

A fully noble metal-free electrocatalyst based on cobalt-polyoxometalate immobilized in layered double hydroxide for water oxidation at neutral pH

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Equipments and Apparatus

X-Ray photoelectron spectra (XPS) were measured by ESCALAB250xi with X-ray monochromatisation. Electrochemical tests were recorded on a CHI760D electrochemical analyser with glassy carbon, Ag/AgCl, and Pt wire electrodes as the working, reference, and auxiliary electrode, respectively, in buffer solutions at room temperature with a scanning rate of 100 mV s⁻¹. Infrared spectra (2–4 wt% sample in KBr pellets) were recorded using a Bruker VERTEX 70v FT-IR spectrometer. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were carried out on JEOL-2100F apparatus at an accelerating voltage of 200 kV. Elemental mapping and energy dispersive X-ray spectroscopy (EDS) were performed with JSM-5160LV-Vantage typed energy spectrometer.

Materials

All chemicals and salts (analytical grade) were used as received without any further purification. Purified water (18.2 MΩ cm) for the preparation of solutions was attained from a Molecular Lab Water Purifier.

Electrochemical Measurements

Electrocatalytic activities of the catalysts (0.07~0.24 mg cm⁻²) were tested in 0.2 M Tris-HCl buffer/ 0.2 M borate buffer / 0.2 M PBS buffer / 0.2 M phosphate buffer / 0.2 M barbitone sodium-HCl buffer with the standard threeelectrode electrochemical glass flask using a CHI660D electrochemical analyzer at room temperature with glassy carbon (or FTO), Ag/AgCl, and Pt wire electrodes as the working, reference, and auxiliary electrode, respectively; scan rate 100 mV/s. In a typical procedure, 2~7 mg of the catalysts were dispersed in 2 mL of 9:1 v/v water/Nafion by sonication to form a homogeneous ink. Typically, 5 μL well-dispersed catalysts were covered on the glassy carbon electrode and then dried in an ambient environment for measurements. The electrocatalyst was prepared with a catalyst loading of 0.07~0.24 mg cm⁻². Linear sweep voltammetry with a scan rate of 100 mV s⁻¹ was conducted in solution using Ag/AgCl (saturated KCl) as the reference electrode, Pt wire as the counter electrode,

and the glassy carbon electrode with various catalysts as the working electrode. The working electrodes were activated for several times until the signals were stabilized. The potentials reported in this work were referenced to the reversible hydrogen electrode (RHE) through RHE calibration: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 \text{ pH}$, overpotential $\eta = E_{\text{vs.RHE}} - 1.23 \text{ V}$. Tafel slopes can be obtained by plotting overpotential η against logarithm of current $\log(J)$ from LSV curves. Electrochemical impedance spectroscopy (EIS) measurements of the various catalysts were carried out using above three electrode systems 1.81 V vs. RHE. The frequency range was 100 000 Hz to 0.1 Hz, and the amplitude of the applied voltage was 5 mV.

Catalyst preparation

Tris-LDH: Tris-LDH was synthesized according to the literature^[1,2]. 13.1 mol of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 6.9 mol $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 mL of H_2O (A). A solution of 24.228 g of Tris in 100 mL of water was added to the solution with gentle stirring, and the aqueous solution was transferred to a 100 mL Teflon-lined stainless autoclave and reacted at 80 °C for 12 h. The final jelly was dissolved in 100 mL Na_2CO_3 solution (0.5 M) with magnetic stirring for 3 h at room temperature. Precipitates were collected by centrifugation and washed with water several times. Finally, the precipitates were kept at 50 °C for 24 h before being naturally cooled in air.

$[\text{PCoW}_{11}\text{O}_{39}]^{5-}$: $[\text{PCoW}_{11}\text{O}_{39}]^{5-}$ was synthesized according to the literature^[3, 4] with some modifications. Na_2HPO_4 (9.1 mmol), Na_2WO_4 (100 mmol) and $\text{Co}(\text{NO}_3)_2$ (12 mmol) were dissolved in 200 mL water with magnetic stirring at room temperature. 1 mol/L of HNO_3 was added slowly to the above system with stirring and resulting in a purple solution with pH 4.8. This mixture was gently stirred for 2 h with 60 °C, then concentrated by rotary evaporation. The solid of $[\text{PCoW}_{11}\text{O}_{39}]^{5-}$ was collected by drying at 50 °C and grinding. The synthesis method of $[\text{PNiW}_{11}\text{O}_{39}]^{5-}$, $[\text{PCuW}_{11}\text{O}_{39}]^{5-}$, $[\text{PMnW}_{11}\text{O}_{39}]^{5-}$ and $[\text{PFeW}_{11}\text{O}_{39}]^{4-}$ is similar to that of $[\text{PCoW}_{11}\text{O}_{39}]^{5-}$, except that 12 mmol nitrate salt of appropriate transition metal was used instead of $\text{Co}(\text{NO}_3)_2$ during the synthesis.

