

Acid-Stable CoWO₄/WO₃-Microrod Coated by a Thin Carbon-Layer as Efficient Pt Co-Catalysts for Methanol Oxidation and Oxygen Reduction

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Synthesis of Pt-CoWO₄/WO₃@NCL-mr Composites

100 mg of CoWO₄/WO₃@NCL-mr was ultrasonically dispersed in aqueous chloroplatinic acid (H₂PtCl₆·6H₂O, A.R.) solution for 15 min to obtain a uniform suspension. Then, pH of the suspension was adjusted to 10 using 1.0 M NaOH solution. Excessive sodium borohydride (NaBH₄, A.R.) solution was used as a reducing agent and the Pt-species in the suspension was slowly reduced at room temperature with vigorous stirring. The suspension was stirred for another 6 h and then allowed to stand for overnight. Next, it was washed with deionized water and ethanol for several times (centrifugation at 4000 rpm) to remove the residual Na⁺ ions and adsorbed water, respectively. The rinsed precipitate was finally desiccated at 40 °C to obtain the catalyst, which was marked as Pt-CoWO₄/WO₃@NCL-mr-X (X = 750, 800, 850 and 900).^[1]

Materials Characterizations

X-ray diffraction (XRD), scanning electron microscopy (SEM), N₂ adsorption/desorption isotherms, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the structure, morphology and composition of the samples. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2500 diffractometer using a CuK α radiation ($k = 1.5406$, 40 kV, 20 mA) under a step scan of 0.02°. Scanning electron microscope (SEM) images were taken at an acceleration voltage of 5.0 kV using an S-4800 scanning electron microscope (Japan). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained using a JEM-2100 electron microscope (JEOL). Surface composition analysis of the prepared catalyst was carried out using XPS (Kratos-AXIS UL TRA DLD, AlK α X-ray source), and the data were fitted using "XPS Peak" software. It was used to analyze the surface components of the catalyst by deconvolution of the C 1s, N 1s, O 1s, W 4f and Pt 4f spectra.^[2,3]

Electrochemical Measurements

All electrochemical tests were recorded at room temperature (25 °C) by a conventional three-electrode battery system with a computer controlled electrochemical workstation (CHI760E, Chenhua, Shanghai). A glassy carbon (GC) rotating disk electrode (RDE) (diameter 3 mm, area 0.07065 cm²) was used as the working electrode, while the reference electrode was a saturated calomel electrode (SCE, +0.2415 V vs. standard hydrogen electrode, 3.0 M KCl) and the counter electrode was a polished platinum sheet (1 cm²) electrode.^[2] All potentials reported in this work are compared to SCE. The catalyst ink was prepared by ultrasonically mixing 5.0 mg of Pt-CoWO₄/WO₃@NCL-mr-850 with 100 μ L of ethanol, 50 μ L of a 5 wt.% Nafion solution for 30 minutes. Then, for the MOR test, 2 μ L of the prepared ink suspension was dropped onto the smooth glassy carbon electrode surface, and a uniform film was formed under natural air-drying conditions. For the ORR test, 5 μ L of ink was dropped onto the electrode. The GC electrode was polished with the Al₂O₃ slurry and washed with deionized water and ethanol before each use. Commercial control Pt/C (10 wt.% Pt on Vulcan carbon black, Hesen Electric Co. Ltd, Shanghai, China) was used for all control catalysts.

