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Supporting Information for:

High-Performance Pt–Co Nanoframes for Fuel Cell Electrocatalysis

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METHODS

Chemicals. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\geq 37.5\%$ Pt basis), cobalt (II) acetate tetrahydrate ($(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$, $\geq 98\%$), oleylamine (technical grade, 70%), oleic acid (technical grade, 90%), hexane ($\geq 98.5\%$), potassium hydroxide (reagent grade, 90%), and Nafion 117 solution ($\sim 5\%$) were purchased from Sigma-Aldrich. Methanol ($\geq 99.8\%$) and chloroform ($\geq 99.8\%$) were purchased from Fisher Scientific. Nitric acid ($\geq 69.0\%$) and perchloric acid (67–72%) were purchased from Honeywell Fluka. Carbon black (Vulcan XC-72) was purchased from Cabot Corporation. Commercial Pt, nominally 20 wt% on carbon black, was purchased from Alfa Aesar.

Characterizations. Transmission electron microscopy (TEM) was carried out using Hitachi H-7650. High-resolution TEM (HRTEM) was acquired by FEI Tecnai F20 at an accelerating voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDX) mapping were performed with FEI TitanX 60-300. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was tested using PerkinElmer Optima 7000 DV. X-ray diffraction (XRD) was measured by Bruker AXS D8 Advance diffractometer with Cu $K\alpha$ source.

Synthesis of Pt–Co rhombic dodecahedra (RD). In a typical synthesis, 20 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 42.1 mg of $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$ were dissolved in 1.2 mL of oleylamine in a small vial by sonication. 6.8 mL of oleylamine and 2 mL of oleic acid were added into a 25 mL three-necked flask under nitrogen (N_2) purging. The solvent solution was first kept under vacuum at 160 °C for

2 minutes to entirely remove water, and then heated to 240 °C under N₂. The precursor solution was injected into the three-necked flask immediately after reaching 240 °C. The color of the solution gradually changed from dark cyan to black at 240 °C. The reaction was stopped at 8 minutes after the injection by carefully transferring the flask into a water bath to quench the growth. The products were washed twice with hexane/ethanol mixture and collected by centrifugation at 12,000 rpm.

Catalyst loading. The Pt–Co RD collected by centrifugation were re-dispersed in chloroform and added to carbon black in a ratio which produced a loading of 8–10wt% Pt. The mixture was shaken in chloroform for 3 minutes to complete the loading process. The loaded sample was washed twice with hexane and collected by centrifugation at 10,000 rpm.

Nitric acid corrosion. The as-loaded Pt–Co RD collected by centrifugation were re-dispersed in 10 mL of nitric acid (2M) aqueous solution by intense sonication. The mixture was heated at 60 °C under vigorous stirring for 1 hour in air to corrode Pt–Co RD into Pt–Co nanoframes (NF). The products were first washed once with pure ethanol and then washed twice with hexane/ethanol mixture. After each wash, the samples were collected by centrifugation at 12,000 rpm.

Preparation for electrochemical measurements. The Pt–Co nanoframe catalyst supported on carbon was dispersed in a mixture of ethanol and Nafion 117 solution (volume ratio of 100:1) with a concentration of 0.5 mg_{catalyst} mL⁻¹. The actual concentration of Pt in the catalyst ink was determined by ICP-OES. The catalyst ink was deposited onto a glassy carbon rotating disk electrode (Pine Instruments, 0.196 cm²) in the appropriate volume to achieve about 5.1 μg_{Pt} cm⁻²

loading density. The commercial Pt/C catalyst had a loading density of $8.2 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$. The electrochemical measurements of both oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) were conducted in a three-compartment glass electrochemical cell with a Pine rotating disk electrode (RDE) set-up and a Biologic VSP potentiostat at room temperature. All potentials are presented versus the reversible hydrogen electrode (RHE).