Co-POM/T-LDH: Co-POM/T-LDH was synthesized according to the

literature^[2, 4, 5] with some modifications. 3.0g Tris-LDH was dissolved in 30 mL of water followed by an addition of 1.0 g/3.0 g/9.0 g $[\text{PCoW}_{11}\text{O}_{39}]^{5-}$, resulting in a purple solution, wherein the mass ratio of the POM to the LDH is 1:3, 1:1 or 3:1. The pH of the mixture was adjusted to between 4.5 and 5.0 by addition of the 1 M HNO_3 solution. This pH is maintained by addition of small amounts of 1 M HNO_3 for a while. The solution was heated at 60 °C for 24 h and then was allowed to cool to room temperature. The desired purple product was isolated by filtration, washed with deionized water and dried under 50 °C. The synthesis methods of **Cu-POM/T-LDH**, **Fe-POM/T-LDH**, **Mn-POM/T-LDH** are similar to that of **Co-POM/T-LDH**, except that $[\text{PCuW}_{11}\text{O}_{39}]^{5-}$, $[\text{PFeW}_{11}\text{O}_{39}]^{4-}$ and $[\text{PMnW}_{11}\text{O}_{39}]^{5-}$ were used instead of $[\text{PCoW}_{11}\text{O}_{39}]^{5-}$ during the synthesis.

Experiment section

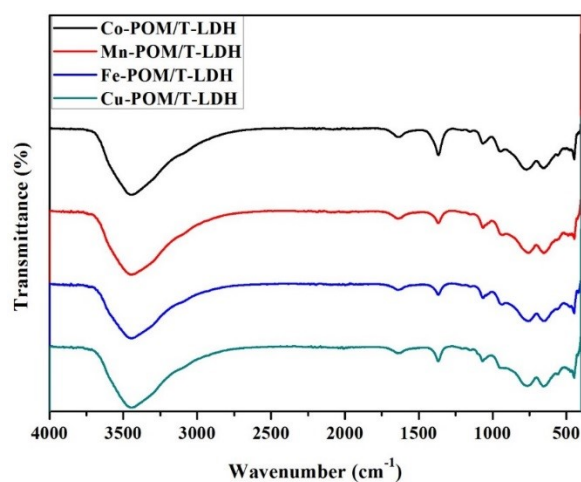


Fig. S1 FT-IR spectrums of POMs/T-LDHs.

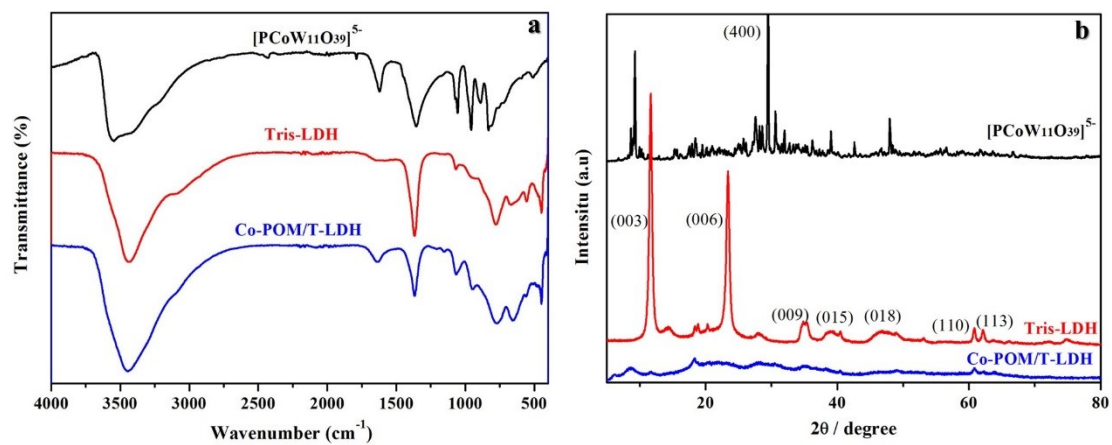


Fig. S2 FTIR spectra (a) and XRD patterns (b) of [PCoW₁₁O₃₉]⁵⁻, Tris-LDH and Co-POM/T-LDH.

