Electronic Supplementary Information

A phosphate tolerant Pt-based oxygen reduction catalyst enabled by synergetic modulation of alloying and surface modification

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Experimental Section

Materials

Commercial Pt/C (40% purchased from Johnson Matthey), ammonium molybdate and ethanol (Chongqing Chuandong Chemical Co., Ltd.), dopamine hydrochloride (Sigma-Aldrich), tris(hydroxymethyl)aminomethane (MERDA technology Co., Ltd. USA), ethylene glycol and perchloric acid (Chengdu Kelong Chemical Reagent Factory), (HClO$_4$ AR), phosphoric acid (Shanghai aladdin biochemical technology Co., Ltd.), deionized water (purification system from Chongqing Huachuang Water Treatment Engineering Co., Ltd.).

All chemical reagents were analytically pure and were used as received without the further purification.

Equipment: magnetic stirrer (Shanghai Meiyingpuyi instrument manufacturing Co., Ltd), vacuum drying oven (Shanghai Qixin science instrument Co., Ltd), vacuum pump (Chongqing Dongyue instrument Co., Ltd), high temperature tube furnace OTF-1200X (Hefei Kejing group), muffle furnace KSL-1200X (Hefei Kejing group).

Preparation of Pt$_3$Co@MoO$_x$-NC

Typically, 20 mL ethylene glycol was added to the mixture of 1.5 g JM Pt/C (40%) and 2 mL H$_2$O. Then 12.88 g ammonium molybdate was added to the mixture with vigorous stirring for 20 min. The mixture was transferred to a round-bottomed flask and followed by an oil bath treatment at 180°C for 3 h. After the mixture cooled down to room temperature, the obtained Pt/C@MoO$_3$ was washed with deionized water and finally dried under vacuum at 60 °C for 12 h. To fabricate a polydopamine coating layer, 200 mg of Pt/C@MoO$_3$ was weighed and put into a beaker. Then, 20 mL tris-HCl solution (0.3 g tris(hydroxymethyl)aminomethane dissolved in 50 mL water）and 40 mg dopamine were added to the beaker with vigorous stirring for 12 h. Then, a certain amount of CoCl$_2$ was added to the solution and stirred for another 12 h. Then the resulting Pt/C@MoO$_x$@PDA@Co^{2+} was further pyrolyzed under 700 °C in the atmosphere of 10% H$_2$/90% N$_2$. After the tube furnace cooling down to room temperature, the obtained Pt$_3$Co@MoO$_x$-NC product was washed with deionized water and finally dried under vacuum at 60 °C for 12 h. The Pt loading of Pt$_3$Co@MoO$_x$-NC is 36.3 wt% as determined by inductively coupled plasma mass spectrometry (ICP-OES:

Agilent 5110).

The reference sample Pt$_3$Co/C was obtained by impregnation reduction. Specifically, a certain amount of JM Pt/C was added to pure water and dispersed ultrasonically, then a certain amount of Co^{2+} was added. And the solution was then dried and the resulting powder was annealed under hydrogen to form an alloy of Pt and Co. The annealing conditions are the same as in the preparation of Pt$_3$Co@MoO$_x$-NC.

The reference sample Pt$_3$Co-NC was also prepared by using commercial Pt/C as precursor without deposition of MoO3 and followed by dopamine polymerization and absorption of Co2+. The Pt@PDA@Co/C was then annealed under the same conditions used for the preparation of Pt$_3$Co@MoO$_x$-NC. (as a reference to the electrochemical test)

To prepare Pt@MoO$_x$/C, an amount of MoO3 and JM Pt/C were added simultaneously to a round-bottomed flask containing ethylene glycol in it. The mixture was then heated to 180°C and stirred for 3h, cooled and filtered to obtain Pt@MoO$_x$/C. (as a reference to XPS)

Pt@MoO$_x$-NC was prepared by the same procedure as Pt$_3$Co@MoO$_x$-NC, except that Co2+ and PDA were not added. (as a reference to the electrochemical test)

To prepare Pt@NC/C, a certain amount of JM Pt/C was weighed as precursor and then coated with PDA. The preparation conditions are the same as for the preparation of Pt$_3$Co@MoO$_x$-NC. Then, the obtained Pt@PDA@C was annealed to obtain Pt@NC/C. The annealing conditions are the same as before. (as a reference to the electrochemical test and XPS)

Characterization

X-ray diffraction data were collected on a Shimadzu X-ray diffractometer (model 6000) using Cu Kα radiation at a step rate of 5°/min. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations were carried out on FEI Tecnai F20 operated at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific K-Alpha. The C 1s peak (284.8 eV) was employed as the reference standard.