Electrochemical measurements for acidic ORR. A saturated Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively, and 0.1 M HClO₄ prepared from 67% HClO₄ was used as the electrolyte. The catalyst was activated by potential cycling in Ar-saturated electrolyte between 0.05–1.02 V with a sweep rate of 100 mV s^{-1} and was held at 0.05 V between measurements. The limits of cyclic voltammetry (CV) were 0.05–1.02 V. Hydrogen underpotential deposition measurements were performed by saturating the electrolyte with Argon (Ar) gas before collecting the CV with a sweep rate of 50 mV s^{-1} . The ORR activity measurements were carried out under oxygen (O₂) purging conditions and with a sweep rate of 20 mV s^{-1} with an RDE rotation rate of 1,600 rpm. The accelerated durability testing (ADT) was conducted by potential cycling in Ar-saturated 0.1 M HClO₄ electrolyte between 0.60 and 1.00 V with a sweep rate of 200 mV s^{-1} . The currents for acidic ORR were corrected for ohmic iR drop.

Electrochemical measurements for alkaline ORR and MOR. The catalyst was first activated by CV in Ar-saturated 0.1 M HClO₄ between 0.05 and 1.02 V with a sweep rate of 100 mV s^{-1} , and then transferred into the alkaline environment. An alkaline Hg/HgO electrode and a graphite rod were used as reference and counter electrodes, respectively, and 1 M KOH was used as the electrolyte. The limits of CV were 0.05–1.10 V, and the RDE rotation rate was always 2,000 rpm

to get rid of bubbles. Hydrogen underpotential deposition measurements were also performed by saturating the electrolyte with Ar gas before collecting the CV with a sweep rate of 50 mV s^{-1} . For alkaline ORR, the activity measurement was carried out under O_2 purging with a sweep rate of 20 mV s^{-1} , and the ADT was conducted by potential cycling in Ar-saturated electrolyte between 0.50 and 1.00 V with a sweep rate of 200 mV s^{-1} for different number of cycles. The currents for alkaline ORR were corrected for ohmic iR drop as well. For alkaline MOR, 1 M methanol was added into the electrolyte as the reactant, and the CV was collected under Ar purging with a sweep rate of 50 mV s^{-1} . Chronoamperometry (CA) was conducted in Ar-saturated electrolyte at 0.67 V for 1,800 seconds. CO-stripping measurements were performed by first purging CO through the electrolyte while holding the potential at 0.05V without the existence of methanol. Ar was then purged to remove CO gas from the electrolyte, and the CV was collected with a sweep rate of 50 mV s^{-1} .