MOR Measurements

For methanol oxidation, a three-electrode cell is used. A saturated calomel electrode (SCE) was used as a reference electrode, a counter electrode was a polished platinum plate (1 cm²) electrode, and a working electrode was a glassy carbon electrode (GCE). The MOR measurement was carried out in a 0.5 M H₂SO₄ aqueous solution containing 0.5 M CH₃OH. The electrochemically active surface area (ECSA) of the catalyst layer was measured in a 0.5 M H₂SO₄ electrolyte at a scan rate of 50 mV s⁻¹ over a potential range of -0.2 to 1.0 V. The ECSA was calculated using the H₂ adsorption-desorption region (as shown in equations (1) and (2)). Stability was estimated by studying the long-term durability of the catalyst in the selected solution by performing a recording chronoamperometry (CA) test in a 0.5 M H₂SO₄ aqueous solution for 3600 s. All CV curves were obtained at a sweep rate of 50 mV s⁻¹, with scanning the potential from -0.2 to 1.0 V vs. SCE and a pre-activated working electrode for 50 cycles. Electrochemical impedance spectroscopy (EIS) was carried out at a frequency range of 10⁵ at 0.62 V to 10⁻² Hz with a sinusoidal perturbation of 10 mV amplitude. For CO stripping experiments, CO was used to saturate a 0.5 M H₂SO₄ aqueous solution for 20 min, and then carried out at a scan rate of 10 mV s⁻¹. All used electrolytes were saturated with pure N₂ to remove dissolved oxygen, which was tested by using a portable oxygen sensing system (NeoFox sport, Ocean Optics).

$$\text{ECSA} = Q_{\text{H}} / (m \times 0.21) \quad (1)$$

$$Q_{\text{H}} = S / v \quad (2)$$

where, Q_{H} is the charge for HAD, S is the integral area of hydrogen stripping peak (AV) and v is the scanning speed (0.05 V s⁻¹); m is the platinum loading on the electrode (mg), and 0.21 is the charge required to oxidize the H₂ monolayer on a bright Pt (mC cm⁻²).^[2]

ORR Measurements

The CV test was carried out from a -0.2 to 1.0 V solution of 0.5 M H₂SO₄ saturated with O₂ at a sweep rate of 0.05 V s⁻¹. The LSV test was carried out in an O₂ saturated 0.5 M H₂SO₄ solution at an electrode speed of 1600 rpm (0.01 V s⁻¹). The tests for electrochemical impedance spectroscopy (EIS) were conducted at 0.8 V (RHE, 1600 rpm) in an O₂-saturated 0.5 M H₂SO₄ electrolyte. The measurement of the rotating disk electrode (RDE) was carried out in an O₂ saturated H₂SO₄ solution and at a scanning rate of 10 mV s⁻¹ and various

rotational speeds of 400 to 2500 rpm. The Koutecky-Levich (K-L) plots (j^{-1} vs. $\omega^{-1/2}$) were obtained in the potential range from 0.10 to 0.25 V according to the RDE results, which were used to calculate the electron transfer numbers (n) from the following equations (3) and (4):

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{nFkC_O} \quad (3)$$

$$B = 0.62nFC_OD_O^{2/3}u^{-1/6} \quad (4)$$

where j , j_L , and j_k are the measured current density, diffusion-limited current density, and kinetic current density, respectively; ω is the angular velocity of rotating electrode; F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$); and k is the electron-transfer rate constant. C_O is the bulk concentration of O_2 in 0.5 M H_2SO_4 ($C_O = 1.2 \times 10^{-6} \text{ mol cm}^{-3}$); D_O is the diffusion coefficient of O_2 in 0.5 M H_2SO_4 ($D_O = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and u is the kinematic viscosity of 0.5 M H_2SO_4 ($u = 0.01 \text{ cm}^2 \text{ s}^{-1}$).^[3]

Rotating ring disk electrode (RRDE) measurements were conducted at an electrode rotation speed of 1600 rpm with a scan rate of 10 mV s^{-1} . A constant ring potential was controlled at 1.2 V in O_2 -saturated 0.5 M H_2SO_4 solution. The electron transfer number (n) and hydrogen peroxide yield (H_2O_2 (%)) were obtained from RRDE voltammograms, determined by the following equations (5) and (6):

$$n = 4I_D/[I_D + (I_R/N)] \quad (5)$$

$$H_2O_2\% = 200(I_R/N)/[I_D + (I_R/N)] \quad (6)$$

Where I_D and I_R are the disk current and the ring current, respectively; N is the collection efficiency of H_2O_2 of Pt ring, and the value is 0.4.^[3]

