in this study, the Gate (Faradaic) current is generally several orders of magnitude smaller than the ETS current (I_G ~1 nA and I_{SD} ~50 µA). Therefore, the on-chip CV current does not affect the ETS current and no additional background subtraction or other mathematical treatment is needed before the data analysis. In rare case when the electrochemical I_G is significant enough to affect the accuracy of I_{SD}, the presented equivalent circuit can be used to subtract the I_G background from the ETS (I_{SD}) channel.

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