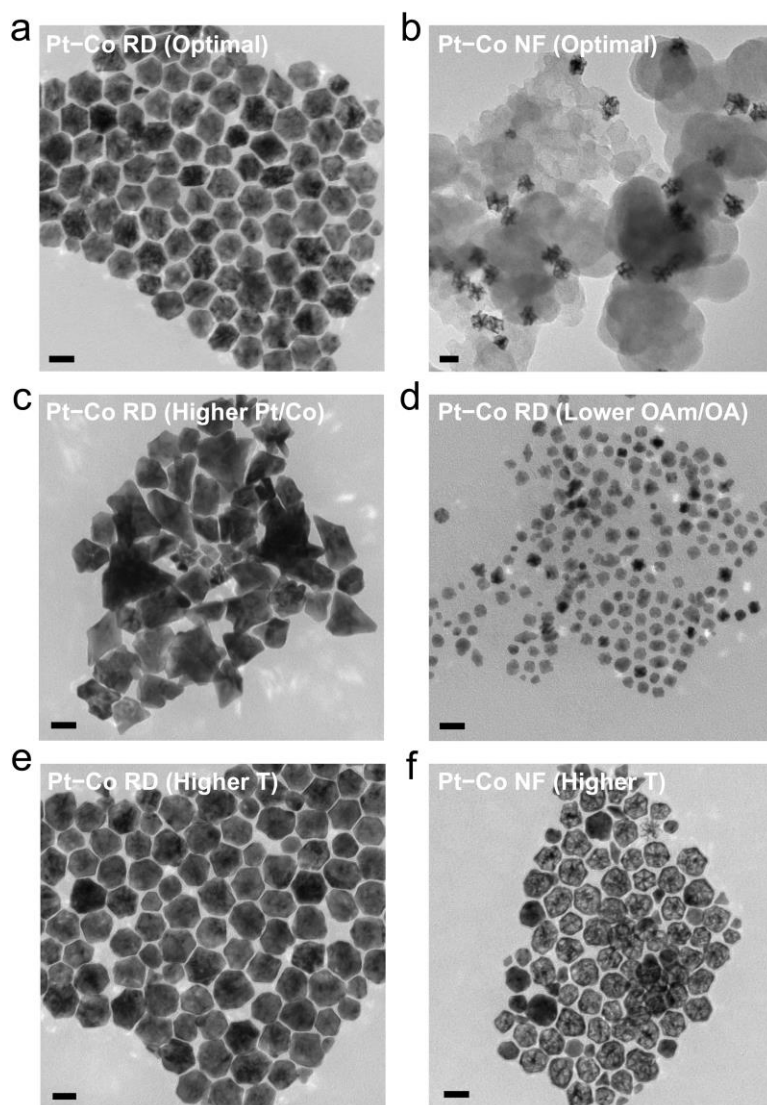


Figure S1. Synthetic optimization of Pt–Co rhombic dodecahedra. TEM images of (a) Pt–Co RD synthesized with the optimal reaction conditions ($T = 240\text{ }^{\circ}\text{C}$, $m_{\text{Pt precursor}}/m_{\text{Co precursor}} = 400/842$, $V_{\text{oleylamine}}/V_{\text{oleic acid}} = 8/2$), (b) Pt–Co NF evolved from (a) using nitric acid corrosion, (c–e) Pt–Co RD prepared with the same conditions as those of (a) except (c) $m_{\text{Pt precursor}}/m_{\text{Co precursor}} = 400/350$, (d) $V_{\text{oleylamine}}/V_{\text{oleic acid}} = 6/4$, and (e) $T = 265\text{ }^{\circ}\text{C}$, and (f) Pt–Co NF obtained by nitric acid corrosion of (e). Scale bar is 20 nm in all images.

