Supporting Information

The Deactivation and Regeneration of Benchmark Pt/C Catalyst toward Oxygen Reduction Reaction in Presence of Poisonous SO₂ and NO

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Experimental Section

Chemicals and materials. Perchloric acid ($HClO_4$, Aladdin, analytically pure), commercial Pt/C catalyst (20 wt%, Johnson Matthey Corp, Vulcan carbon XC-72, product code: Hispec 3000, analytically pure), anhydrous sodium sulfite (Na_2SO_3, Dupont, analytically pure), sodium nitrite ($NaNO_2$, Dupont, analytically pure), 5.0 wt% Nafion aqueous solution (Dupont) were purchased and used without further purification. Deionized water (18.2 MΩ cm, Mill-Q Corp.) was used in all the experiments.

Electrochemical measurements. All the electrochemical measurements were conducted in a three-electrode system equipped with a Pine AFMSRX disk rotator and an electrochemical workstation (CH Instruments Inc.) at room temperature (25 °C). A Pt foil and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The catalyst ink was prepared by ultrasonically dispersing 12 mg of the catalyst in the solvent containing 9 mL water, 3 mL isopropanol alcohol and 12 μL Nafion (5 wt%). The ratio of ionomer-to-catalyst is 1:21.7. The working electrode was prepared by dropping 10 μL of the catalyst ink onto a glassy carbon rotating disk electrode (RDE) (geometric area: ~0.196 cm^2) followed by drying it at room temperature in air to yield a smooth thin film that covered the entire electrode surface. The ORR kinetic current density of catalyst was calculated according to Koutecky-Levich equation, as shown in equation. S1

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \qquad (S1)$$

where i, i_k and i_d represent the current of apparent current density, kinetic current

density and limited diffusion current density, respectively.

The procedures to complete the SO_2 adsorption (poisoning) on Pt surfaces were reported in our previous publication.[1] There is an equilibrium between SO_3^{2-} and SO_2 in sulfur dioxide stock solution (0.1 M Na_2SO_3 + 0.1 M $HClO_4$); the equilibrium equations are

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+ \qquad pKa=1.82 \qquad (S2)$$

$$HSO_3^- + H^+ \rightleftharpoons SO_3^{2-} + 2H^+ \qquad pKa=7.26 \qquad (S3)$$

According to the chemical equilibrium constants, it can be calculated that, in 0.1 M $HClO_4$ electrolyte, the concentration of SO_2 is millions of times that of SO_3^{2-}. Therefore, the primary S-containing species are SO_2 molecules, so that the actual concentration of the SO_2 can be calculated on the basis of the total amount of S(IV) initially dissolved in the stock solution. Then the stock solution was diluted to different concentrations by deoxygenated 0.1 M $HClO_4$ electrolyte and homogenized by bubbling Ar. The Pt/C catalyst was poisoned by holding the electrode at 0.65 V in the 1 mM Na_2SO_3 + 0.1M $HClO_4$ electrolyte for 1 min, which was denoted as s-Pt/C.

The NO-poisoned Pt/C was prepared by a similar method and denoted as n-Pt/C, i.e., holding the electrode at 0.65 V in the 1 mM $NaNO_2$ + 0.1 M $HClO_4$ electrolyte for 1 min.[2, 3] Pt electrode immersed in acidic $NaNO_2$ solution can catalyze the following reactions S4-5, resulting in the formation of NO adsorption layer on the electrode surface. This method has been widely used to pre-adsorb NO monolayer on Pt group metal surfaces.[4]

$$HNO_2 + H^+ + e^- \rightarrow NO + H_2O \qquad (S4)$$

$$3HNO_2 \rightarrow NO_3^- + 2NO + H_3O^+ \qquad (S5)$$

For the SO_2 and NO coadsorption experiment, the electrode was held at 0.65 V in a

mixed electrolyte consisting of Na_2SO_3, $NaNO_2$ and 0.1M $HClO_4$ for 1 min. The concentration of Na_2SO_3 was fixed as 1 mM while that of $NaNO_2$ was x times of Na_2SO_3. The corresponding electrode was denoted as s_1n_x-Pt/C. The poisoned Pt/C electrodes were then rinsed with water and immersed into fresh 0.1 M $HClO_4$ electrolyte for further tests. All the potentials were reported with respect to the reversible hydrogen electrode (RHE) in this work. The potential of Ag/AgCl electrode vs. RHE was determined by a two-electrode system where Ag/AgCl electrode was used as the working electrode, the platinum plate with saturated hydrogen (i.e., RHE) was used as the counter and reference electrode.

