

## **Electronic Supplementary Information**

### **Ultrathin nanosheets constructed CoMoO<sub>4</sub> porous flower with high activity for electrocatalytic oxygen evolution**

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## I. Experimental Section

**Chemicals.** Cobalt (II) chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ), urea and ethanol were purchased from Shanghai Chemical Reagent Co. Ltd. The iridium oxide ( $\text{IrO}_2$ ) was purchased from Strem Chemicals, Inc. Nafion (5 wt%) was obtained from Sigma-Aldrich. Ultrapure water ( $18.2 \Omega \text{ cm}^{-2}$  resistivity) was used for all aqueous solution. All chemicals were of analytical grade and used as received without further purification.

**Hydrothermal synthesis of  $\text{CoMoO}_4$  sample.** In a typical procedure,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol),  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (0.071 mmol) and  $\text{CO}(\text{NH}_2)_2$  (5 mmol) were dissolved in 36 mL of deionized (DI) water and stirred to form a clear solution at room temperature. The as-formed homogenous solution was then transferred into a Teflon-lined stainless steel autoclave, which was sealed, maintained at  $120 \text{ }^\circ\text{C}$  for 12 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  $60 \text{ }^\circ\text{C}$  for 12 h.

**Synthesis of  $\text{Co}_3\text{O}_4$  sample.** The comparative  $\text{Co}_3\text{O}_4$  sample was prepared by a facile two-step method. After a similar hydrothermal process without adding  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  described above, the product was calcined in air at  $400 \text{ }^\circ\text{C}$  for 3 h. The resulting powders can be collected after the tube furnace cooling down to room temperature.

**Hydrothermal synthesis of  $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$  sample.** The pure  $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$  sample was prepared by a similar hydrothermal process without adding  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  described above. Product was collected by centrifugation at 5000 rpm for 5 min, washed with DI water and ethanol and dried at  $60 \text{ }^\circ\text{C}$  for 12 h.

**Electrochemical measurements.** 4 mg of catalyst powder and 40  $\mu\text{L}$  Nafion solution (5 wt%) were dispersed in 1 mL of 4:1 v/v water/ethanol by at least 30 min sonication to form a homogeneous ink. Then 5  $\mu\text{L}$  of the catalyst ink was loaded onto a glassy carbon electrode of 3 mm in diameter (loading  $0.285 \text{ mg cm}^{-2}$ ). For comparison, the electrodes were also modified with  $\text{IrO}_2$ . Finally, the as-prepared catalyst films were dried at room temperature.

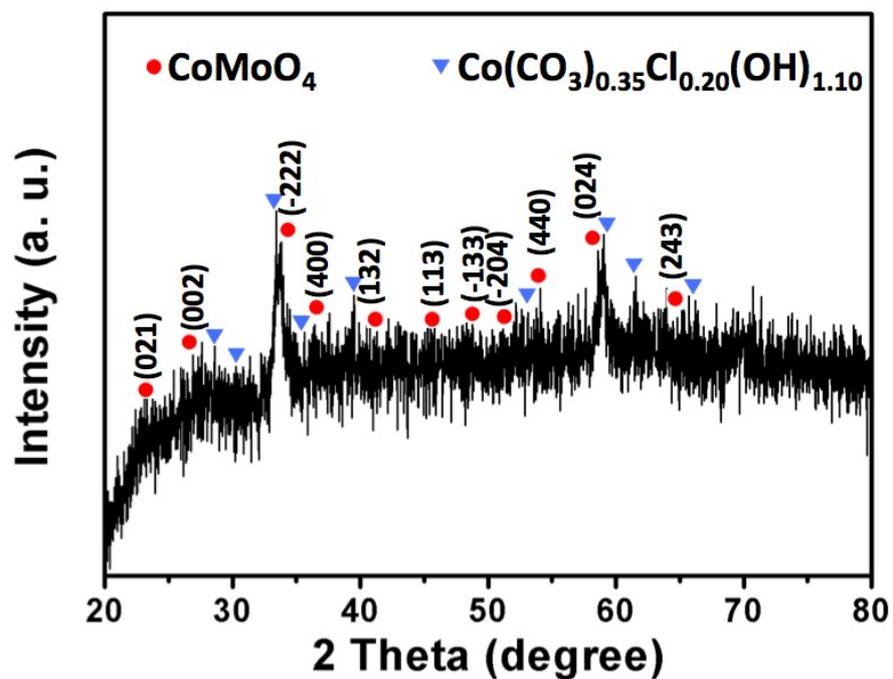
All electrochemical studies were performed using a CHI 660 potentiostat (CH Instruments, China) in a three-electrode setup in 1 M KOH aqueous solution. The reference electrode and counter electrode were Ag/AgCl electrode (3.5 M KCl) and platinum mesh, respectively.

