Supporting Information for

Interfacial Electronic Structure Modulation Enables $CoMoO_x/CoO_x/RuO_x$ an Advanced Oxygen Evolution Electrocatalysis

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Experimental section

Synthesis of ZIF-67

In a typical synthesis, 58.3 mg of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 2 mL of deionized water containing 1 mg of cetyltrimethylammonium bromide (CTAB). Then this solution was rapidly injected into 15 mL of aqueous solution containing 908 mg of 2-methylimidazole and stirred at room temperature for 20 min. The product was collected by centrifugation and washed by ethanol for several times.

Synthesis of $CoMoO_4$-$Co(OH)_2$

22 mg freshly prepared ZIF-67 nanocubes were dispersed in 10 mL ethanol to form solution A, and 100 mg of Na_2MoO_4 was dissolved in 10 mL H_2O + 10 mL ethanol to form solution B. Subsequently, solution A was injected into solution B rapidly with continuous stirring at 80 °C for 2 h. After being cooled to room temperature, the

product was rinsed by ethanol several times and separated by centrifugation.

Synthesis of Ru-$CoMoO_4$-$Co(OH)_2$

The freshly prepared $CoMoO_4$-$Co(OH)_2$ nanoboxes were dispersed in 10 mL of ethanol by ultrasound. At the same time, 2 mg of $RuCl_3$ was dissolved in a solution containing 2 mL of H_2O. $RuCl_3$ solution was added to the $CoMoO_4$-$Co(OH)_2$ solution drop by drop with continuous stirring for 5h at room temperature. After that, the product were collected by centrifugation and washing 3 times with ethanol.

Synthesis of $CoMoRuO_x$

To obtain $CoMoRuO_x$, 10 mg of the as-prepared Ru-$CoMoO_4$-$Co(OH)_2$ were annealed in air at different temperatures (300°C, 350 °C, 400°C) for 2 h with a ramp rate of 2 °C min^{-1}. The finally obtained catalyst was named as $CoMoRuO_x$-a (a represents the temperature) for easy distinction.

Characterizations

The chemical compositions of the all samples were determined by SEM-energy-dispersive-X-ray spectroscopy (SEM-EDS). Low-magnification transmission electron microscopy (TEM) was performed on a HITACHI HT7700 at 120 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and HRTEM was recorded on a FEI TecnaiG2F2 FEI Talos F200X S/TEM with a field-emission gun at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on SSI S-Probe XPS Spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å).

Electrochemical tests

All electrochemical measurements were performed on CHI660 workstation (Chenhua, Shanghai) by using the three-electrode system. The system consisted of a graphite rod counter electrode, Ag/AgCl reference electrode, and a glassy carbon electrode (GCE) as working electrode. To prepare the catalyst ink, 6 mg catalysts were added into a mixture solution including 1.6 mL of isopropanol, 0.4 mL of H_2O and 20 μL Nafion. After 30 min sonication, 20 μL catalyst ink was deposited on glassy carbon electrode (diameter 5 mm, area: 0.196 cm^2) as a working electrode. The polarization curves were performed in 1 M KOH solution without iR compensation. The Tafel slopes were derived from polarization curves. Prolonged CP tests were conducted at the current density of 10 mA cm^{-2}. Electrochemical water splitting was tested by using a two-electrode system.

Calculation of ECSA

The calculation of the electrochemical surface areas (ECSA) are based on the measured double layer capacitance of the catalysts modified electrode in 1.0 M KOH according to previous published report. Briefly, a potential range where no apparent Faradaic process happened was determined firstly using the static CV. The charging current i_c was measured from the CVs at different scan rates. The relation between i_c, the scan rate (ν) and the double layer capacitance (C_{DL}) was given in eq 1. Therefore, the C_{DL} is then calculated according to: C_{DL}=d (Δj (0 V vs. RHE))/2dv.

$$i_c = \nu C_{DL} \qquad (1)$$

For the estimation of ECSA, a specific capacitance (C_S) value C_S = 0.040 mF cm^{-2} in