In-situ **ATR-SEIRAS.** A Nicolet iS50 FT-IR spectrometer equipped with a liquid nitrogen-cooled MCT detector was used for *in-situ* SEIRAS measurements and was operated at an incident angle of ca. 65° with the optical accessory developed by Shanghai Yuanfang Technology Co. Ltd. A Pt film electrodeposited on Au/Si was used as the working electrode, which was reported in details previously.[5] An SCE and a Pt mesh were used as the reference and counter electrodes, respectively. Real-time spectra were collected during the potential sweep at 5 mV s^{-1} at a resolution of 4 cm^{-1}. All of the spectra in this paper are shown in absorbance units defined as $-\log (I/I_0)$, where I and I_0 represent the intensities of the reflected radiation of the sample and reference spectra, respectively. All of the experiments were performed at room temperature.

Transmission electron microscopy (TEM). TEM images were taken on an FEI Tecnai G2F30 with an acceleration voltage of 300 kV.

Computational method. The modeling and theoretical simulation were carried out

using Density Functional Theory (DFT) with a plane-wave based pseudopotential formalism. Exchange correlation effects were described self-consistently using the generalized gradient approximation (GGA-PBE). Bulk platinum was established based on a face-centered cubic structure with a lattice parameter of 3.97Å. 4*4 supercells were constructed to avoid adsorptive molecular interactions. Pt(111) surface was separated from its periodic images by a vacuum space of 15 Å. We used a plane-wave cutoff energy of 300 eV and a $(8 \times 8 \times 1)$ Monkhorst-Pack mesh of k points to sample the Pt(111). The adsorption energy of SO_2 was calculated as

$$E_{ads} = -\left(E_{SO_2 - Pt(111)} - E_{Pt(111)} - E_{SO_2}\right)$$

(1)