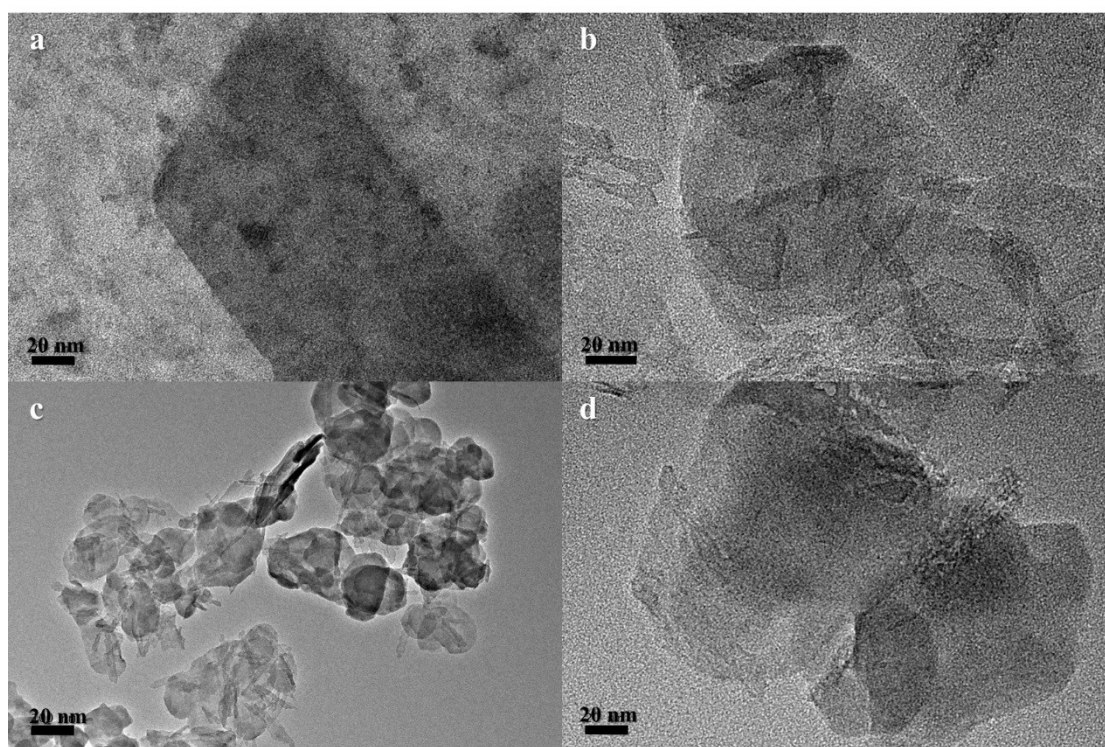


Fig. S3 TEM images of [PCoW₁₁O₃₉]⁵⁻ (a), Tris-LDH (b) and Co-POM/T-LDH (cd).

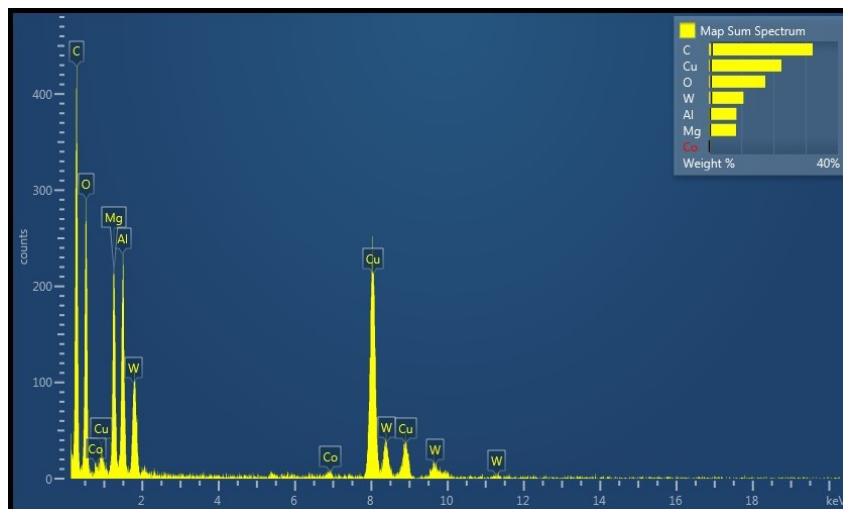


Fig. S4 EDS spectrum of Co-POM/T-LDH.