Table S1. Electrochemically Active Surface Area (ECSA) Calculated from Cyclic Voltammetric Curves in Figure 4, R_{CT} (Ω), Onset Potential, Peak Potential, and Current Density of Commercial Pt/C and Five As-prepared Pt-CoWO₄/WO₃@NCL-Mr-X (X = 750, 800, 850 And 900) Catalysts in Acid Media

Catalysts	ECSA ($\text{m}^2 \text{g}^{-1}_{\text{Pt}}$)	R_{CT} (Ω)	Onset potential (V)	Peak potential (V)
Pt/C	114.47	89.02	0.335	0.569
Pt-CoWO ₄ /WO ₃ @NCL-mr-900	48.57	90.74	0.197	0.6036
Pt-CoWO ₄ /WO ₃ @NCL-mr-850	225.8	77.77	0.141	0.628
Pt-CoWO ₄ /WO ₃ @NCL-mr-800	15.7	129.31	0.362	0.571
Pt-CoWO ₄ /WO ₃ @NCL-mr-750	60.19	142.39	0.411	0.546

Table S2. Summarized Mass Activities for Pt-CoWO₄/WO₃@NCL-mr-850 and Other Recently-reported Catalysts

Catalysts	Conditions	Mass activity (mA mg ⁻¹ _{Pt})	References
Pt-CoWO ₄ /WO ₃ @NCL-mr-850	0.5MH ₂ SO ₄ +0.5MCH ₃ OH	2208	This work
Pt-Au/CNs(1: 0.1)	0.5MH ₂ SO ₄ +1.0MCH ₃ OH	566	4
@M-TiN/N-G(5)/Pt(13.5)	0.5MH ₂ SO ₄ +1.0MCH ₃ OH	739	5
Pd ₁ Pt ₄ DNS	0.1MHClO ₄ +1.0MCH ₃ OH	1660	6
PtRu NW	0.1MHClO ₄ +0.5MCH ₃ OH	820	7
Pt-Ni (trace)/GNs	0.5MH ₂ SO ₄ +1.0MCH ₃ OH	1009.98	8
CuPt _{2.22} NWs	0.1MHClO ₄ +0.5MCH ₃ OH	1710	9
Pt ₅ PdCu ₅	0.5MH ₂ SO ₄ +0.5MCH ₃ OH	970	10

Table S3. Onset Potentials, Half-wave Potentials (V vs. SCE) and Limiting Current Density of Pt/C and Pt-CoWO₄/WO₃@NCL-mr-850 for ORR

Catalysts	Onset potentials (V)	Half-wave potentials (V)	Limiting current density (mA cm ⁻²)
Pt-CoWO ₄ /WO ₃ @NCL-mr-850	0.54	0.46	-3.28
Pt/C	0.50	0.41	-4.87

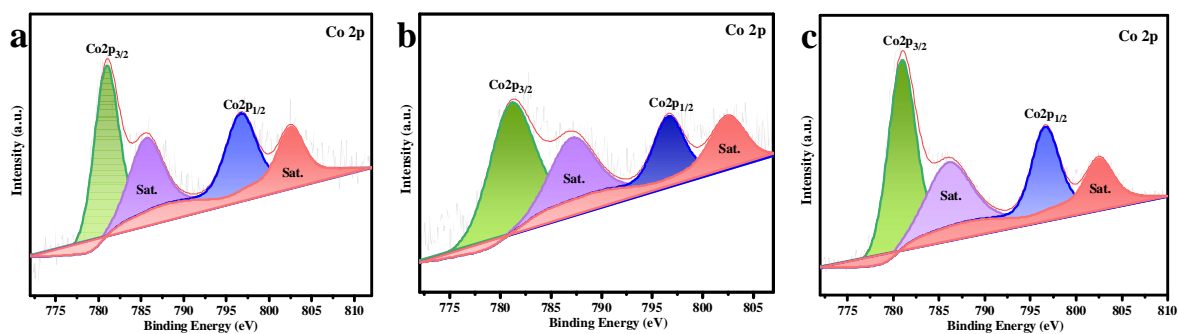


Figure S1. High resolution XPS spectra of Co 2p Pt-CoWO₄/WO₃@NCL-mr-750 (a), Pt-CoWO₄/WO₃@NCL-mr-800 (b) and Pt-CoWO₄/WO₃@NCL-mr-900 (c).

