# **Electronic Supplementary Material (ESI)**

Humid atmospheric pressure plasma jets exposed micro-defects on

CoMoO<sub>4</sub> nanosheets with enhanced OER performance

## I. Material preparation

### **Raw materials**

Cobalt (II) acetate tetrahydrate (Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O), Sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O), Anhydrous ethanol were purchased from Shanghai Chemical Reagent Co. Ltd. The iridium oxide (RuO<sub>2</sub>) was purchased from Pharmaceutical Group Co. Ltd. All prepared solutions are deionized water (18.2  $\Omega$ •cm<sup>-2</sup> resistivity). All chemicals were of analytical grade and used as received without further purification.

## Synthesis of CoMoO<sub>4</sub>

In this work, Co and Mo sources are derived from 0.1 mmol of  $Co(CH_3COO)_2 \cdot 4H_2O$ and 0.1 mmol of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, transfer to a beaker, add 35 mL of deionized water, sonicate for 10 min. to be completely mixed and dissolved to form a homogeneous solution. The stirred mixed solution was transferred to a 50 mL PTFE liner, and the acid-treated carbon fiber cloth (CC) was placed in a reaction vessel at 154 °C hydrothermal reaction for 4 hours in a blast drying oven. The CC substrate (2 × 2 cm<sup>2</sup>) was rinsed by ultrasonication with ethanol and water for several times to get rid of impurities on the surface, and then was activated by nitric acid (40 %) for 4 h. The hydrated form of cobalt molybdate formed on CC. Thereafter, the obtained-product was washed with deionized water several times to remove surface enriched product. Dry overnight, then transferred to a muffle furnace and heated with nitrogen (or argon) at 400 °C for 2 h. Cobalt molybdate formed on the CC can be indicated from the Xray diffraction (XRD) information.

#### Plasma treatment of CoMoO<sub>4</sub>

For modification, the fabric was then processed by atmospheric pressure plasma jets (APPJs) sustained in argon/ 0.1% water vapour mixture for 30, 60, 120 and 180 seconds, respectively. The plasma parameters were a power supply voltage of 15 kV and a frequency of 20 KHz. The samples of treated fabric prepared by this method were designated as Name-30s, Name-60s, Name-120s and Name-180s, respectively.

#### Working electrode and Electrochemical measurements

The prepared electrode material is cut into an electrode  $(2 \times 2 \text{ cm}^2)$ , one of the sections is cut into a strip, leaving a section  $(1 \times 1 \text{ cm}^2)$  for testing, which can be directly clamped on the electrode holder of the platinum sheet to prepare a three-electrode test. By observing the loading mass of cobalt molybdate on the CC, RuO<sub>2</sub> with the same mass density was coated on the Glassy carbon (GC).

All electrochemical tests were performed at the Autolab electrochemical workstation (PGSTAT 302N, Metrohm China Ltd.) in 1M KOH aqueous solution with three electrodes. Characterization of OER electrochemical performance was examined by linear sweep voltammetry (LSV) and iR compensated with a sweep rate of 5 mV s<sup>-1</sup> after cyclic voltammetry curve (CV) activation. All the potentials in our test results

were calculated and calibrated to the reversible hydrogen electrode (RHE), as follows:  $E_{vsRHE} = E_{vs.SCE} + 0.059 \times pH + 0.242V$ 

Electrochemical impedance measurements were carried out in the FRA impedance potentiostatic when the working electrode was biased at overpotential of 320 mV from 100 KHz to 0.1Hz with an AC voltage of 2 mV. In order to obtain the surface area of electrochemical activity to measure the electrochemical capacitance, the scanning range of potential is  $1.12 \sim 1.22$  V(vs.RHE), and the scanning rate ranges from 2mV/s to 10mV/s, respectively. The Galvanostatic measurement (j = 10 mA/cm<sup>2</sup>) was performed to evaluate the long-term stability.

## **Physical characterization**

Samples prepared with D/Max-2550 PC X - ray diffractometer (XRD, Rigaku, Cu-Ka radiation) and scanning electron microscope (SEM, S-4800), and transmission electron microscope (TEM, JEM-2100F) characterization. The characteristic peaks of X-ray photoelectron spectra (XPS) were collected using a PHI Quantum-2000 electron spectrometer (Ulvac-Phi, Japan) with 150 W monochromatized Al Ka radiation (1486.6 eV) were used to compare the valence state changes of samples. The peak of C 1s binding energy at 284.8 eV was taken as an internal standard.

## II. Supplementary Experimental Figures



Figure S1. The XRD of CoMoO<sub>4</sub> powder, CoMoO<sub>4</sub> on the CC and humid atmospheric pressure plasma jets treated for 60 seconds CoMoO<sub>4</sub>. In order to better understand the XRD result of supported cobalt molybdate, a target of CoMoO<sub>4</sub> powders which not supported on CC was collected as the comparison sample, the result get senior anastomotic with each other.

According to the definition of the Bragg's Law

$$2d\sin \mathbb{Q} = n\lambda$$

d - crystal plane spacing;  $\Theta$  - the Angle between the X-ray and crystal plane;  $\lambda$  - the wavelength of the X-ray; and n - the diffraction series.



Figure S2. (a-d) SEM images of the plasma treatment of  $CoMoO_4$  for 30 seconds, 60 seconds, 120 seconds and 180 seconds.