The electrocatalytic activity of the catalysts towards OER was examined by polarization curves using linear sweep voltammetry (LSV) with a sweep rate of 5 mV

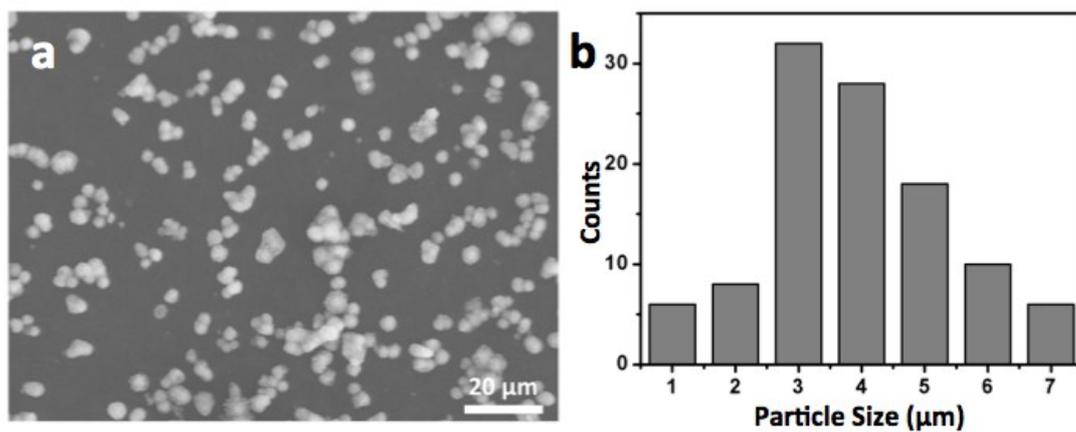
s<sup>-1</sup> in 1 M KOH at room temperature. All of the potentials in our manuscript were calibrated to a reversible hydrogen electrode (RHE) by following calculations:  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.205$ . All LSV polarization curves were not corrected. AC impedance measurements were carried out in the same configuration when the working electrode was biased at overpotential of 350 mV from 10<sup>5</sup> Hz to 1 Hz with an AC voltage of 5 mV. Galvanostatic measurement ( $j = 10 \text{ mA/cm}^2$ ) was performed to evaluate the long-term stability.

**Characterizations.** The morphology and structure of the samples were characterized by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEM 2100, 200 kV). Brunauer-Emmett-Teller (BET) surface area measurements were performed at 77K on a Micromeritics ASAS 2460 adsorption analyzer in N<sub>2</sub>-adsorption mode. The sample was degassed at 150 °C for 24 h under vacuum prior to the measurements. The crystal structure was determined by X-ray diffraction (XRD, D/max2550V). Further, the chemical states of the elements in catalysts were studied by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD), and the binding energy of C 1s peak at 284.8 eV was taken as an internal standard.

## II. Supporting Figures



**Figure S1.** XRD pattern of the as-prepared sample. Circle:  $\text{CoMoO}_4$  (JCPDS card No. 21-0868). Triangle:  $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$  (JCPDS No. 38-0547).