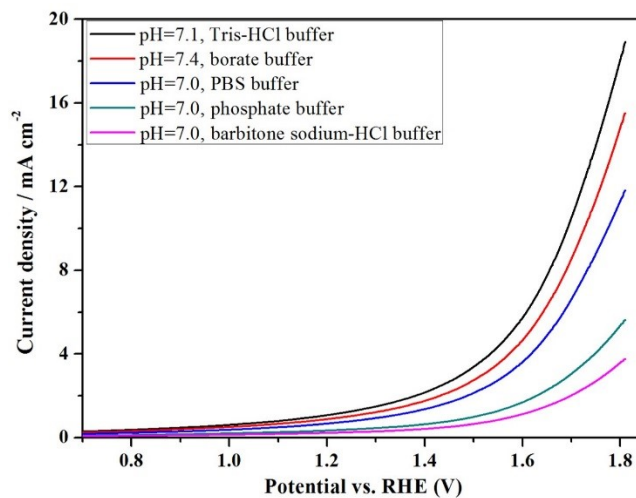


Fig. S5 LSVs of Co-POM/T-LDH (1:1) use different kinds of buffers. Conditions: 0.18 mg/cm² catalyst, no NaNO₃.

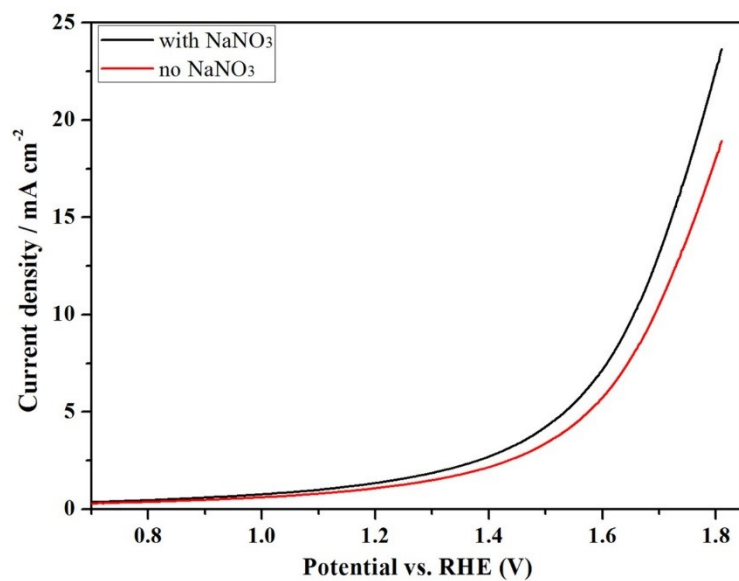


Fig. S6 LSVs of Co-POM/T-LDH (1:1) using NaNO₃. Conditions: 0.18 mg/cm² catalyst, 0.2 M Tris-HCl buffer (pH=7.1), 5 mM NaNO₃.

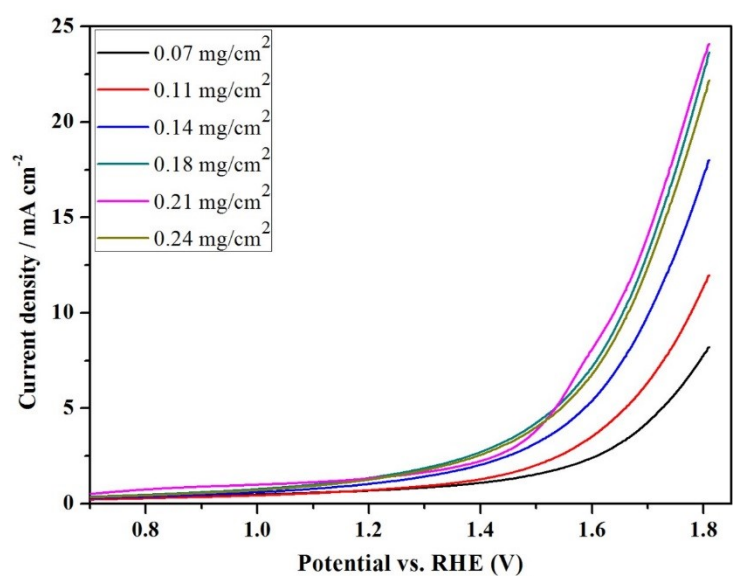


Fig. S7 LSVs of Co-POM/T-LDH (1:1) at different concentrations. Conditions: 0.2 M Tris-HCl buffer (pH=7.1), 5 mM NaNO₃.