1.0 M KOH.

$$ECSA = C_{DL} / C_S \qquad (2)$$

Supporting Figures and Tables

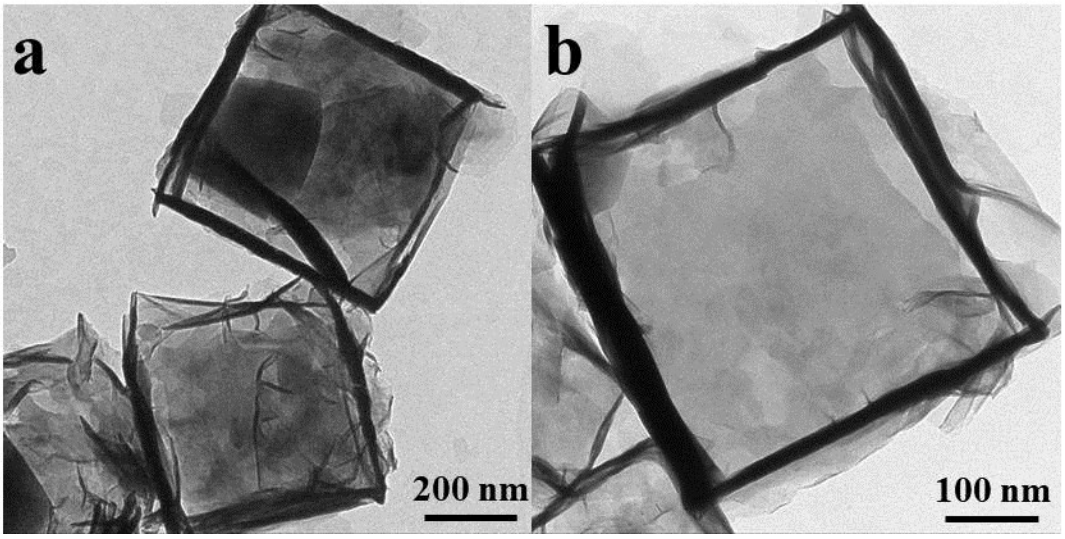

Fig.S1 Representative TEM images of the $CoMoO_4$-$Co(OH)_2$.

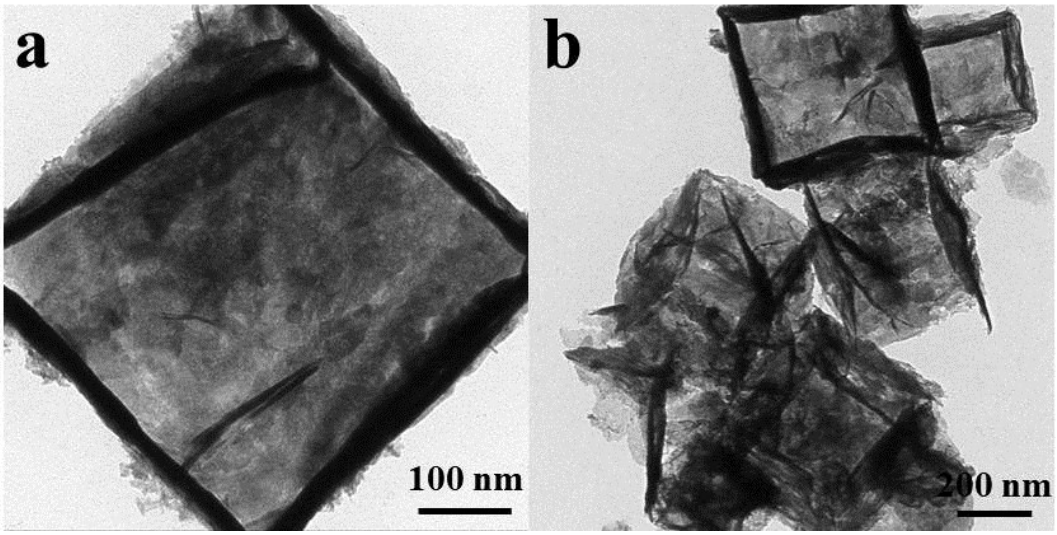

Fig.S2 Representative TEM images of the heterostructured $CoMoRuO_x$ nanoboxes.