**Figure S2.** (a) SEM image of synthesized  $\text{CoMoO}_4$  micro-flowers. (b) The particle size histogram of synthesized  $\text{CoMoO}_4$  micro-flowers obtained from (a).

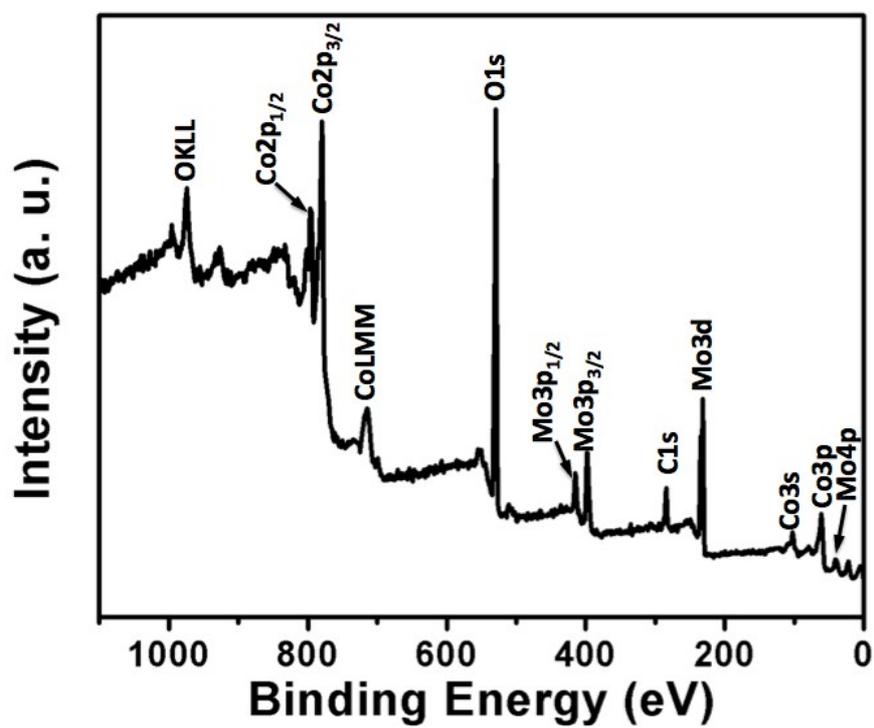
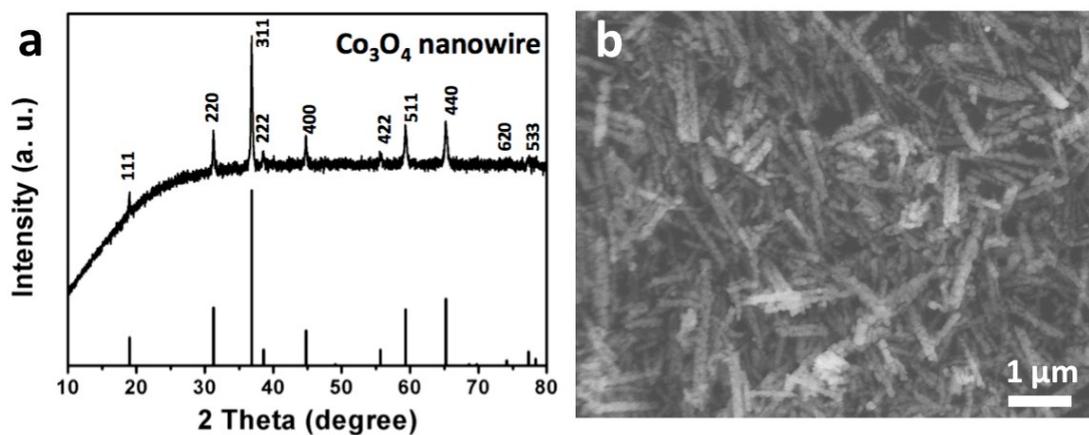
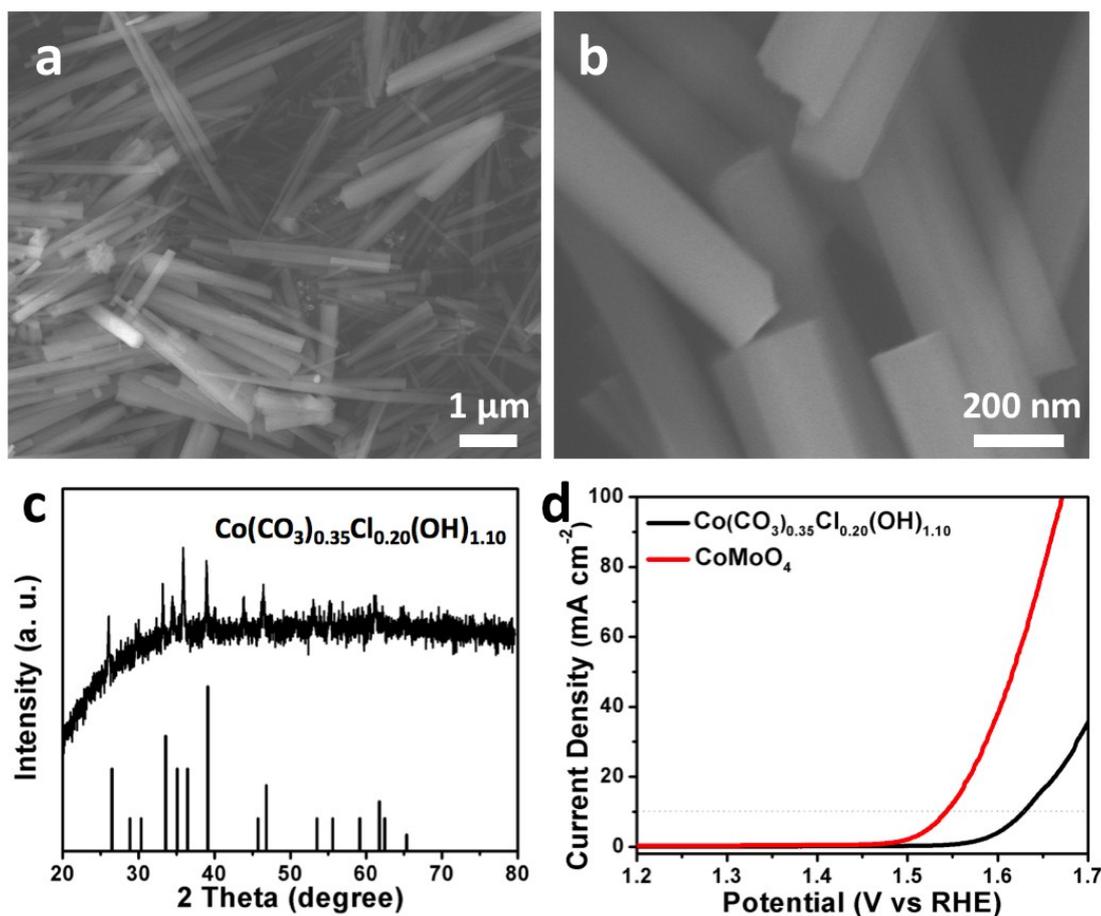