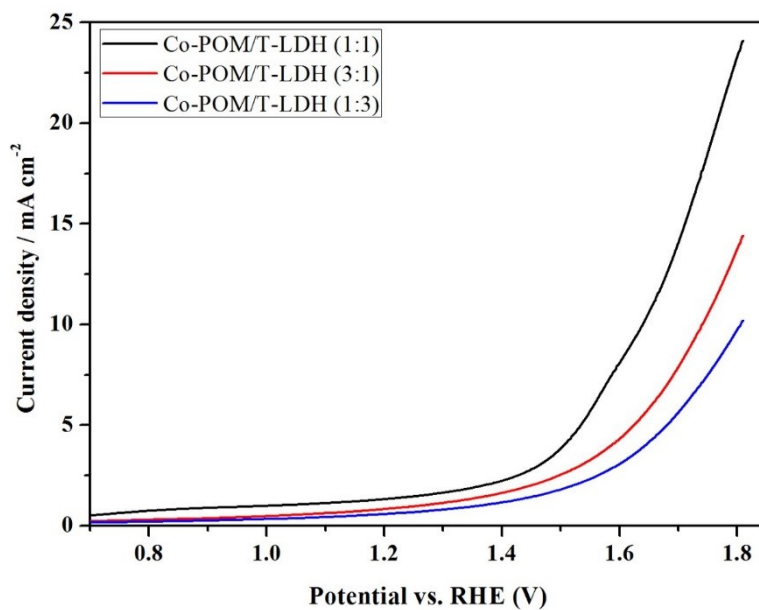


Fig. S8 LSV curves of **Co-POM/T-LDH** with different mass ratio of POMs to LDHs: POM: LDH= 1:1 (black), POM: LDH= 3:1 (red), POM: LDH= 1:3 (blue). Conditions: 0.21 mg/cm² catalyst, 0.2 M Tris-HCl buffer (pH=7.1), 5 mM NaNO₃.

Table S1. Determination of metal element ratio in **Co-POM/T-LDH** obtained by ICP-AES.

Samples	Co to Mg ratio (before the addition of HNO ₃)	Co to Mg ratio (before wash steps)	Co to Mg ratio (final product)
Co-POM/T-LDH (1:1)	1:7.9	1:8.8	1:15.7

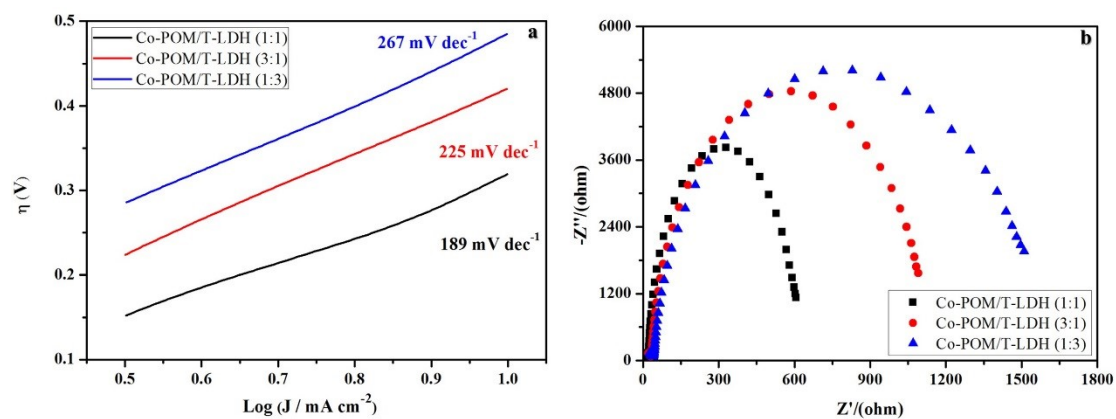


Fig. S9 (a) Tafel plots of Co-POM/T-LDH with different mass ratio of POMs to LDHs: POM: LDH= 1:1 (black), POM: LDH= 3:1 (red), POM: LDH= 1:3 (blue). (b) Nyquist diagrams of EIS for Co-POM/T-LDH with different mass ratio of POMs to LDHs: POM: LDH= 1:1 (black), POM: LDH= 3:1 (red), POM: LDH= 1:3 (blue).

