Electronic Supplementary Information

Experimental section

Materials: Nickel foam (NF) and carbon cloth (CC) were provided by Hongshan District, Wuhan Instrument Surgical Instruments business. Calcium Chloride (CaCl₂) was purchased from Beijing Chemical Works. Sodium Molybdat Dihydrat (Na₂MoO₄·2H₂O) was purchased from Aladdin Ltd. (Shanghai, China). Ruthenium (III) chloride hydrate (RuCl₃·3H₂O) was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. The water used throughout all experiments was purified through a Millipore system. All the reagents were used as received without further purification.

Preparation of CaMoO₄/NF and CaMoO₄/CC: CaMoO₄/NF and CaMoO₄/CC were prepared as follows. Prior to the synthesis, NF was treated by ultrasonication in 3.0 M HCl solution for 10 min to remove the possible surface oxide layer and cleaned with ethanol and deionized water, and CC was first treated with concentrated HNO₃, ethanol and deionized water by sonication to achieve a clean surface. 40 mL CaCl₂ aqueous solution (0.5 mol L⁻¹) was added into 40 mL Na₂MoO₄·2H₂O aqueous solution (0.5 mol L⁻¹) with the assistance of strong magnetic stirring to form a homogeneous solution at room temperature. After gentle stirring for 15 min, the solution was transferred to two 50 mL Teflon-lined stainless steel autoclave. Various substrates (3 × 3 cm) such as NF and CC were respectively immersed into the reaction solution. The autoclave was sealed and maintained at 160 °C for 6 h in an electric oven and then cooled down to room temperature. After the reaction, the samples were collected and rinsed with ultrapure water several times, followed by drying at 60 °C for 12 h.

Preparation of CaMoO₄ powder/NF: Prior to the synthesis, NF was treated by ultrasonication in 3.0 M HCl solution for 10 min to remove the possible surface oxide layer and cleaned with ethanol and deionized water. Then, The washed NF substrates and the deionized water were together transferred into an 50 mL Teflon-lined stainless steel autoclave and reacted at 160 °C for 6 h. The autoclave was cooled down to room temperature naturally, and the treated NF were collected and rinsed with deionized

water mixture several times before drying in a vacuum oven at 60 °C overnight. 20 mL CaCl₂ aqueous solution (0.5 mol L⁻¹) was added into 20 mL Na₂MoO₄:2H₂O aqueous solution (0.5 mol L⁻¹) with the assistance of strong magnetic stirring to form a homogeneous solution at room temperature. The as-formed homogenous solution was then transferred into a Teflon-lined stainless steel autoclave, which was sealed, maintained at 160 °C for 6 h, and then allowed to cool to room temperature naturally. Product was collected by centrifugation at 5000 rpm for 5 min, washed with DI water and ethanol and dried at 60 °C for 12 h. The as-prepared CaMoO₄ powder (0.01 g) was dispersed into a solution of Nafion, ethanol and water with a volume ratio of 10/250/250 via sonication, and deposited onto treated NF with a loading of 2.38 mg cm⁻².

Synthesis of RuO_2/NF : RuO₂ was prepared according to previous work.¹ Briefly, 2.61 g RuCl₃·3H₂O was dissolved in 100 mL distilled water and stirred for 10 min at 100 °C. Then, 30 mL NaOH solution (1.0 M) was added to the solution and kept vigorously stirring for 45 min at 100 °C. After that, the above solution was centrifuged for 10 min and filtered. The precipitates were collected and washed with distilled water several times. Finally, the product was dried at 80 °C overnight and then annealed at 350 °C for 1 h in air atmosphere. The as-prepared RuO₂ powder (0.01 g) was dispersed into a solution of Nafion, ethanol and water with a volume ratio of 10/250/250 via sonication, and deposited onto NF with a loading of 2.38 mg cm⁻².