Electrochemical measurements

All electrochemical tests were performed by employing a Princeton electrochemical workstation (Versa STAT 4) in a 3-electrode cell with a glassy carbon rotating disk (working electrode), carbon rod (counter electrode) and Ag/AgCl (reference electrode). Before each measurement, the potential of the Ag/AgCl electrode was calibrated and then converted to a reversible hydrogen electrode (RHE).

2 mg of Pt$_3$Co@MoO$_x$-NC (Pt 36% wt.) and JM Pt/C 40% (Pt loading = 36% wt. measured by ICP) were weighed respectively. The catalyst was then transferred to a 10 mL centrifuge tube and 800 μL ethanol was added. The suspension was treated with ultrasound to uniformly disperse the catalyst. After 10 min, 10 μL Nafion (5 wt%) was added to the tube and underwent ultrasonic treatment for another 10 min. Finally, 8 μL inks of Pt/C and Pt$_3$Co@MoO$_x$-NC were deposited on the working electrode

respectively (Pt loading = 7.2 µg).

The cyclic voltammetry (CV) was performed in N_2 saturated 0.1 M $HClO_4$ at a scan rate of 50 mV/s. The CO stripping curves were obtained using the same procedure of CV except that the scan rate was changed to 10 mV/s. The linear sweep voltammetry (LSV) was performed in O_2 saturated 0.1 M $HClO_4$ at 10 mV/s, 1600 rpm for the ORR test.

The specific kinetic current densities (J_k) associated with the intrinsic activity of catalysts was calculated by the following equation:

$$J_k = \frac{J * J_D}{J_D - J}$$

Where J is the measured current density at 0.9 V (vs. RHE), J_D is the diffusion-limited current density, respectively.

The mass activity (MA) is calculated by the following equation:

$$MA = \frac{J_K * 0.19625}{[Pt]}$$

Where the constant 0.19625 is the area of working electrode, [Pt] is the mass of Pt on the working electrode.

The electrochemical surface area (ECSA) was obtained by the following equation

$$ECSA\text{-}CO = \frac{Q_{CO}}{0.42\text{mC/cm}^2 * [Pt]}$$

$$ECSA\text{-}H_{upd} = \frac{Q_{H2}}{0.42\text{mC/cm}^2 * [Pt]}$$

Where Q_{CO} is the integrated charge of CO stripping peak area. $Q_{H\text{-}upd}$ is the integrated charge of H_2 area after reducing the current of electrical double layer. 0.21 mc/cm^2 is the charge of monolayer adsorption of hydrogen on Pt. 0.42 mc/cm^2 is the electrical charge associated with monolayer adsorption of CO on Pt. [Pt] is the mass of Pt on the working electrode.

The specific activity (SA) is calculated by the following equation:

$$SA = j_k / \frac{Q_{CO}}{0.42\text{mC/cm}^2}$$
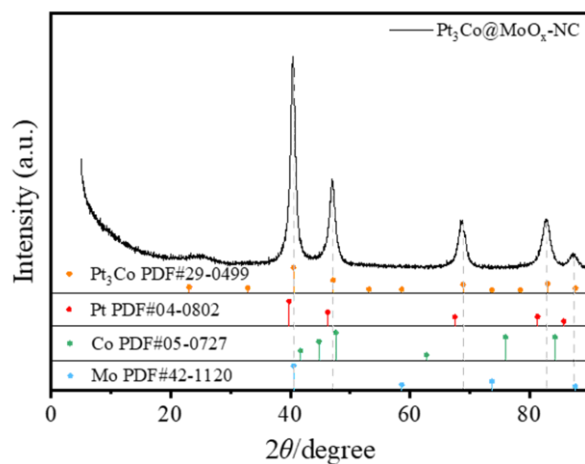
Figures and table
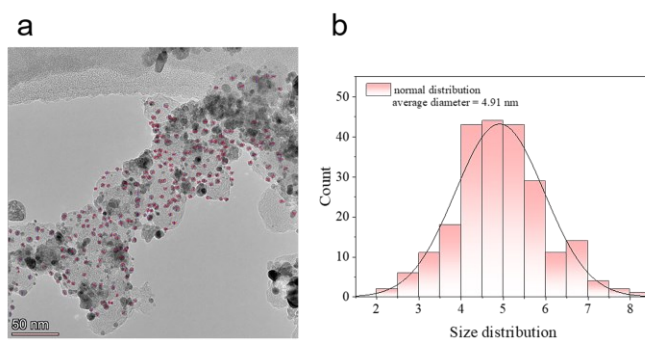

Figure S1. The XRD pattern of $Pt_3Co@MoO_x$-NC.