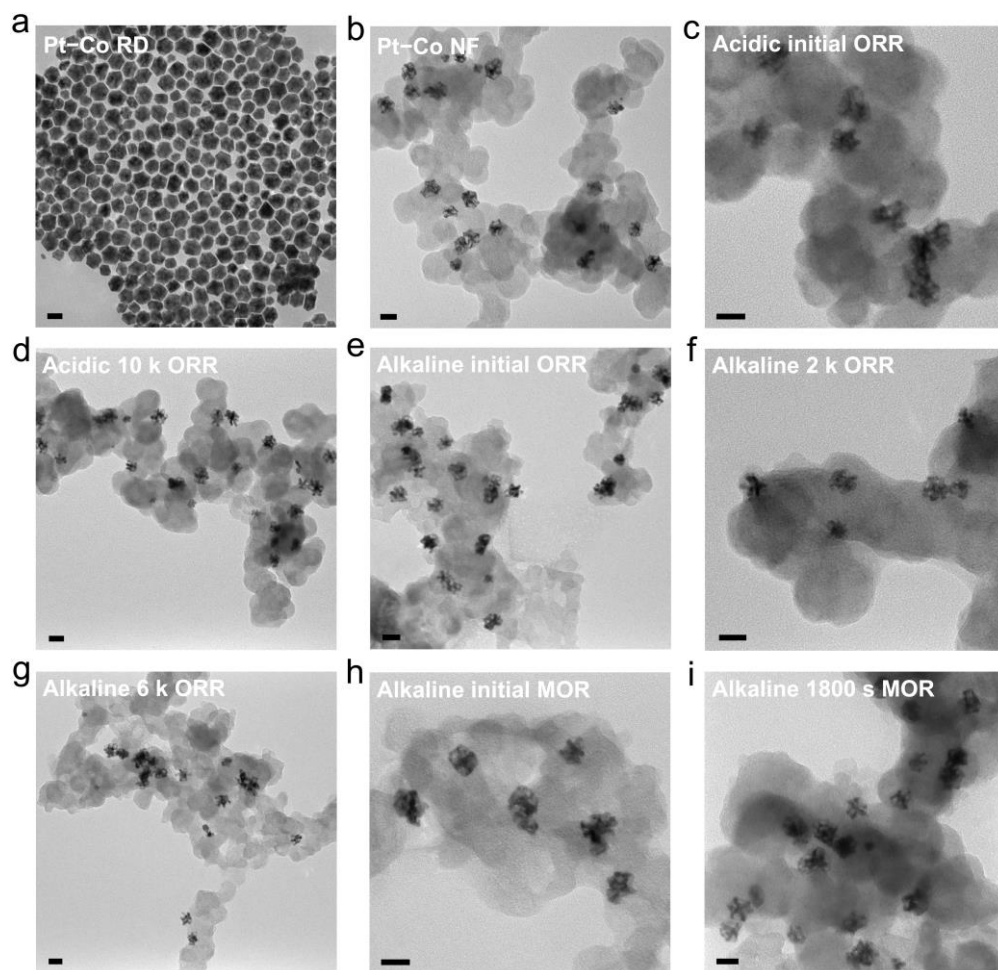


Figure S2. Additional TEM images of Pt–Co nanoframe electrocatalysts. TEM images of (a) as-synthesized Pt–Co RD, (b–h) Pt–Co NF after (b) nitric acid corrosion, (c) initial and (d) 10,000 cycles of acidic ORR, (e) initial, (f) 2,000 cycles of and (g) 6,000 cycles of alkaline ORR, (h) initial and (i) 1800 s of alkaline MOR. Scale bar is 20 nm in all images.

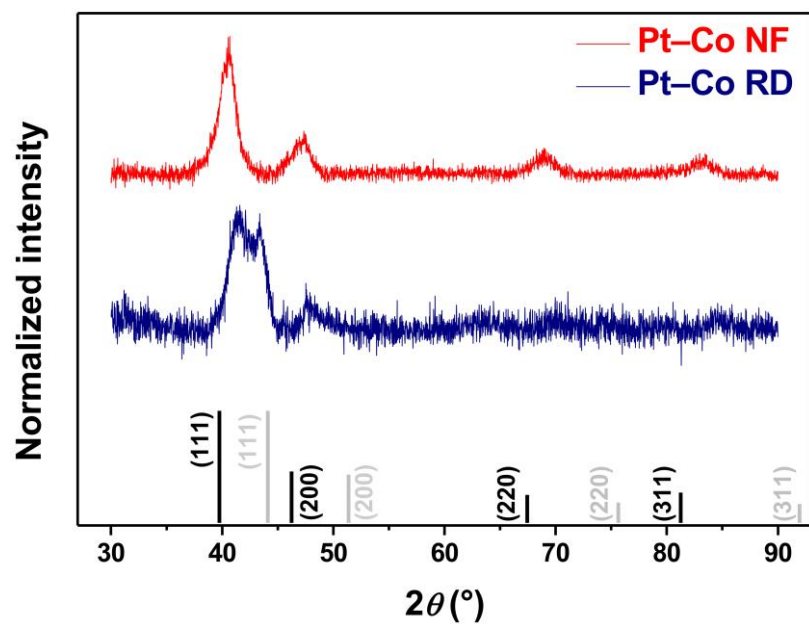


Figure S3. XRD patterns of Pt–Co rhombic dodecahedra and nanoframes. Black line, Pt, PDF#03-065-2868; grey line, Co, PDF#01-071-4651.