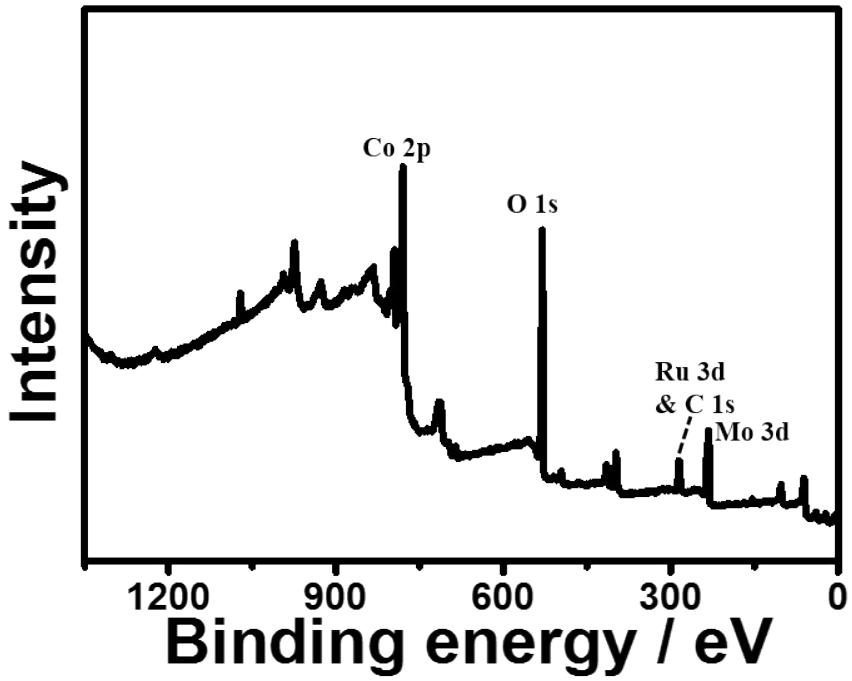

Fig.S3 Survey spectrum of the heterostructured $CoMoRuO_x$ nanoboxes.

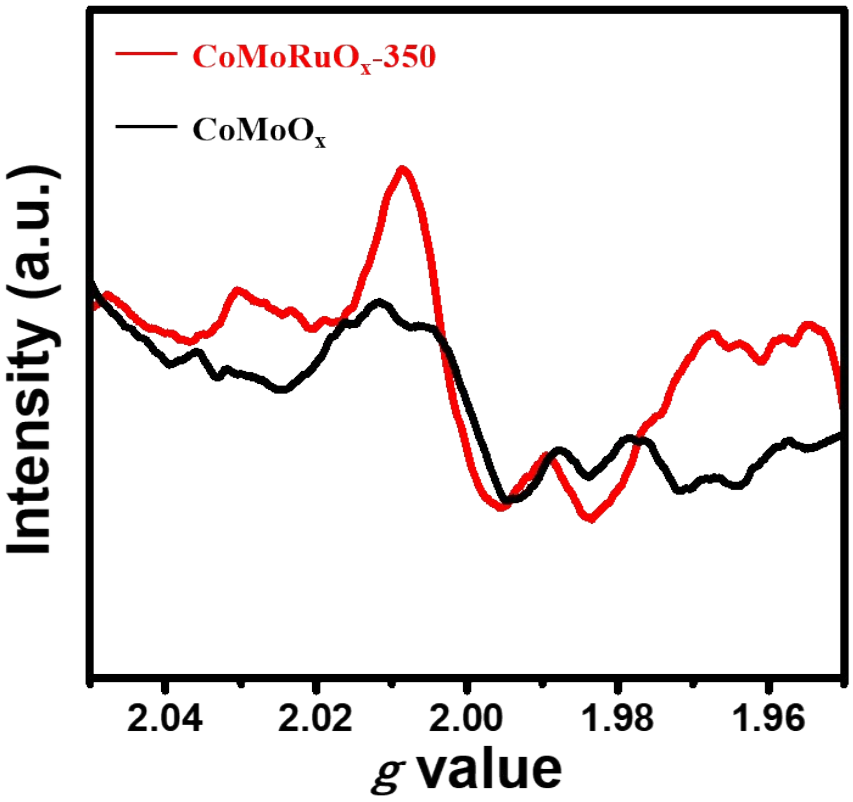

Fig.S4 EPR spectra of the $CoMoRuO_x$ and $CoMoO_x$.