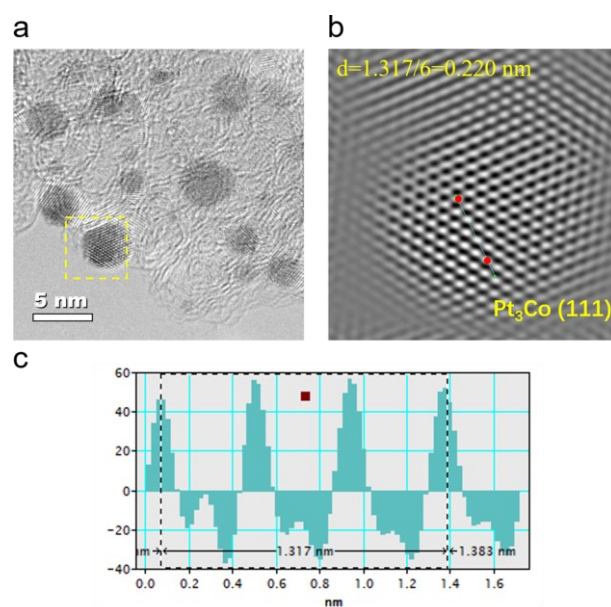Figure S2. The TEM image of $Pt_3Co@MoO_x$-NC and the corresponding size distribution histogram.

Figure S3. The HRTEM image of a Pt particle in $Pt_3Co@MoO_x$-NC and the corresponding lattice spacing.
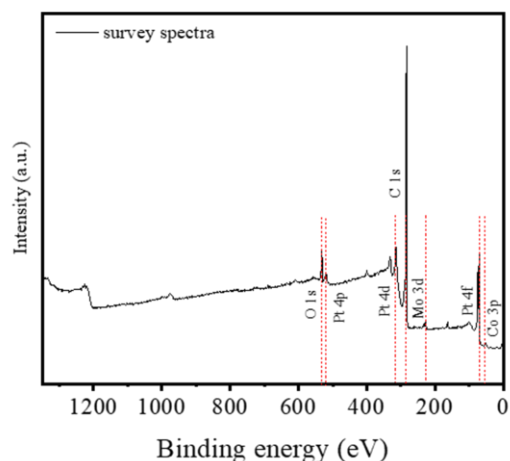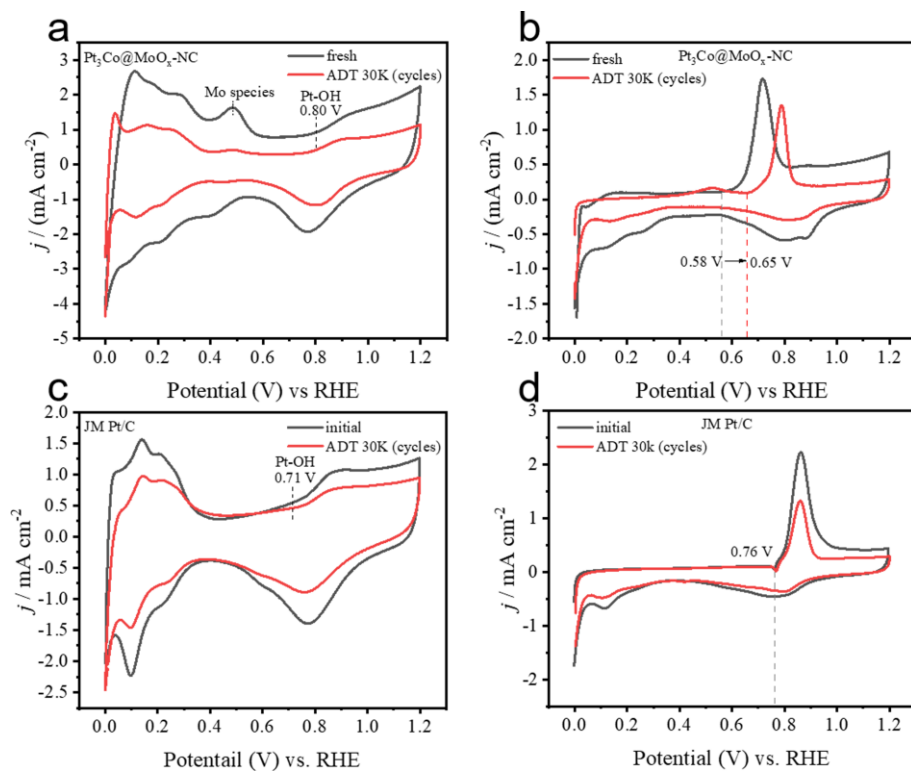
Figure S4. The XPS survey spectrum of $Pt_3Co@MoO_x$-NC.