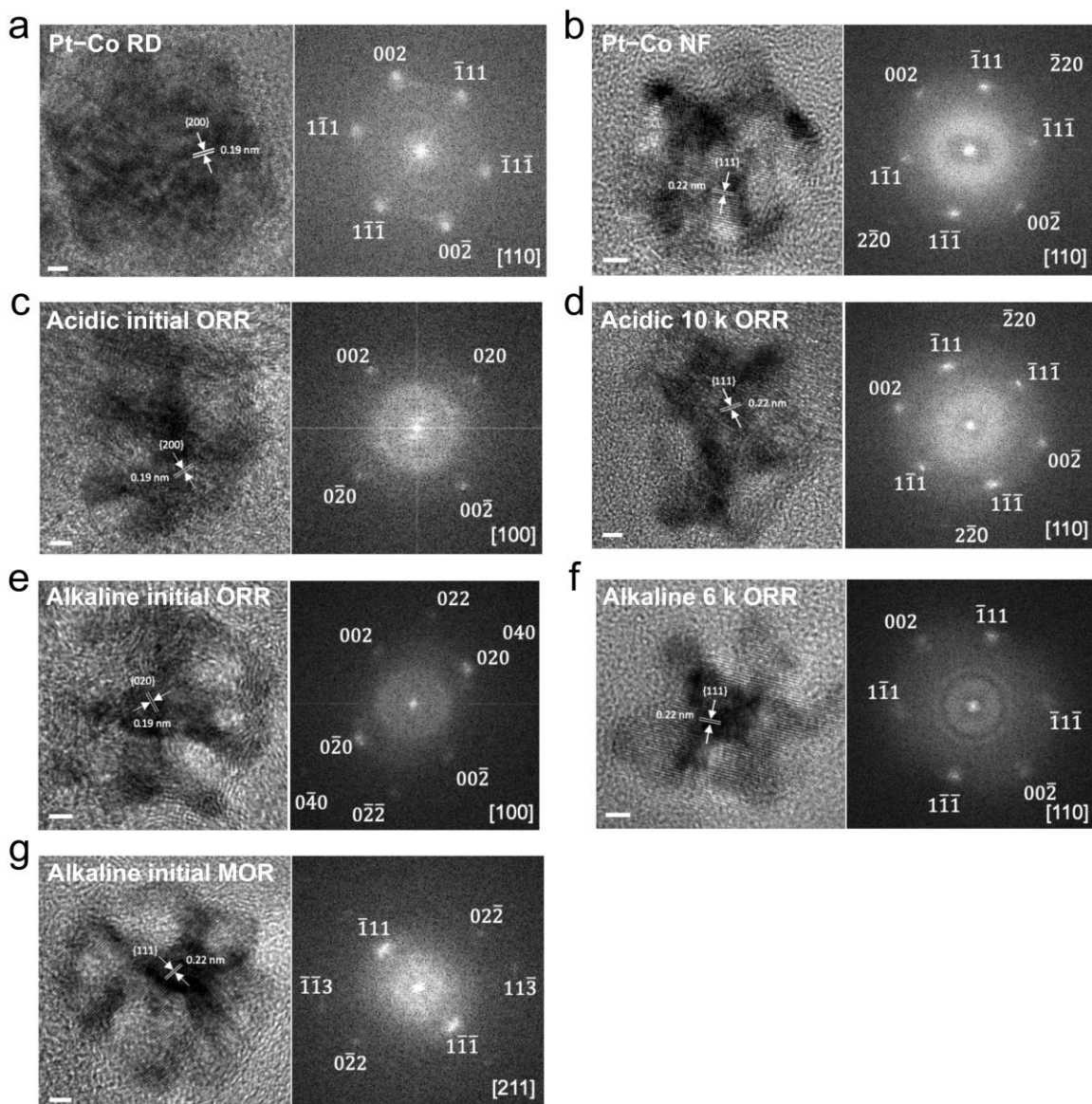


Figure S4. HRTEM images and FFT of Pt–Co nanoframe electrocatalysts. HRTEM images and FFT of (a) as-synthesized Pt–Co RD, (b–g) Pt–Co NF after (b) nitric acid corrosion, (c) initial and (d) 10,000 cycles of acidic ORR, (e) initial and (f) 6,000 cycles of alkaline ORR, and (g) initial alkaline MOR. Scale bar is 2 nm in all images.

