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Supporting Information

Safeguarding CoMnMo-oxide nanosheets in acidic oxygen evolution reaction *via* an atomic layer deposited TiO₂ conformal coating

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Reference RuO_2 *catalysts film preparation:* A 10 mg portion of commercially available ruthenium oxide (RuO₂) catalyst powder was dispersed in 2000 µL of a Nafion-ethanol-water solution (5% Nafion, with an ethanol-to-water volume ratio of 1:1). The mixture was sonicated for 60 minutes to ensure a uniform and homogeneous suspension. Meanwhile, a carbon paper substrate was cleaned by soaking in ethanol and sonicating for 30 minutes. The catalyst suspension was then evenly applied onto the pre-treated carbon paper using a micropipette, creating a 1.0 cm × 1.0 cm coated area on both sides. The total catalyst loading was 2.0 mg (1.0 mg per side). Finally, the coated carbon paper was left to dry in air-dried and stored for subsequent use.

Structural characterization: X-ray diffraction (XRD) measurements were performed using a PANalytical X'Pert diffractometer with Cu-K α radiation ($\lambda = 0.154$ nm). The X-ray source was operated at 40 kV and 40 mA. Morphological analysis was carried out using field-emission scanning electron microscopy (FE-SEM), while transmission electron microscopy (TEM) was conducted on a Talos F200X microscope. For TEM imaging, the CoMnMo–O₄/TiO₂/CP sample was dispersed in ethanol via ultrasonication, drop-casted onto carbon-coated copper grids, and airdried. X-ray photoelectron spectroscopy (XPS) was performed for the composition analysis of the catalyst samples by using a Thermo Scientific Escalab 250Xi system. The binding energy scale was referenced to the C 1s peak at 284.60 eV. An Al-K α X-ray source (1486.60 eV) was used for excitation. Both survey and high-resolution spectra were collected with a pass energy of 50 eV, using step sizes of 1.0 eV and 0.1 eV, respectively.

Electrochemical measurements: The OER performance was evaluated in 0.5 M H₂SO₄ using a three-electrode setup connected to an electrochemical workstation (BioLogic EC Lab). A platinum plate acted as the counter electrode, and an Ag/AgCl was the reference electrode. All potentials were converted to the reversible hydrogen electrode (RHE) scale using the equation:

$E_{RHE}(V) = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$

Linear sweep voltammetry (LSV) was conducted at 5 mV s⁻¹ to assess OER activity. The working electrode consisted of a 1.0×1.0 cm carbon paper coated with CoMnMo-O₄/TiO₂ films.

Measurements took place in 50 mL of 0.5 M H₂SO₄ at room temperature. Before data collection, the electrodes were stabilized via 100 cyclic voltammetry (CV) cycles at 100 mV.s⁻¹. The OER performance of CoMnMo-O₄/CP and CoMnMo-O₄/TiO₂/CP was benchmarked against commercial RuO₂. Long-term stability was examined via chronopotentiometry (CP) at a fixed current density. *In-situ* electrochemical impedance spectroscopy (EIS) was performed at a frequency range of 0.001 Hz to 10 kHz with a 10-mV amplitude under the bias of 340 mV OER overpotential. The electrochemical double-layer capacitance (C_{dl}) was determined by cyclic voltammetry (CV) in a non-Faradaic potential window at varying scan rates (5–60 mV s⁻¹) to estimate the ECSA.



Figure S1. SEM views of top surface of (a) CoMnMo–O₄, (b) CoMnMo–O₄/TiO₂-500, (c) CoMnMo–O₄/TiO₂-750, and (d) CoMnMo–O₄/TiO₂-1000 films deposited on a carbon fiber paper.



Figure S2. (a) Double layer capacitance (C_{dl}) estimation by the slope of the straight lines obtained by plotting average current density (Δj) versus scanning rates of the cyclic voltammograms measured in 0.5 M H₂SO₄ solution, as shown in (b) – (e).