Figure S5. (a) The CV curves for $Pt_3Co@MoO_x$–NC before and after ADT. (b) The CO stripping curves for $Pt_3Co@MoO_x$–NC before and after ADT. (c) The CV curves for JM Pt/C before and after ADT. (d) The CO stripping curves for JM Pt/C before and after ADT.
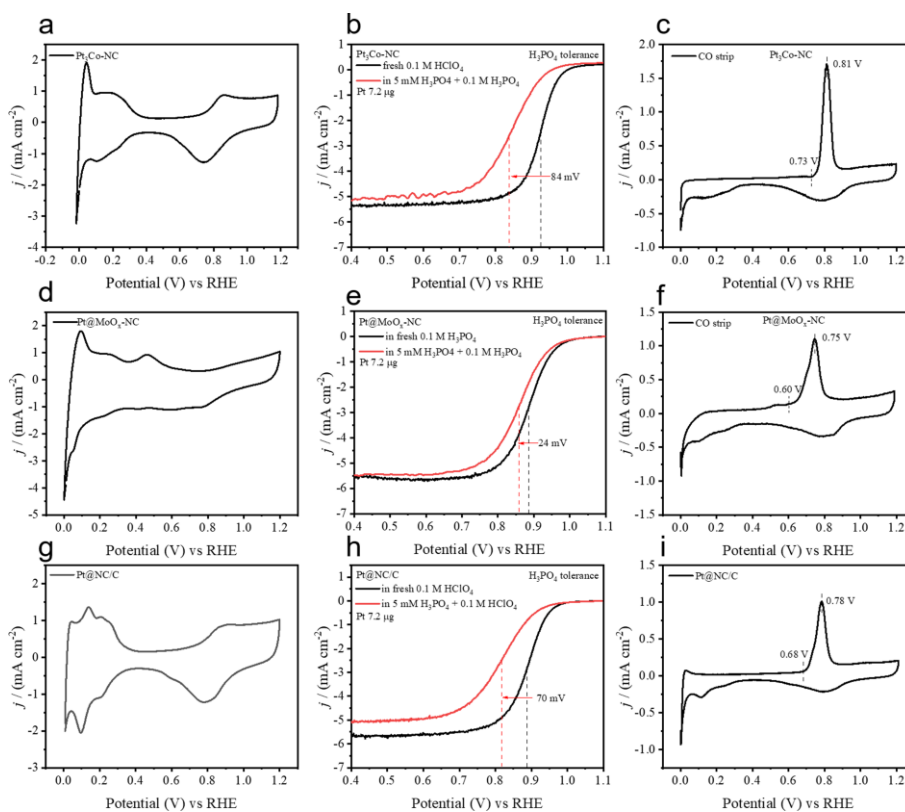
Figure S6. (a, d, g) The CV curves of Pt₃Co-NC, Pt@MoOₓ-NC and Pt@NC/C in 0.1M HClO₄. (b, e, h) The ORR polarization curves of Pt₃Co-NC, Pt@MoOₓ-NC and Pt@NC/C in 0.1M HClO₄ and 0.1M HClO₄ + 5 mM H₃PO₄. (c, f, i) The CO stripping curves of Pt₃Co-NC, Pt@MoOₓ-NC and Pt@NC/C.

Table S1. The MA, SA and ECSA of different catalysts under different conditions.

Catalysts	MA fresh (A/mg)	MA ADT (A/mg)	MA in H_3PO_4 (A/mg)	SA fresh (mA/cm²)	SA ADT (mA/cm²)	SA in H_3PO_4 (mA/cm²)	ECSA-CO fresh (m²/g)	ECSA-CO ADT (m²/g)	ECSA-H₂ fresh (m²/g)	ECSA-H₂ ADT (m²/g)
Pt₃Co@MoOx-NC	0.62	0.41	0.25	0.89	0.92	0.35	69.8	44.6	64.7	54.2
JM Pt/C	0.21	0.10	0.04	0.42	0.41	0.072	55.3	25.5	57.2	33.3
Pt@NC/C	0.10	N/A	0.02	0.27	N/A	0.053	37.1	N/A	66.1	N/A
Pt₃Co-NC	0.32	N/A	0.03	0.60	N/A	0.055	52.8	N/A	68.7	N/A
Pt@MoO₃-NC	0.096	N/A	0.05	0.22	N/A	0.11	44.2	N/A	67.1	N/A