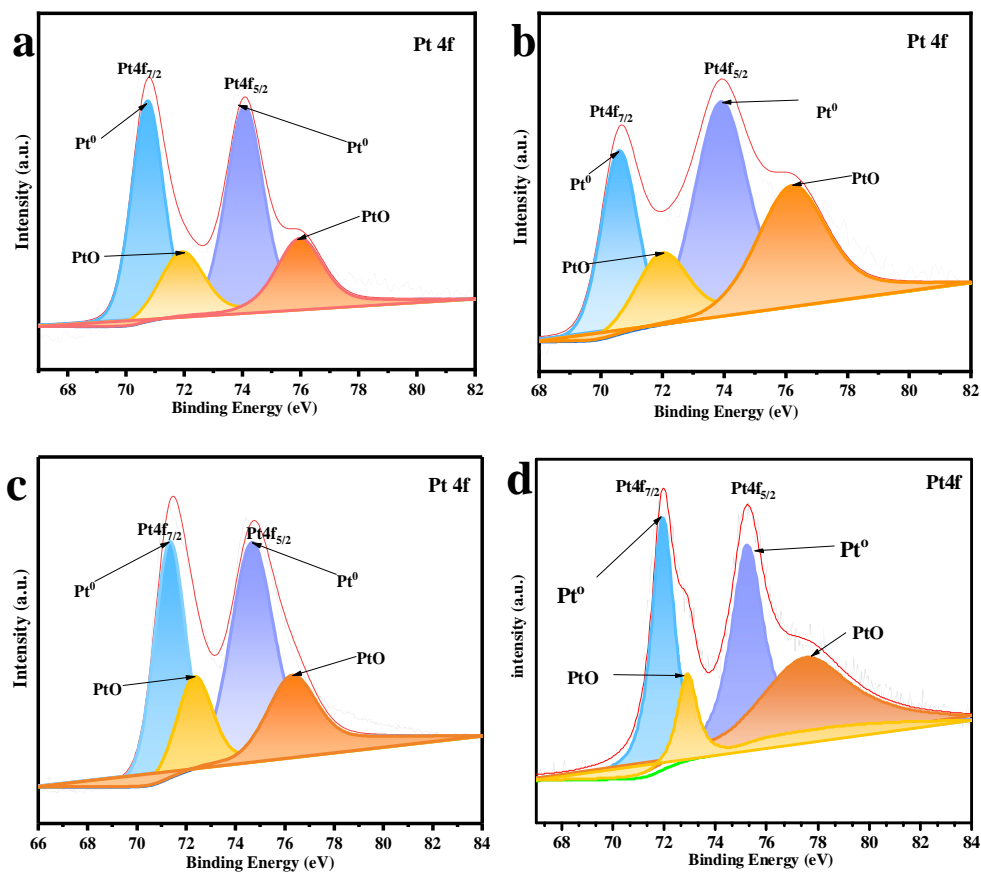


Figure S2. High resolution XPS spectra of Pt 4f Pt-CoWO₄/WO₃@NCL-mr-750 (a), Pt-CoWO₄/WO₃@NCL-mr-800 (b), Pt-CoWO₄/WO₃@NCL-mr-900 (c) and Pt/C (d).