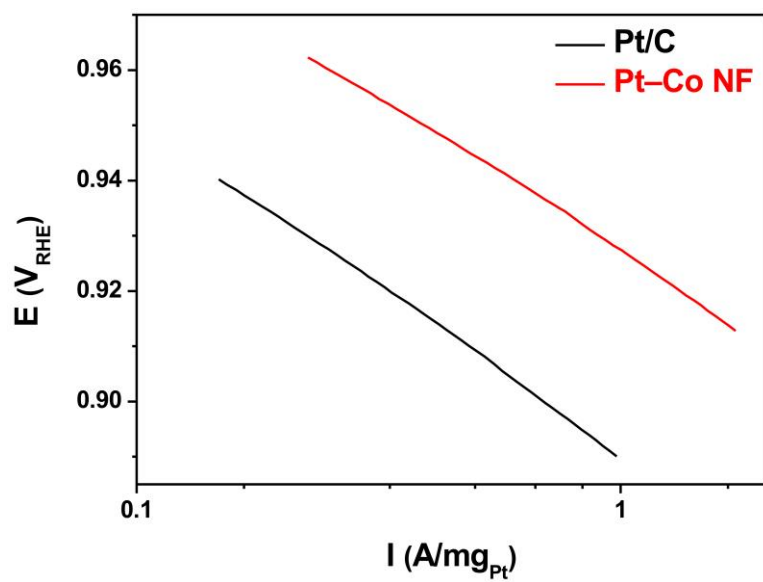


Figure S5. Acidic ORR mass activity Tafel plots of Pt–Co nanoframes and commercial Pt/C.

The corresponding Tafel slopes are 60 and 66 mV decade⁻¹ for Pt–Co nanoframes and commercial Pt/C, respectively.

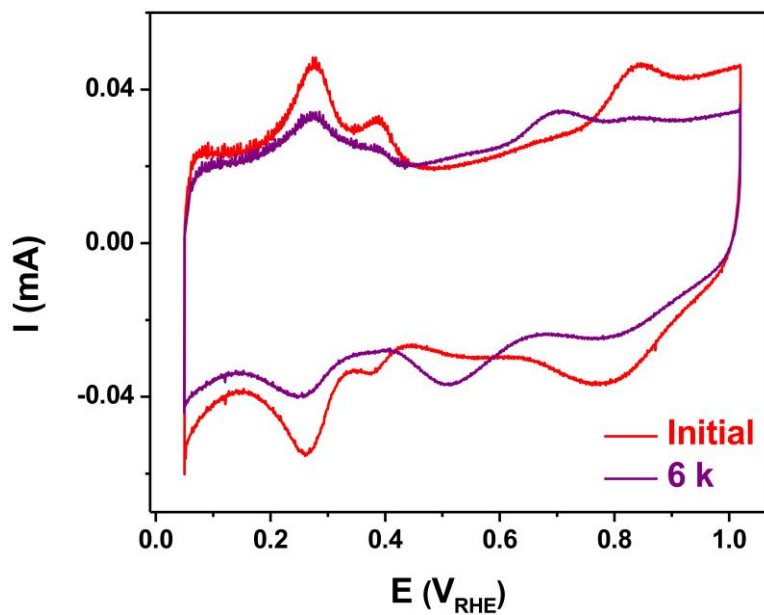


Figure S6. CV curves of Pt–Co nanoframes after initial and 6,000 cycles of alkaline ORR.

CV was performed in Ar-saturated 1 M KOH with a sweep rate of 50 mV s⁻¹.

Table S1. Compositions of Pt–Co nanoframe electrocatalysts.

	ICP	EDX
Pt–Co RD	Pt ₂₁ Co ₇₉	Pt ₂₃ Co ₇₇
Pt–Co NF	Pt ₈₃ Co ₁₇	Pt ₈₂ Co ₁₈
Acidic initial ORR	N/A	Pt ₈₂ Co ₁₈
Acidic 10 k ORR	N/A	Pt ₈₅ Co ₁₅
Alkaline initial ORR	N/A	Pt ₈₃ Co ₁₇
Alkaline 6k ORR	N/A	Pt ₈₆ Co ₁₄
Alkaline initial MOR	N/A	Pt ₈₃ Co ₁₇

Table S2. MOR stability of Pt–Co nanoframes.

@0.67V_{RHE}

I (A mg _{Pt} ⁻¹)	t = 0 s	t = 1,000 s	t = 1,800 s
Pt–Co NF	1.08	0.47	0.33
Pt/C	0.31	0.05	0.02