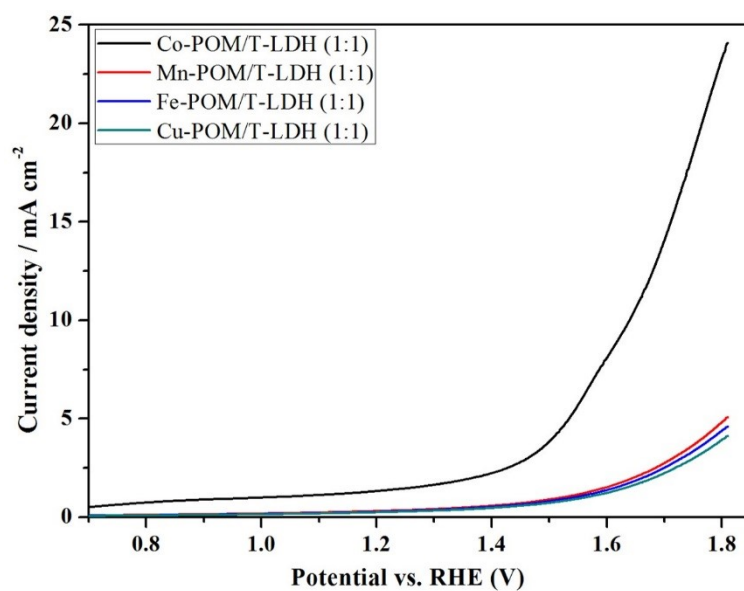


Fig. S10 LSV curves of four POMs/T-LDHs. Conditions: 0.21 mg/cm² catalyst, 0.2 M Tris-HCl buffer (pH=7.1), 5 mM NaNO₃.

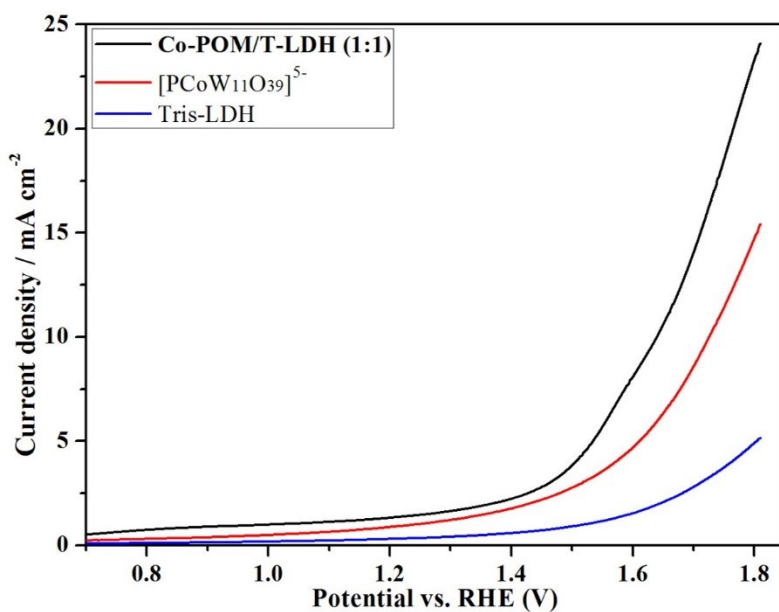


Fig. S11 LSV curves of Co-POM/T-LDH (black), [PCoW₁₁O₃₉]⁵⁻ (red), Tris-MgAl-LDH (blue). Conditions: 0.21 mg/cm² catalyst, 0.2 M Tris-HCl buffer (pH=7.1), 5 mM NaNO₃.