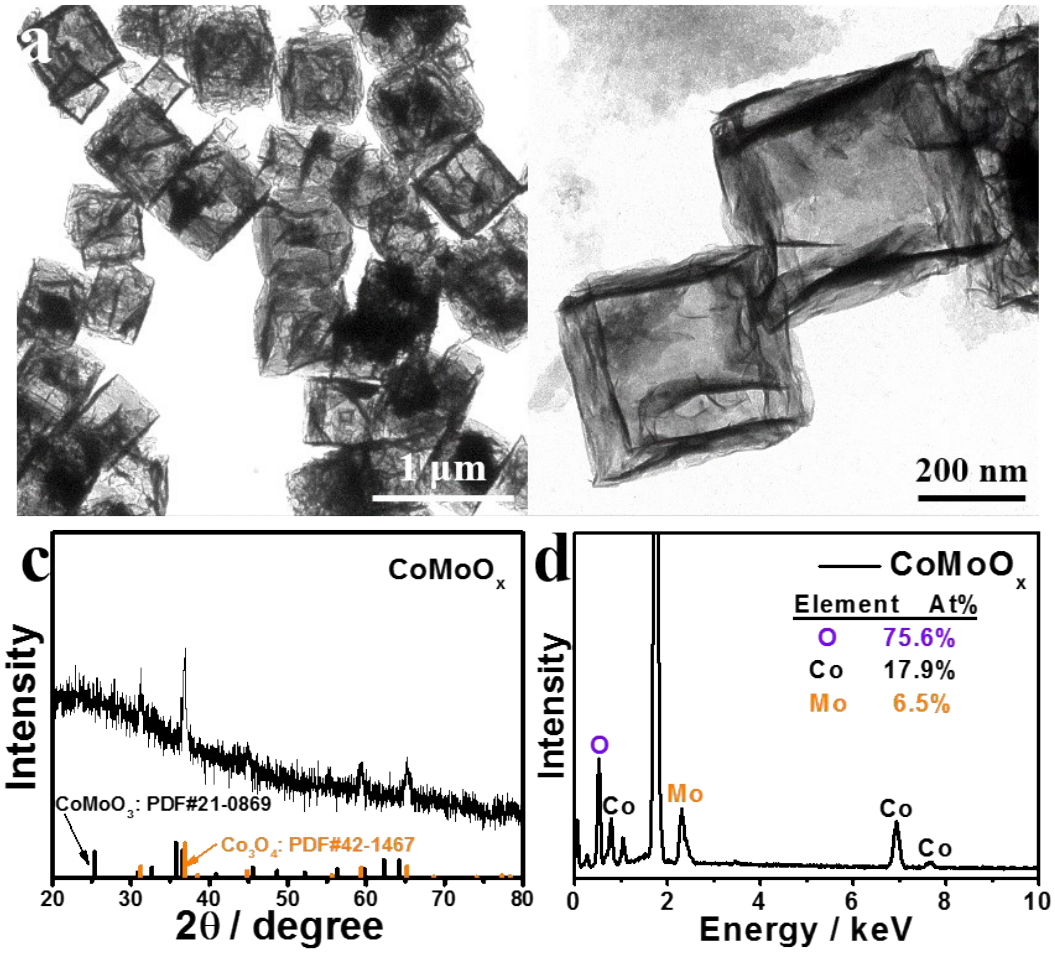

Fig.S5 (a, b) Representative TEM images of the $CoMoO_x$ nanoboxes. (c) XRD pattern and (d) EDS spectrum of the $CoMoO_x$ nanoboxes.