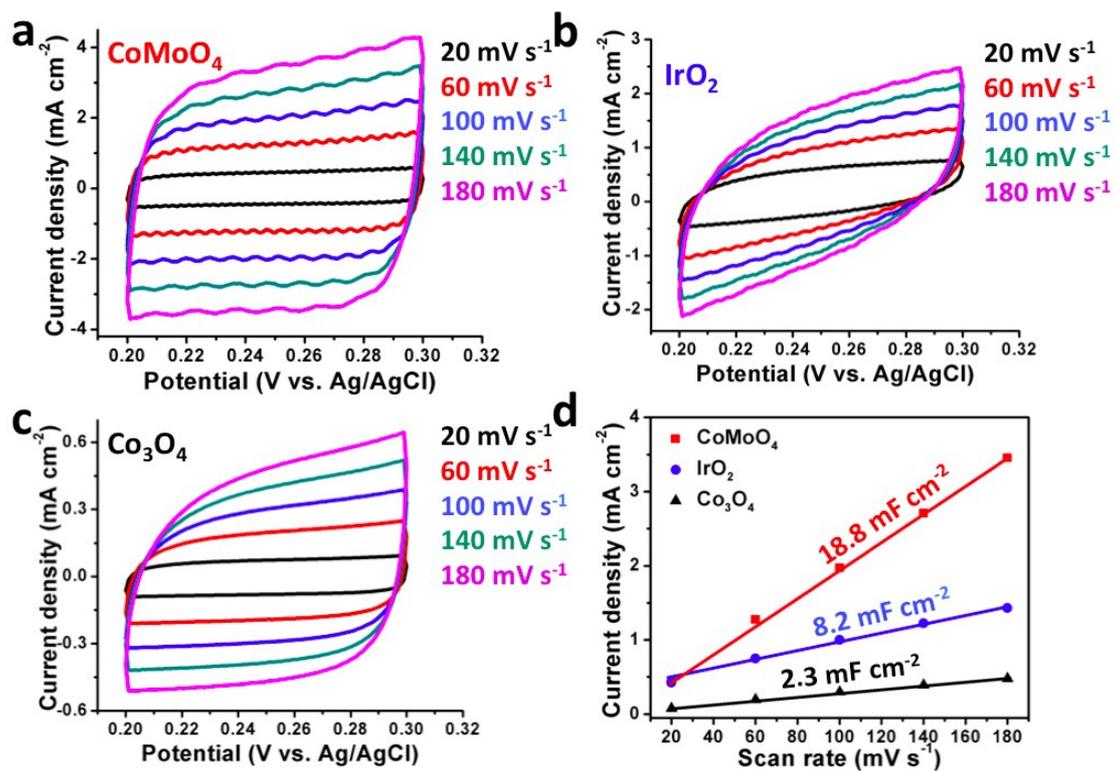
Figure S3. XPS survey spectrum of as-prepared CoMoO<sub>4</sub> sample.