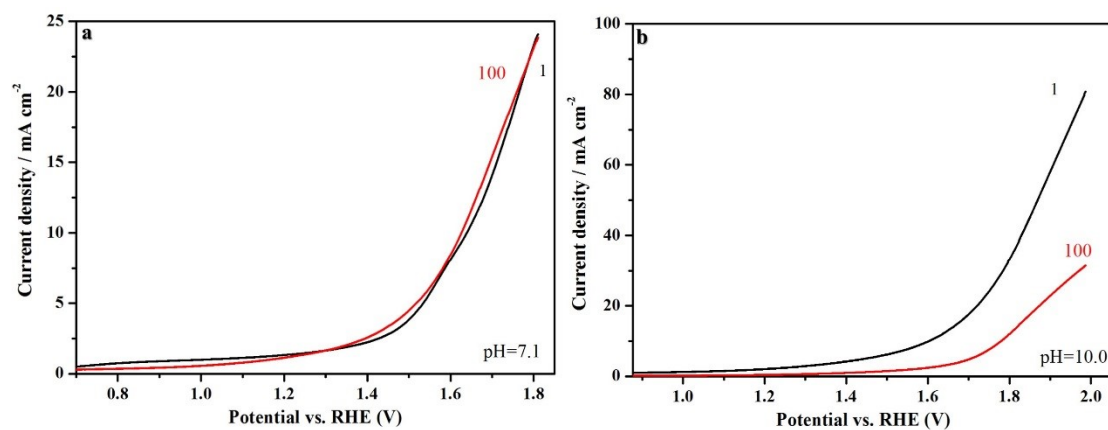


Fig. S12 LSV curves of Co-POM/T-LDH for 100 times of voltammetry cycling in neutral condition at pH 7.1 (a) and 100 cycles under basic condition at pH 10.0 (b). Conditions: 0.21 mg/cm² catalyst, 0.2 M Tris-HCl buffer (pH=7.1), 0.2 M borate buffer (pH=10.0), 5 mM NaNO₃.

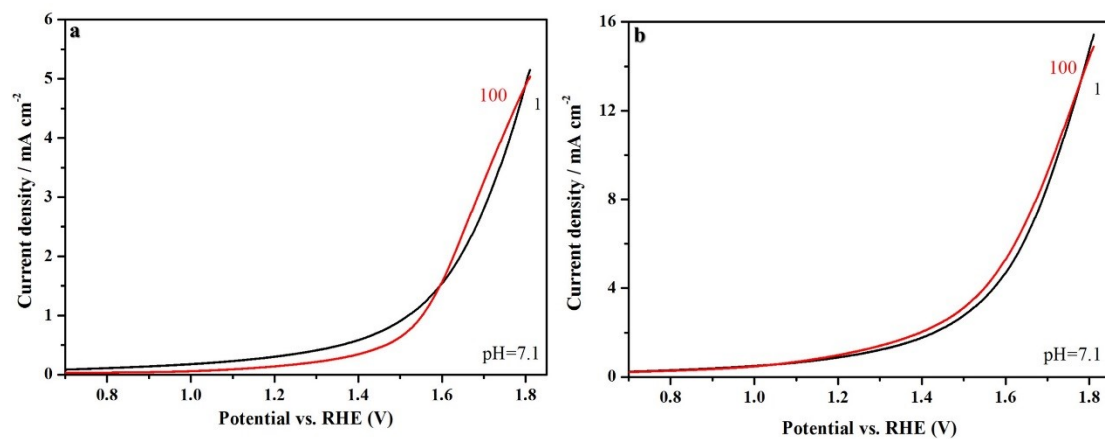


Fig. S13 LSV curves of [PCoW₁₁O₃₉]⁵⁻ (a) and Tris-LDH (b) for 100 times of voltammetry cycling in neutral condition at pH 7.1. Conditions: 0.21 mg/cm² catalyst, 0.2 M Tris-HCl buffer (pH=7.1), 5 mM NaNO₃.

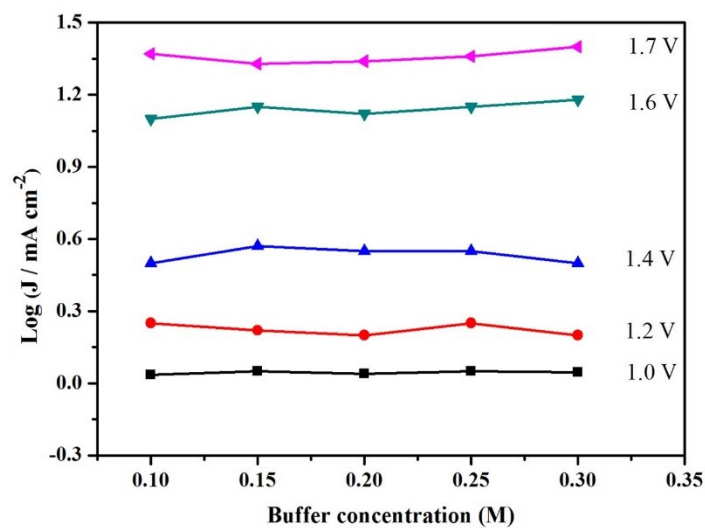


Fig. S14 Tris-HCl buffer concentrations dependency of current at a constant applied potential (1.0, 1.2, 1.4, 1.6 and 1.7 V vs RHE) at pH 7.1.