where $E_{SO_2 - Pt(111)}$, $E_{Pt(111)}$, E_{SO_2} are the energies of the SO_2 molecule adsorbed on the Pt(111) surface, the Pt(111) surface, and the SO_2 molecule in the gas phase, respectively.
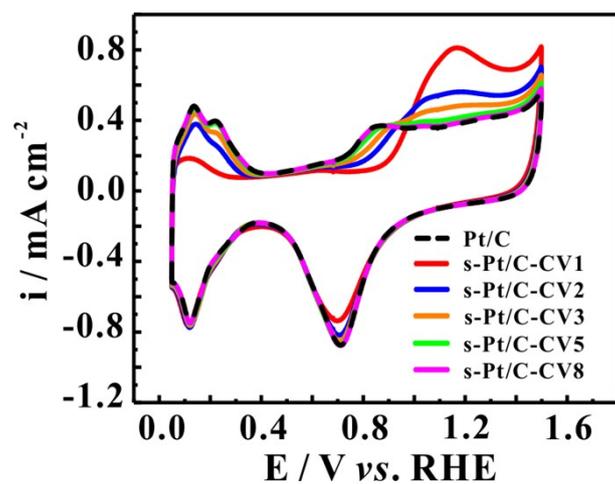
Figure S1 CV curves of a fresh Pt/C and an s-Pt/C in an Ar-saturated 0.1 M HClO$_4$ solution at a scan rate of 50 mV s^{-1}.
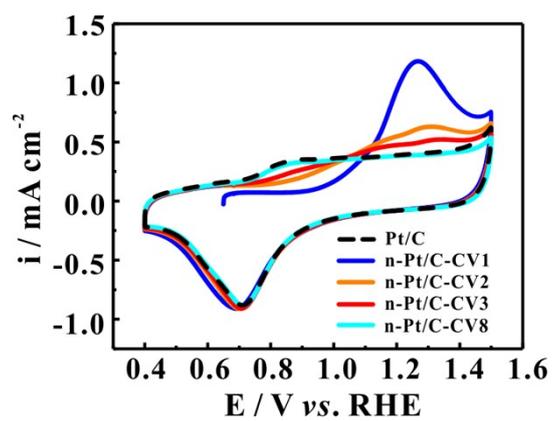
Figure S2 CV curves of fresh Pt/C and n-Pt/C catalysts in Ar-saturated 0.1 M HClO$_4$ solution at a scan rate of 50 mV s^{-1}: the potential scan procedure is 0.65 V→1.5 V→0.4 V.
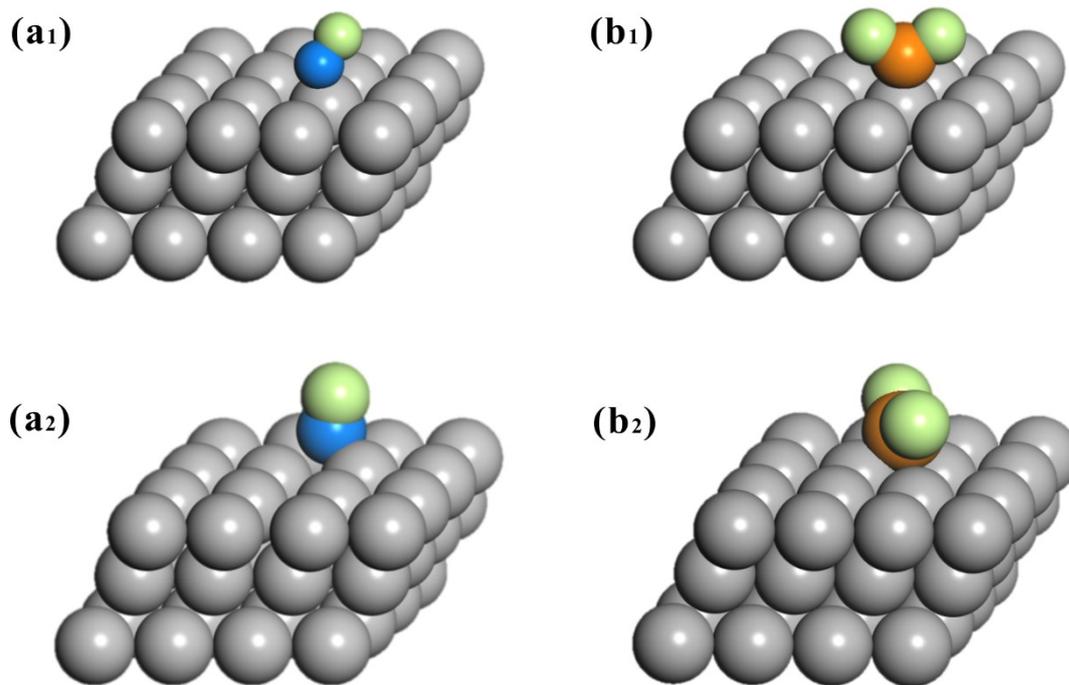
Figure S3 Diagrams of Pt(111) surface shown with two adsorption structures for SO_2 and NO, where a, b correspond to the atop site and bridge site. Gray, yellow, blue and green balls represent Pt, S, N and O atoms, respectively (The ball size does not represent the actual atomic size).
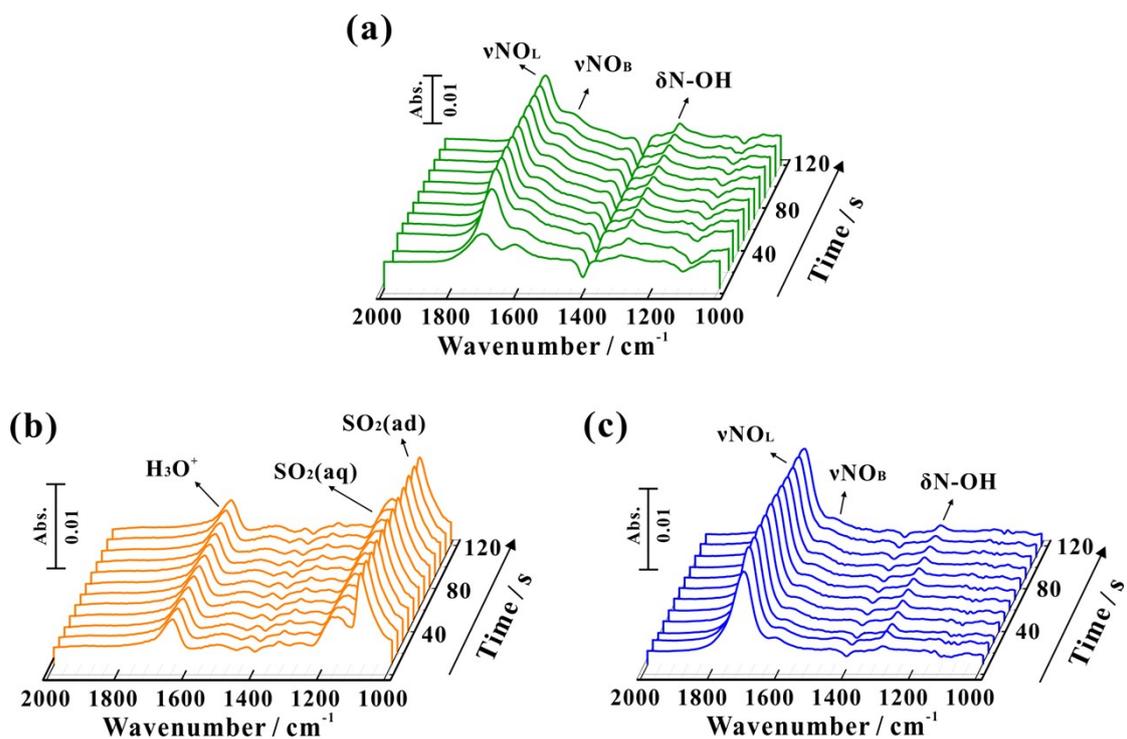
Figure S4 *In situ* ATR-SEIRA spectra of polycrystalline Pt electrode at 0.65 V in (a) 0.1 M HClO$_4$ + 1mM Na$_2$SO$_3$ + 3mM NaNO$_2$; (b) 0.1 M HClO$_4$ + 1mM Na$_2$SO$_3$ and (c) 0.1 M HClO$_4$ + 1mM NaNO$_2$ solution. The reference spectrums were taken at 0.65 V in 0.1 M HClO$_4$.