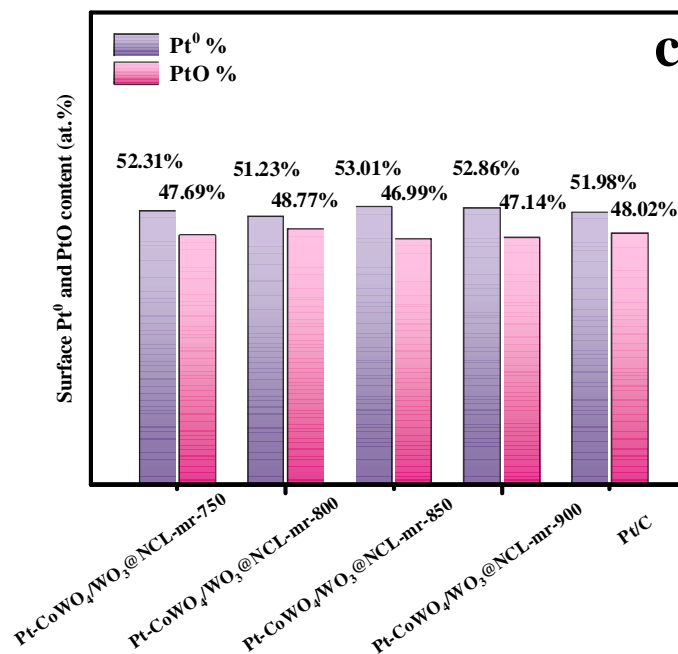


Figure S3. Percentage contents of Pt⁰ and PtO in Pt-CoWO₄/WO₃@NCL-mr-X (X = 750, 800, 850, 900 and Pt/C) (c).

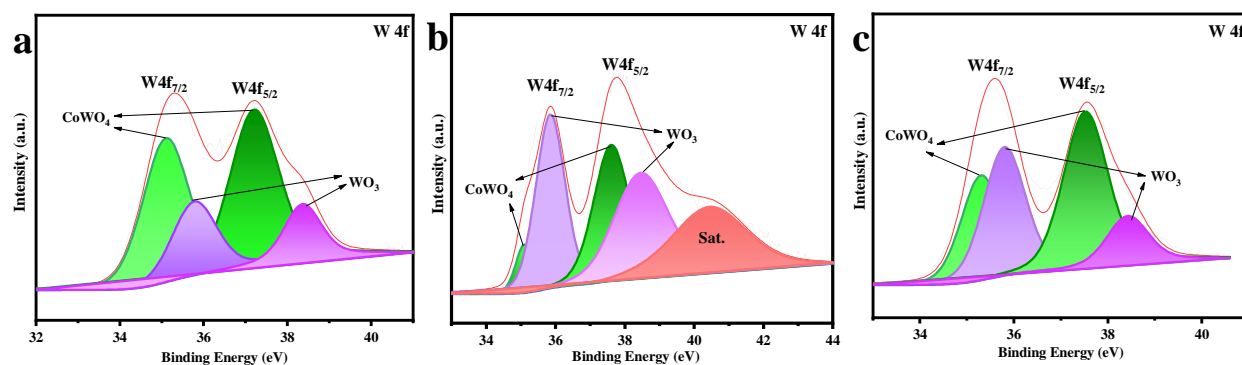


Figure S4. High resolution XPS spectra of W 4f Pt-CoWO₄/WO₃@NCL-mr-750 (a), Pt-CoWO₄/WO₃@NCL-mr-800 (b) and Pt-CoWO₄/WO₃@NCL-mr-900 (c).