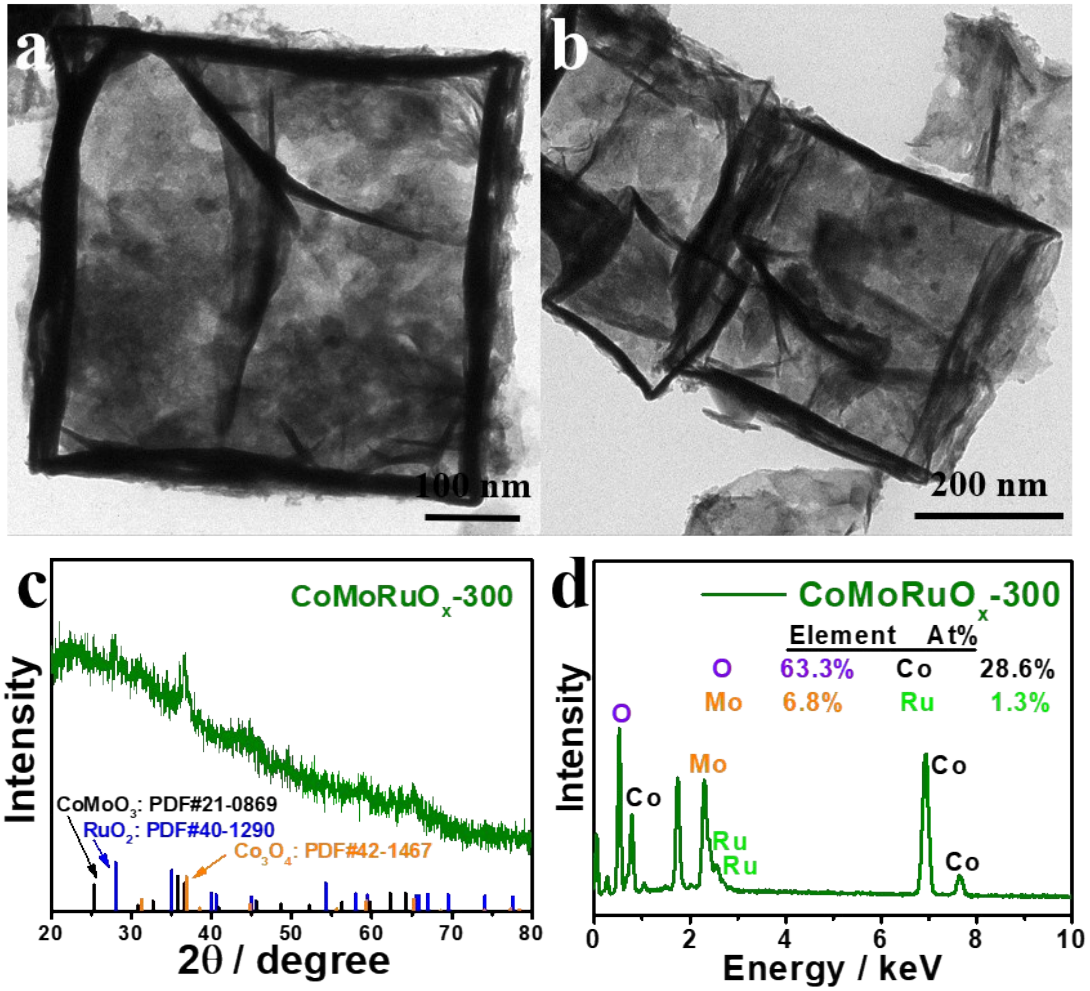

Fig.S6 (a, b) Representative TEM images of the $CoMoRuO_x$-300 nanoboxes. (c) XRD pattern and (d) EDS spectrum of the $CoMoRuO_x$-300 nanoboxes.