Characterizations: XRD patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM measurements were performed on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were carried out on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS data were acquired on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. **Electrochemical measurements:** Electrochemical measurements were performed

with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system. CaMoO₄/NF electrode (geometric area = 0.5×0.5 cm²) was used as the working electrode. A graphite rod and an Hg/HgO were used as the counter electrode and the reference electrode, and KOH used as electrolyte, respectively. The temperature of solution was kept at 25 °C for all the measurements via the adjustment of air condition and heating support, which ensured the variation of diffusion coefficient below 1%. The potentials reported in this work were calibrated to RHE other than especially explained, using the following equation: E (RHE) = E (Hg/HgO) + (0.098 + 0.059 pH) V.

Calculation of Double-layer capacitance (C_{dl}), roughness factor (R_f), intrinsic activity, and mass activity: C_{dl} is estimated by applying the equation:²

$$C_{\rm dl} = \Delta j/2 \cdot v = (j_{\rm a} - j_{\rm c})/2 \cdot v$$

where j_a and j_c are the anodic and cathodic current density, respectively, recorded at a potential of +0.9954 V vs. RHE, and v is the scan rate (Fig. S3). The ideal plane electrode has a C_{dl} of 40 µF cm⁻², and R_f can be calculated using the equation:³

$$R_f = C_{dl}/40$$

the j_{specific} is calculated by the equation:^{4,5}

where
$$j_{\text{specific}} = j/R_{\text{f}}$$

where *j* is the OER current density at a potential of 350 mv.

The mass activity (mA mg⁻¹) values of catalysts for OER were calculated at $\eta = 350$ mV:

mass activity = $j/m_{loading}$.



Fig. S1. EDX spectrum for CaMoO₄/NF.



Fig. S2. (a) LSV curves of bare CC, CaMoO₄/CC and CaMoO₄/NF for water oxidation. (b) mass activities for CaMoO₄/CC and CaMoO₄/NF at η = 350 mV.



Fig. S3. CV curves and corresponding capacitive current densities at +0.9954 V vs. RHE against scan rate for CaMoO₄/CC (a,b), CaMoO₄ powder/NF (c,d) and CaMoO₄/NF (e,f).

Table S1. Comparison of water oxidation performance for CaMoO₄/NF with other non-noble-metal OER electrocatalysts in alkaline media.

Catalyst	J (mA cm ⁻²)	η (mV)	j _{specific} (mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	mass activity at η = 350 mV (mA mg ⁻¹)	Electrolyte	Ref.
CaMoO ₄ /NF	50	345	0.81 (η	135	24	1.0 M KOH	This work
	100	400	= 350 mV)				
CaMoO ₄ /CC	50	422	0.25 (η		15		
	100	450	= 350 mV)		15		
$Cu_x Co_y O_4 (y/x = 8)$	50	504				1.0 M KOH	6
NiMoO ₄ Nanotubes	100	445		126		1.0 M KOH	7
CuCo ₂ O ₄	10	400		67		1.0 M KOH	8
Fe(OH) ₃ :Cu(OH) ₂ /CF	10	~365	0.035(η	42		1.0 M KOH	9
	100	~407	= 370 mV)				
$Zn_xCo_{3-x}O_4-1:3$	50	400	$0.056(\eta) = 520 \text{ mV}$	51	20	1.0 M KOH	10
Co@CoO/G	50	400		83	12.5	1.0 M KOH	11
Porous Co ₃ O ₄ nanosheets	10	368		59	30	1.0 M KOH	12
α -Co(OH) ₂	50	440		76		1.0 M KOH	13
Co(OH) ₂ /Ti	50	644				1.0 M KOH	14
mCo ₃ O ₄	10	420		72		1.0 M KOH	15
CoOx film	10	403		42		1.0 M KOH	16
NiO/CoN PINWs	50	~355		35		1.0 M KOH	17
Ni(OH) ₂ bulk	20	347		47	21	1.0 M KOH	18
NiOx nanoparticles				54			
Ni(OH) ₂	50	380				1.0 M KOH	19
NiCo _{2.7} (OH) _x	10	350		65		1.0 M KOH	20
γ-CoOOH bulk	10	374		55		1.0 M KOH	21

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