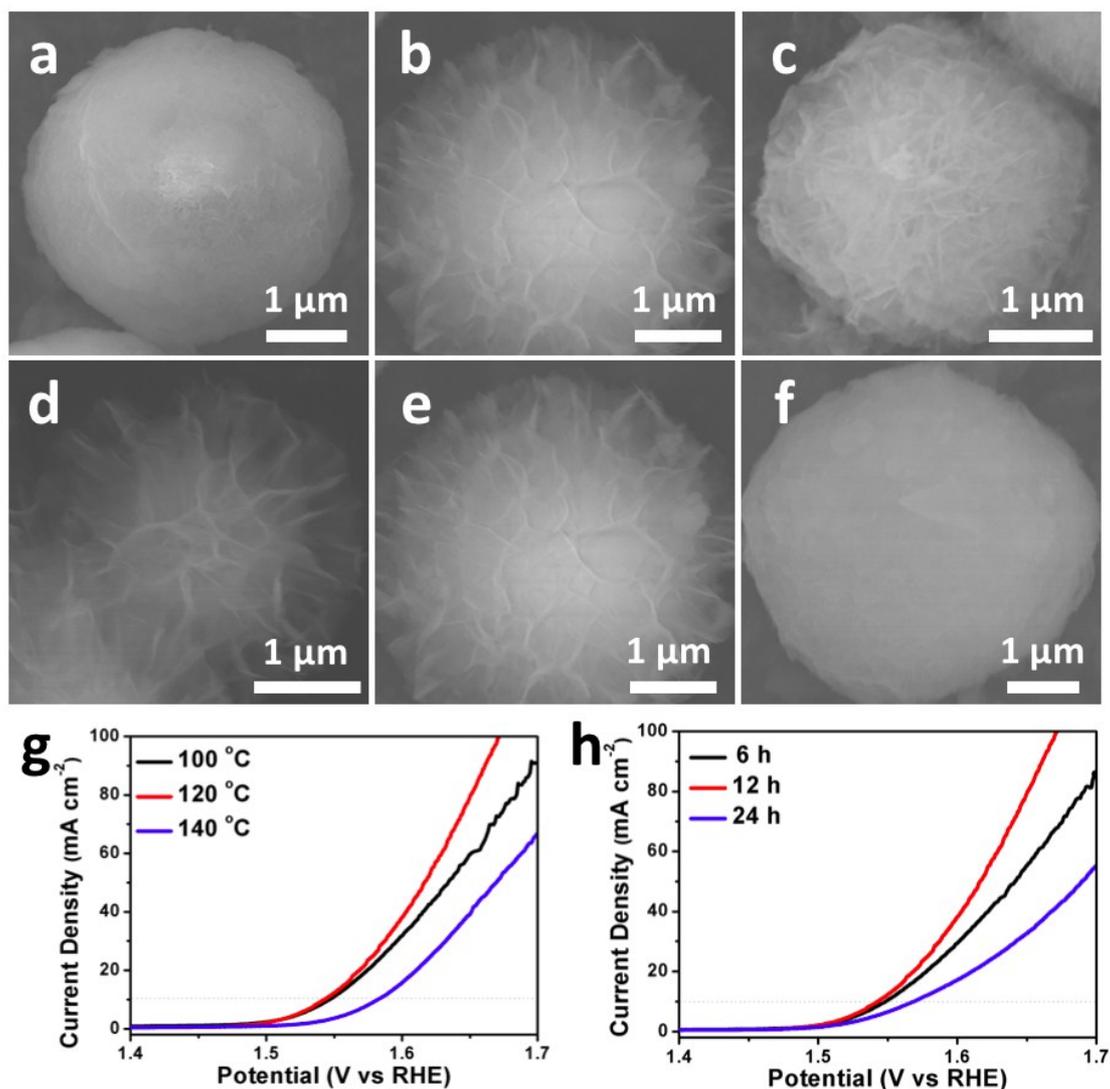
**Figure S4.** (a) XRD pattern of  $\text{Co}_3\text{O}_4$  sample. All the diffraction peaks of the prepared  $\text{Co}_3\text{O}_4$  sample can be indexed to the cubic  $\text{Co}_3\text{O}_4$  (JCPDS No. 43-1003). (b) SEM image of  $\text{Co}_3\text{O}_4$  sample.