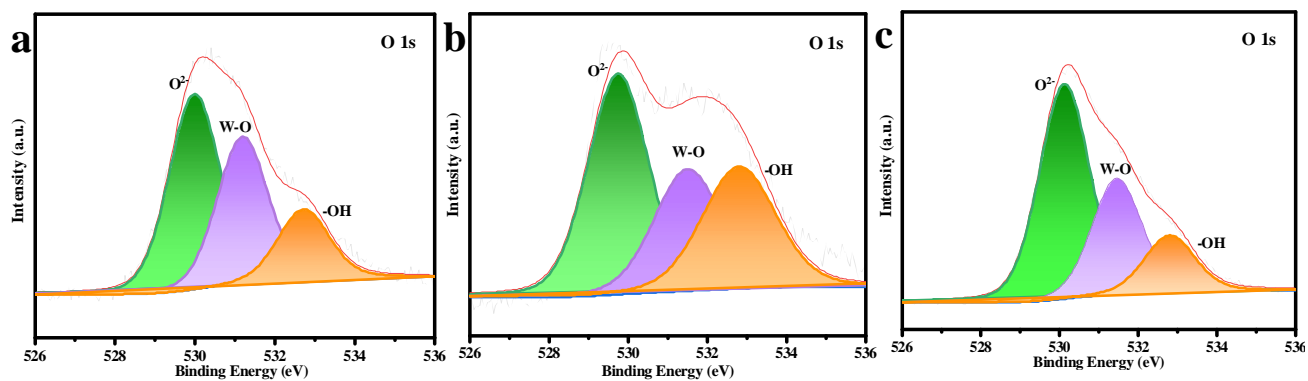


Figure S5. High resolution XPS spectra of O 1s Pt-CoWO₄/WO₃@NCL-mr-750 (a), Pt-CoWO₄/WO₃@NCL-mr-800 (b) and Pt-CoWO₄/WO₃@NCL-mr-900 (c).

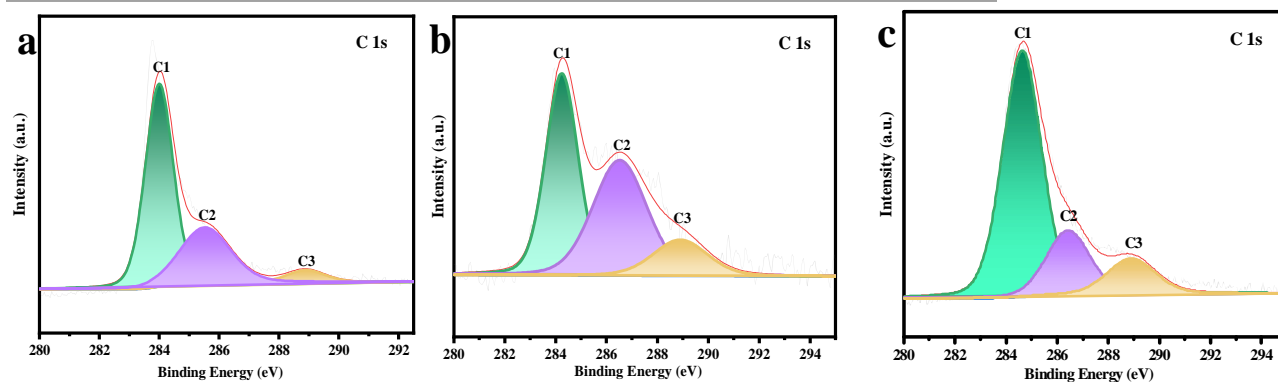


Figure S6. High resolution XPS spectra of C 1s Pt-CoWO₄/WO₃@NCL-mr-750 (a), Pt-CoWO₄/WO₃@NCL-mr-800 (b) and Pt-CoWO₄/WO₃@NCL-mr-900 (c).