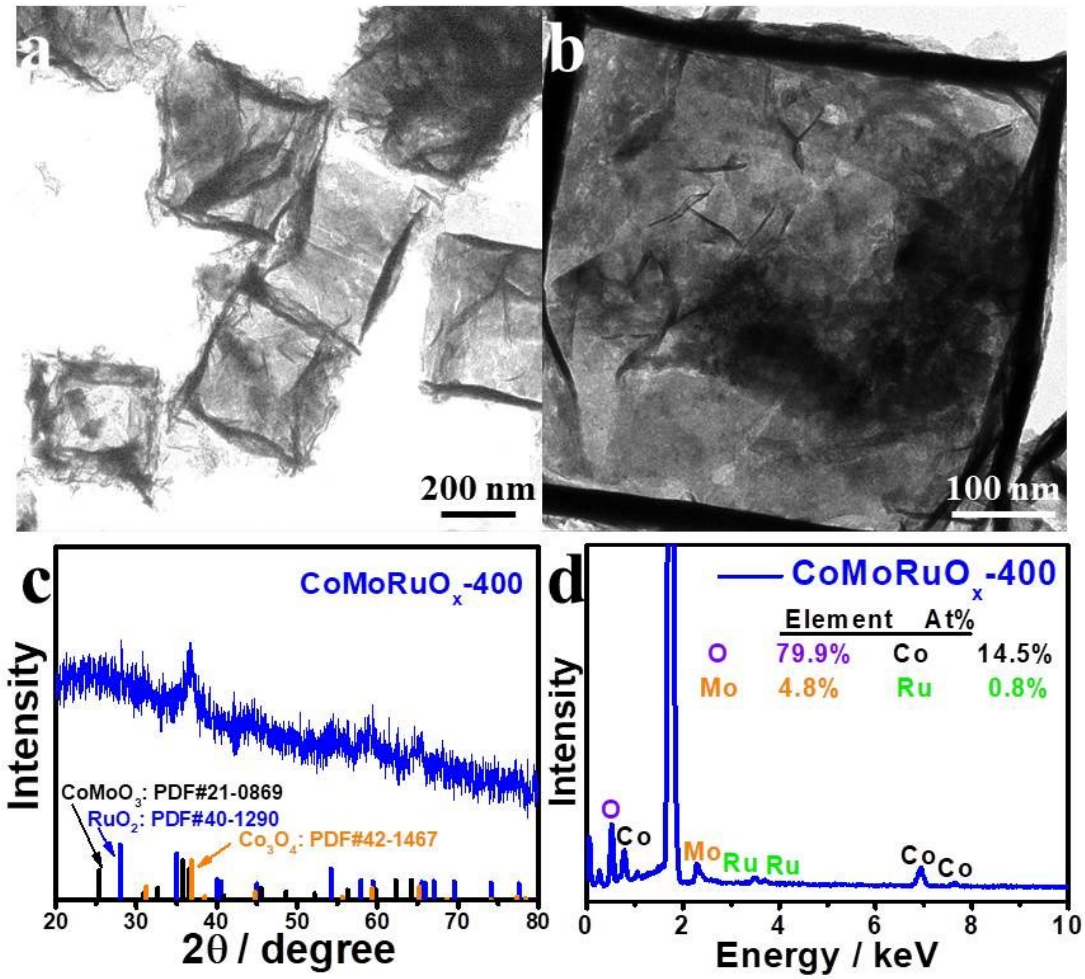

Fig.S7 (a, b) Representative TEM images of the $CoMoRuO_x$-400 nanoboxes. (c) XRD pattern and (d) EDS spectrum of the $CoMoRuO_x$-400 nanoboxes.