**Figure S5.** (a) Low-magnification and (b) high-magnification SEM images of pure  $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$  nanowires. (c) XRD pattern of the  $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$  nanowires, All the diffraction peaks of the prepared  $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$  sample can be indexed to the standard card of  $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$  (JCDPS No. 38-0547). (d) Polarization curves for OER on pure  $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$  nanowires and  $\text{CoMoO}_4$  micro-flowers, which shows that  $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$  nanowires have little OER activity.



**Figure S6.** (a-c) EDLC curves of CoMoO<sub>4</sub>, IrO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> respectively at different scan rates in a potential window where no Faradaic process occur (0.2-0.3 V vs. Ag/AgCl). (d) Plots of current densities at 0.25 V vs scan rates of CoMoO<sub>4</sub>, IrO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> respectively.



**Figure S7.** SEM images of the CoMoO<sub>4</sub> procedure with different hydrothermal reaction conditions: (a) at 100 °C for 12h, (b) at 120 °C for 12h, (c) at 140 °C for 12h, (d) at 120 °C for 6h, (e) at 120 °C for 12h, (f) at 120 °C for 24h; (g) is the corresponding polarization curves for OER of (a-c); and (h) is the corresponding polarization curves for OER of (d-f).

To study the formation mechanism of the spherical CoMoO<sub>4</sub> architecture, a series of experiments with different reaction conditions were carried out. Under hydrothermal environment at 120 °C, the CoMoO<sub>4</sub> crystallites began to grow along the layered plane and assembled to form sphere-shape structures as the reaction continued, leading to the formation of hierarchical CoMoO<sub>4</sub> micro-flowers. As shown in Fig. S7, the reaction temperature and the reaction time can affect the morphology of the synthesized CoMoO<sub>4</sub> product. Of which, the product obtained at 120 °C for 12 h has the morphology of sphere constructed by ultrathin nanosheets. Moreover, benefitting from the high specific surface area and constituent nanosheet with an ultrathin thickness, it exhibits superior electrocatalytic activity.

**Table. S1. Comparison of the electrocatalytic activity of CoMoO<sub>4</sub> to recently reported Co-based OER electrocatalysts in basic electrolyte<sup>†</sup>**

Catalysts (mg/cm <sup>2</sup> )	Electrolyte	Onset potential (mV)	Overpotential at 10 mA/cm <sup>2</sup> (mV)	Tafel (mV/decade)	Ref.
Co <sub>3</sub> O <sub>4</sub> /N-rmGO/Ni foam (1.0)	1M KOH	/	310	67	<i>Nat. Mater.</i> , 2011, 10, 780-786.
<b>CoMoO<sub>4</sub> (0.285)</b>	<b>1M KOH</b>	<b>235</b>	<b>312</b>	<b>56</b>	<b>this work</b>
CoSe <sub>2</sub> (0.142)	0.1M KOH	/	320	44	<i>J. Am. Chem. Soc.</i> , 2014, 136, 15670-15675.
(Ln <sub>0.5</sub> Ba <sub>0.5</sub> )CoO <sub>3-x</sub> (0.25)	0.1M KOH	/	~330 (Ln=Pr)	/	<i>Nat. Commun.</i> , 2013, 4, 2439.
crumpled graphene-CoO (0.7)	1M KOH	/	340	71	<i>Energy Environ. Sci.</i> , 2014, 7, 609-616.
NiCo <sub>2.7</sub> (OH) <sub>x</sub>	1M KOH	250	350	65	<i>Adv. Energy Mater.</i> , 2015, 5, 1402031.
CoMn-LDH (0.142)	1M KOH	/	350	43	<i>J. Am. Chem. Soc.</i> , 2014, 136, 16481-16484.
CoCo-NS (0.07)	1M KOH	307	353	45	<i>Nat. Commun.</i> , 2014, 5, 4477.
Ba <sub>0.5</sub> Sr <sub>0.5</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3-x</sub>	0.1M KOH	314	~362	~48	<i>Science</i> , 2011, 134, 1383-1385.
exfoliated NiCo LDH /carbon paper (0.08)	1M KOH	/	367	40	<i>Nano Lett.</i> , 2015, 15, 1421-1427
reduced Co <sub>3</sub> O <sub>4</sub> (0.136)	1M KOH	290	~410	72	<i>Adv. Energy Mater.</i> , 2014, 4, 1400696.
SrNb <sub>0.1</sub> Co <sub>0.7</sub> Fe <sub>0.2</sub> O <sub>3-δ</sub>	0.1M KOH	260	420	90	<i>Angew. Chem. Int. Ed.</i> , 2015, 54, 1-6.
Mn <sub>3</sub> O <sub>4</sub> /CoSe <sub>2</sub> (0.2)	0.1M KOH	/	450	49	<i>J. Am. Chem. Soc.</i> , 2012, 134, 2930-2933.
mesoporous Co <sub>3</sub> O <sub>4</sub>	1M KOH	/	476	/	<i>Nano Res.</i> , 2013, 6, 47-54.
Au/mCo <sub>3</sub> O <sub>4</sub>	0.1M KOH	300	650	46	<i>ChemSusChem</i> , 2014, 7, 82-86.

<sup>†</sup> The table was built by the column of the overpotential that reaches to the current density of 10 mA cm<sup>-2</sup> in a descending order.