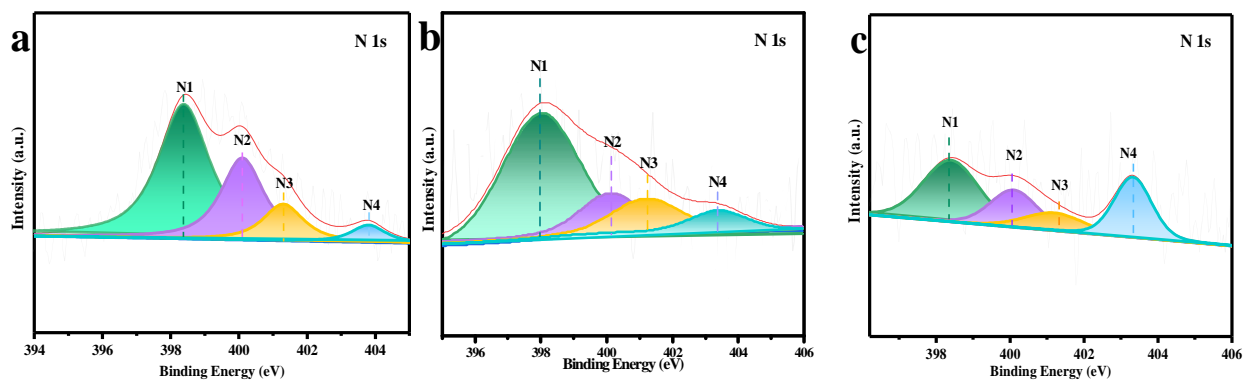


Figure S7. High resolution XPS spectra of N 1s Pt-CoWO₄/WO₃@NCL-mr-750 (a), Pt-CoWO₄/WO₃@NCL-mr-800 (b) and Pt-CoWO₄/WO₃@NCL-mr-900 (c).

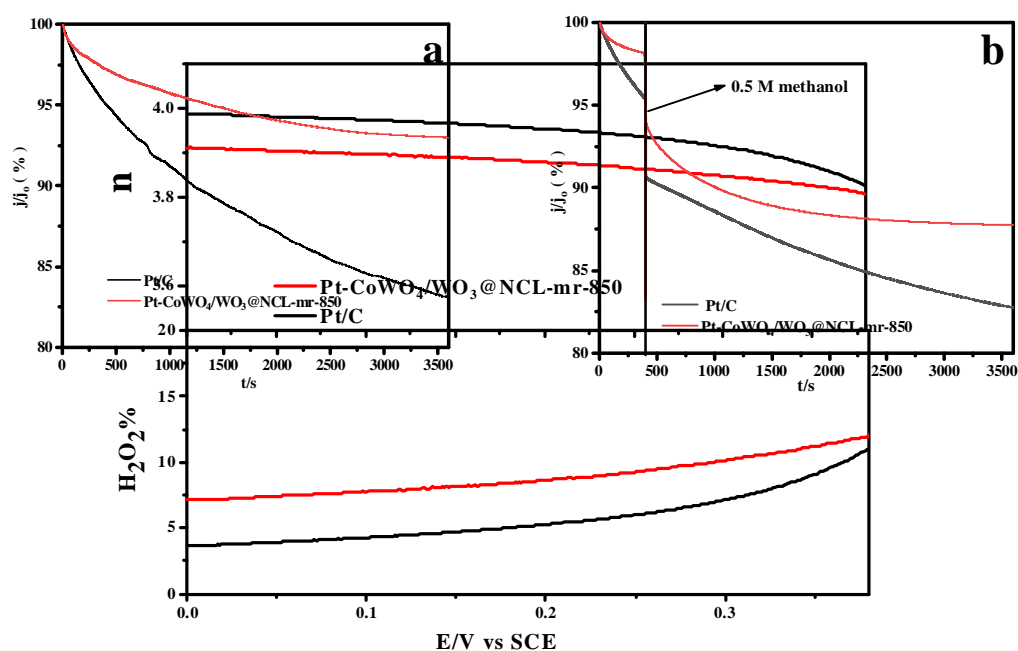


Figure S8. Number of transferred electrons and the H₂O₂ yields.

Figure S9. Current-time (i-t) chronoamperometric responses of Pt-CoWO₄/WO₃@NCL-mr-850 and Pt/C in the O₂-saturated 0.5 M H₂SO₄ at 1600 rpm (a); Current-time (i-t) chronoamperometric responses of Pt-CoWO₄/WO₃@NCL-mr-850 and Pt/C with the addition of 0.5 M methanol in the O₂-saturated 0.5 M H₂SO₄ at 1600 rpm (b).

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