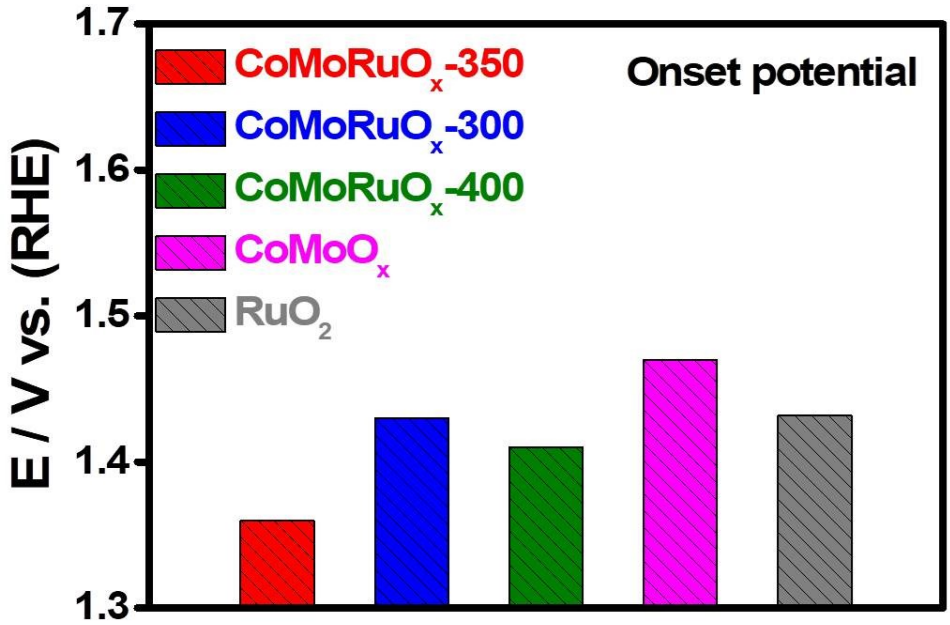

Fig.S8 Histogram of the onset potentials of different electrocatalysts toward OER.

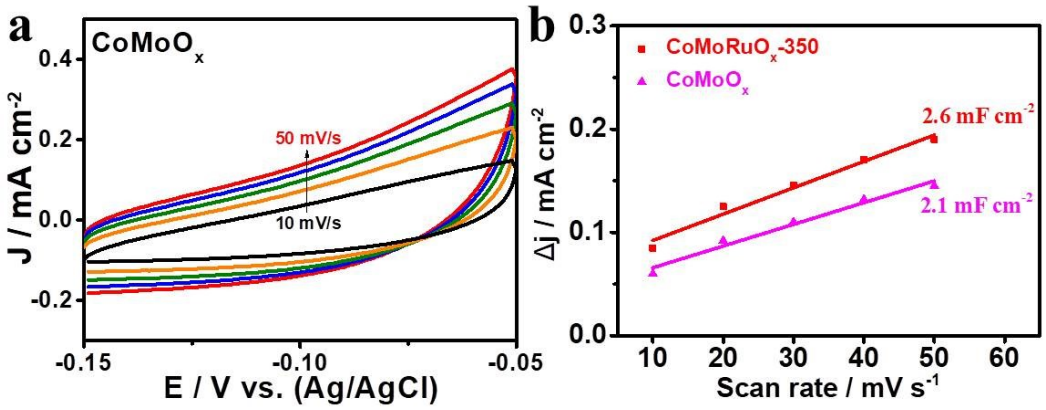

Fig.S9 (a) CV curves of $CoMoO_x$ in 1 M KOH solution at different scan rates. (b) Double layer currents of different catalysts versus scan rate.