Samples	C _{dl} (mF)	ECSA (cm ⁻²)
CoMoMn–O ₄	1.27	31.75
CoMoMn–O ₄ /TiO ₂ -500	19.28	482.00
CoMoMn–O ₄ /TiO ₂ -750	31.38	784.50
CoMoMn–O ₄ /TiO ₂ -1000	24.64	616.00

Table S1. Double layer capacitance (C_{dl}) and ECSA of various catalytic films measured in 0.5 M H_2SO_4 solution.



Figure S3. XPS spectra of CoMnMo-O₄ (top) and CoMnMo-O₄/TiO₂ (bottom) films.

Table S2. Corrosion potential and corrosion current density obtained from Tafel extrapolation curves of the sample films, as shown in figure 7b.

Samples	E _{corrosion} (V vs RHE)	J _{corrosion} (mA cm ⁻²)
CoMoMn–O ₄	-0.1813	8.45
CoMoMn–O ₄ /TiO ₂ -500	-0.0651	1.77
CoMoMn–O ₄ /TiO ₂ -750	+0.0076	0.28
CoMoMn–O ₄ /TiO ₂ -1000	+0.0462	0.06



Figure S4. LSV curves of various catalytic films in 0.5 M H₂SO₄ solution at 5 mV.s⁻¹.



Figure S5. XPS spectra of CoMnMo $-O_4/TiO_2$ -1000 film measured after the long-term stability test for 12 hours, as shown in figure 7a.



Figure S6. (a) XRD patterns, and (b) SEM image of CoMnMo–O₄/TiO₂-1000 film measured after the long-term stability test for 12 hours, as shown in figure 7a.



Figure S7. XPS spectra of CoMnMo–O₄/TiO₂-1000 film measured after the long-term stability test for 24 hours, as shown in figure 7a.



Figure S8. (a) XRD patterns, and (b) SEM image of CoMnMo–O₄/TiO₂-1000 film measured after the long-term stability test for 24 hours, as shown in figure 7a.

Table S3. The comparison of the electrocatalytic performance of $CoMoMn-O_4/TiO_2$ catalyst with others.

No	Catalysts	Electrolyte	Stability time (h)	J	η	References
			@10mAcm ⁻²	(mAcm ⁻²)	(mV)	
	CoMnMo-O ₄ /TiO ₂ -		8.4	10	260	This work
	750					
	CoMnMo-O ₄ /TiO ₂ -	0.5M	14	10	320	
	1000	H_2SO_4				
			24	10	350	
	RuO ₂					
1	Mo-Co ₉ S ₈ @C	0.5M	24	10	370	Adv. Energy
		H_2SO_4				Mater. 2020, 10,
						1903137
2	40wt%IrO2/TSO	0.5M	10	10	271	ACS Sustainable
		H_2SO_4				Chem. Eng.
						2023, 11, 1121
3	RuO ₂ /Co ₃ O ₄ -	0.1M	120	10	217	ACS Sustainable
	B ₃ DC	HClO ₄				Chem. Eng.
						2024, 12, 2313

4	Co ₃ O ₄ /Co _{1-x} RuxO ₂	0.5M H ₂ SO ₄	24	10	240	J. Mater. Chem. A, 2021, 9, 10385
5	Na-Co ₃ O ₄ (AA)	0.5M H ₂ SO ₄	200	10	360	Chem. Eng. J. 2024, 500, 156846
6	CoMn ₁ O	0.5M H ₂ SO ₄	20	10	415	Acta Phys Chim. Sin. 2024, 40, 2305021
7	Mn-Co ₃ O ₄	0.5 M H ₂ SO ₄	12	10	460	Chem. Eng. J. 2024, 482, 148926
8	LaMn–Co ₃ O ₄ /CC	0.5 M H ₂ SO ₄	24	10	370	Int. J. Hydrogen Energy 2024, 83, 682
9	Mn-Co ₃ O ₄ @CN	0.5 M H ₂ SO ₄	50 @200 mAcm ⁻²	10	395	Angew. Chem. Int. Ed. 2024 e202319462
10	DA_IrOx/TiO ₂ _4	0.05 M H ₂ SO ₄	100 @ 2Acm ⁻²	10	316	ACS Catal. 2025, 15, 5435