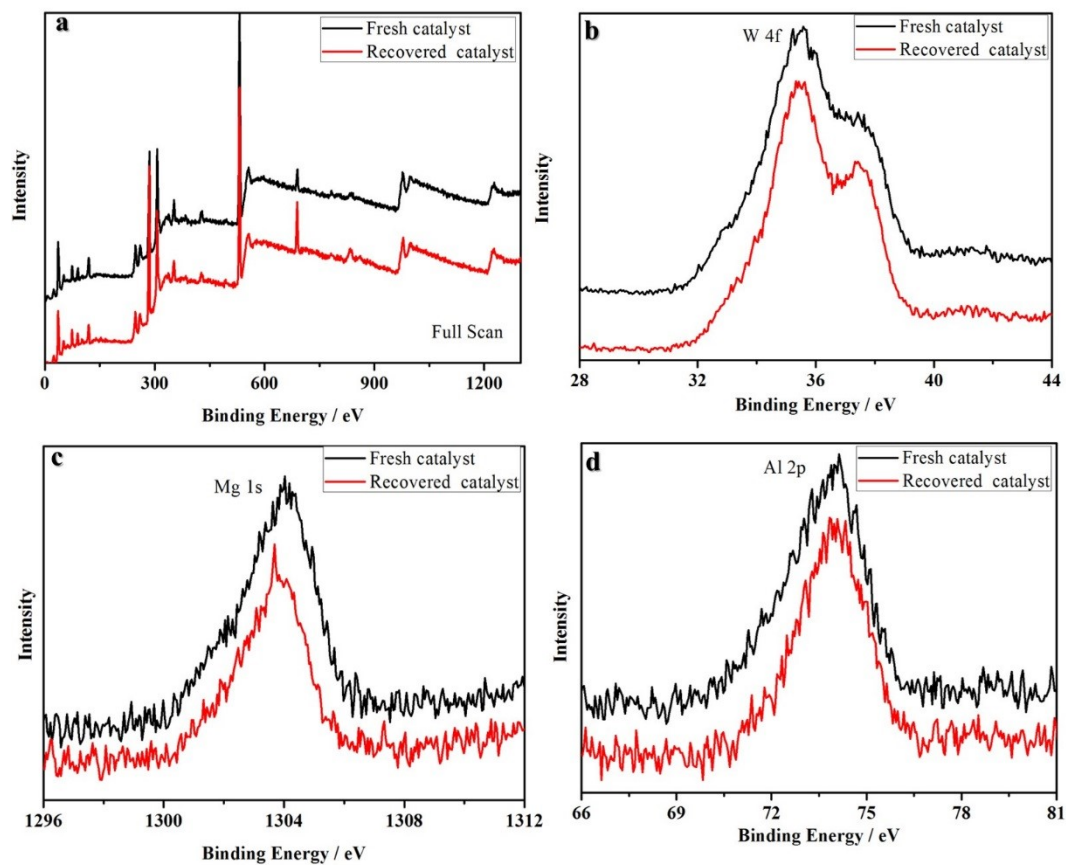


Fig. S15 XPS of Co-POM/T-LDH before and after the reaction in the energy regions of (a) full scan, (b) W 4f, (c) Mg 1s and (d) Al 2p.

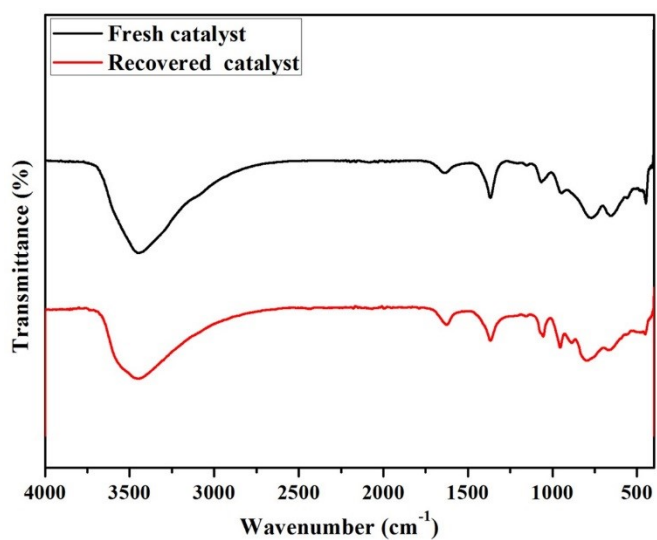


Fig. S16 FTIR of Co-POM/T-LDH before and after water electrolysis.

References

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