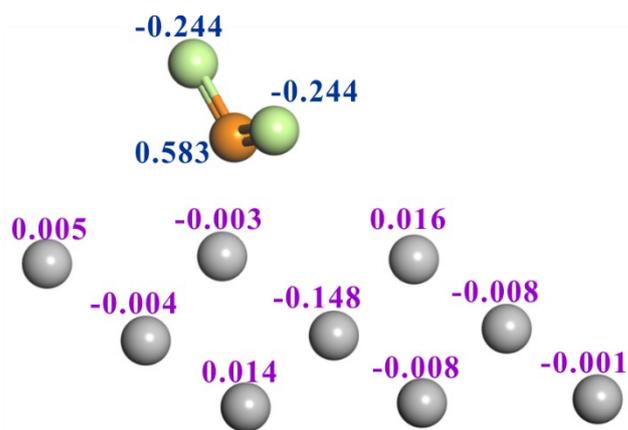
Figure S5 Charge distribution for SO_2/Pt(111) (The ball size does not represent the actual atomic size).
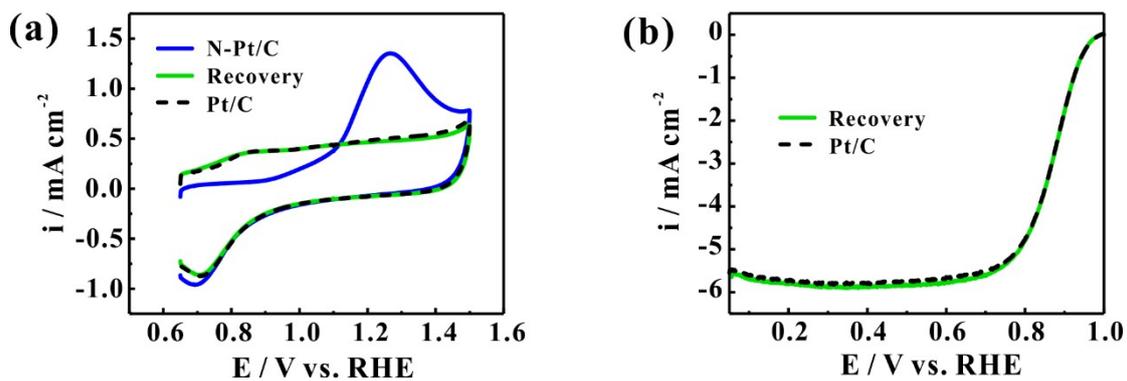
Figure S6 (a) CV curves of fresh Pt/C, n-Pt/C and n-Pt/C after potentiostatic at 0.2 V for 5 s (Recovery) in Ar-saturated 0.1 M HClO$_4$ solution at a scan rate of 50 mV s^{-1}: the potential scan procedure is 0.65 V→1.5 V→0.65 V; (b) LSV curves of fresh Pt/C and N-Pt/C after potentiostatic at 0.2 V for 5 s (Recovery) (scan rate:10 mV s^{-1}) in O$_2$-saturated 0.1 M HClO$_4$ solution at a rotation rate of 1600 rpm.

Table S1. IR Peak Assignments in this work

Wavernumber (cm^{-1})	Assignment
~1710	Linear-bonded NO (NO$_L$) on Pt(111) [2, 6]
~1630	Bridge-bonded NO (NO$_B$) on Pt(100) [2, 6]
~1610	δ(HOH) of interfacial water [6, 7]
~1285	δ(N–OH) bending of adsorbed HNO$_2$ [9]
~1460	δN–H mode of dissolved NH$_4^+$ [2, 10]
~1330	Asymmetric N–O stretching of NO$_3^-$ in solution [2]
~1091	S-O stretching of adsorbed SO$_2$ [11-13]
~1170	Symmetric S-O stretching of SO$_2$ in solution [11-13]
~1650	Interfacial hydronium (H$_3$O$^+$) [7]

Supplementary References

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