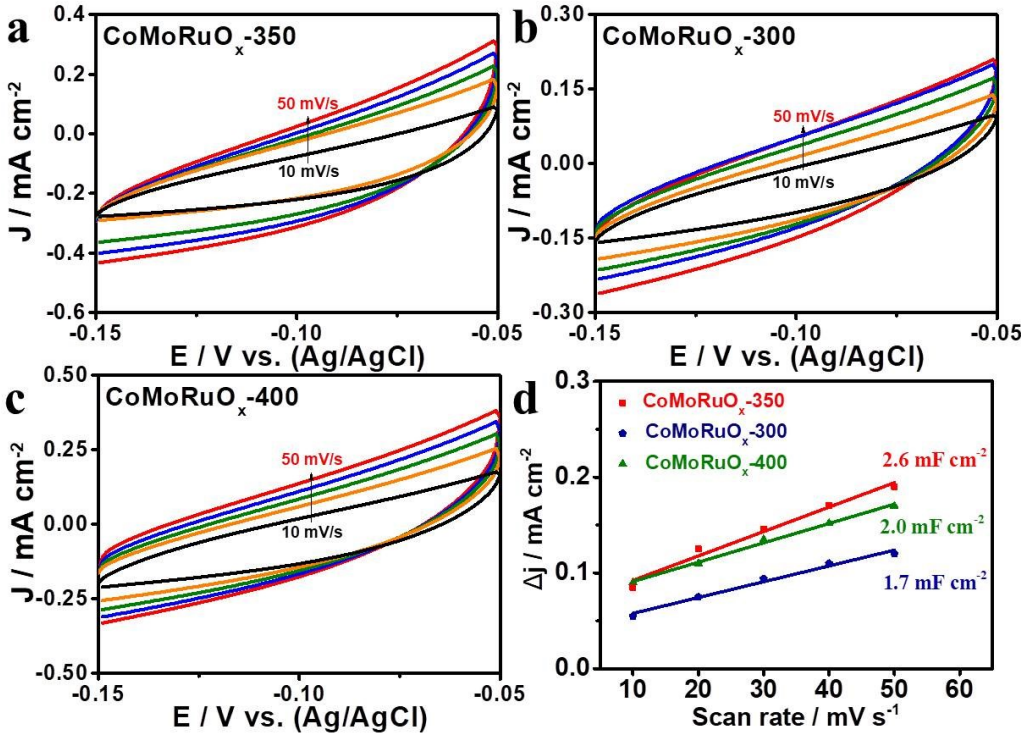

Fig.S10 CV curves of (a) $CoMoRuO_x$-350, (b) $CoMoRuO_x$-300, and (c) $CoMoRuO_x$-400 in 1 M KOH solution at different scan rates. (d) Double layer currents of different catalysts versus scan rate.

Table S1 OER activity comparison of different electrocatalysts.

Catalyst	**η(mV)**	**Electrolyte**	**Reference**
$CoMoRuO_x$	**250**	1.0 M KOH	**This work**
$CoVO_x$-300	330	1.0 M KOH	Appl. Catal. B: Environ. 2020, 265, 118605
Ru SAs/AC-FeCoNi	205	1.0 M KOH	Adv. Energy Mater. 2020, 2002816
VO-$(Co, Fe)_3O_4$/CC	286	1.0 M KOH	Appl. Surf. Sci. 2020, 529, 147125
Ru-NiCoP/NF	216	1.0 M KOH	Appl. Catal. B: Environ. 2020, 279, 119396
1-RuO_2/CeO_2	350	1.0 M KOH	Int. J. Hydrog. Energy 2020, 45, 18635-18644
NiMoRuO (CC)	280	1.0 M KOH	Chem. Eng. J. DOI:10.1016/j.cej.2020.127686
N_1-CoP@NPCNFs-900	266	1.0 M KOH	J. Alloys Compd. 2021, 854, 156830
Co_3O_4-24 h	296	1.0 M KOH	J. Colloid Interface Sci. 2021, 582, 322-332
N-$NiCoP_x$/NCF	298	1.0 M KOH	Chem. Eng. J. 2020, 402, 126257
Co/β-Mo_2C@N-CNTs	356	1.0 M KOH	Angew. Chem. Int. Ed. 2019, 58, 4923–4928
FeCo@C	302	1.0 M KOH	Int. J. Hydrog. Energy 2020, 45, 26574-26582
Co_3O_4/Fe_2O_3	310	1.0 M KOH	Chem. Eng. J. 2019, 355, 336-340
$Co_3O_4/Co_{0.85}Se/Co_9Se_8$	360	1.0 M KOH	Inorg. Chem. 2020, 59, 17326
CoOx/CoNy@$CN_{z,700}$	280	1.0 M KOH	Appl. Catal. B: Environ. 2020, 279, 119407
C-CoP-1/12	321	1.0 M KOH	Nanoscale 2019, 11, 17084–17092
Co_3O_4-MoS_2	298	1.0 M KOH	J. Alloys Compd. 2021, 853, 156946
Co-Mo_2C@NCNT	377	1.0 M KOH	ACS Sustain. Chem. Eng. 2018, 6, 9912–9920

Table S2 EIS fitting parameters from equivalent circuits of samples during electrocatalytic process.

Samples	R_s / Ω cm^{-2}	R_0 / Ω cm^{-2}	Q / S s-n	R_{ct} / Ω cm^{-2}	Q_1 / S s-n
$CoMoRuO_x$	7.2	2.5	4.60E-2	3.6	0.21E-3
$CoMoO_x$	6.8	7.4	2.14E-2	394	2.73E-3