Figure S3. Electrochemical impedance analysis for  $RuO_2$ , pristine CoMoO<sub>4</sub> and CoMoO<sub>4</sub> treated by plasma for 30 seconds, 60 seconds, 120 seconds and 180 seconds at overpotential 320 mV, and add equivalent circuit diagram.



Figure S4.  $CoMoO_4$  plasma with 60s' linear sweep voltammetry (LSV) curves compared to  $RuO_2$  at 20 mA cm<sup>-2</sup>.



Figure S5, (a-e) diagrams are pristine  $CoMoO_4$ ,  $CoMoO_4$ -30s,  $CoMoO_4$ -60s,  $CoMoO_4$ -120s and  $CoMoO_4$ -180s scan rates increasing from 2 to 10 mV s<sup>-1</sup>, respectively. utilize cyclic volt-ampere characteristic curves at different sweep speeds double-layer capacitance to measure ECSA. (f) The peak oxidation current is selected at 1.18V compare with the Reversible Hydrogen Electrode relationship with the scan rate curve pristine CoMoO\_4, CoMoO\_4-30s, CoMoO\_4-60s, CoMoO\_4-120s and CoMoO\_4-180s.

For various materials with double layer capacitance ECSA is calculated from  $C_{dl}$  according to:

$$ECSA = \frac{C_{dl}}{C_s} \ (Eq1)$$

![](_page_6_Figure_0.jpeg)

The structure of  $\text{CoMoO}_4$  obtained from CrystalMaKer® 2.2.4

Figure S6. Crystal structure of  $CoMoO_4$ ,<sup>s1</sup> Atoms: red = surface oxygens, blue = cobalt, gray = molybdenum. The Volume = 642.8 Å<sup>3</sup>.

#active sites per real surface area :  

$$A^{COMOO_4-60s}_{ECSA} = \frac{63.5mFcm^{-2}}{40 \ uFcm^{-2}percm^2} = 1587cm^2$$

$$A^{COMOO_4-0}_{ECSA} = \frac{36.3mFcm^{-2}}{40 \ uFcm^{-2}percm^2} = 907cm^2$$
Turnover frequency (TOF) calculation of the catalysis with Eq 2:  
TOF per sites =  $\frac{total \ oxygen \ turnovers \ cm^{-2} \times geometric \ area}{activesites \ cm^{-2} \times geometric \ area}$ 

For accurate active site it is difficult to determine the direct, In Figure S6, the Monoclinic crystal cell of cobalt molybdate contains  $CoO_6$  octahedra and  $MoO_4$  tetrahedra constituted. It can be approximated that four active center sites are provided by 2  $CoO_6$  and 2  $MoO_4$ . So, the definition of the active sites that obtained a close value relevant with real number of atoms per real surface area. We get some experience from previous scholars.<sup>\$2, \$3, \$4</sub></sup>

Number of active sites per square specific surface area:

activeties  

$$= \left( \frac{4 \quad (atoms \ active \ center) \quad unit \ cell^{-1}}{642.8 \text{\AA}^3 \ unit \ cell^{-1}} \right)^{\frac{2}{3}} = 3.38316 \times 10^{14}$$

$$cm^{-2} \qquad (Eq3)$$

$$TOF \ per \ sites = \frac{total \ oxygen \ turnovers \ cm^{-2} \times geometric \ area}{active sites \ cm^{-2} \times geometric \ area} \ (Eq4)$$

Convert the total oxygen conversion frequency calculated from the current density, as follows:

$$O_{2}(per \ mA/cm^{-2}) = \left(j\frac{mA}{cm^{2}}\right) \left(\frac{1C \ s^{-1}}{1000 \ mA}\right) \left(\frac{1mol \ e^{-1}}{96485.3C}\right) \left(\frac{1mol \ O_{2}}{4mol \ e^{-1}}\right) \left(\frac{6.022 \times 10^{23} O_{2} \ mol}{1mol \ O_{2}}\right) = 1.56 \times 10^{15} O_{2}$$

$$s^{-1} cm^{-2} \ per \ (mA \ cm^{-2}) \quad (Eq5)$$

Converted to a new TOF calculation formula according to the definition formula *Eq4*:

$$TOF = \frac{1.56 \times 10^{15} O_2 \, s^{-1} cm^{-2} \, per \, (mA \, cm^{-2}) \, \times |j|}{3.38316 \times 10^{14} \, atoms \, cm^{-2} \times A_{ECSA}} \quad (Eq6)$$

Water oxidation (OER) electrocatalytic reaction relates the current and overpotential expressed by the Tafel equation:

 $\eta = a + b * log|j| (Eq7)$ 

At the overpotential of 350 mV, the TOF value of the pristine  $CoMoO_4$  is 0.024  $O_2$  s<sup>-1</sup>, but the  $CoMoO_4$ -60s get a better value is 0.1184  $O_2$  s<sup>-1</sup>.

#OER mechanism under alkaline conditions

 $\begin{array}{ll} M+OH^- \rightarrow MOH & Eq8.1\\ MOH+OH^- \rightarrow MO+H_2O & Eq8.2\\ 2MO\rightarrow 2M+O_2 & Eq8.3\\ \\ \text{or,}\\ MO+OH^- \rightarrow MOOH+e^- & Eq8.4\\ MOOH+OH^- \rightarrow M+O_2+H_2O & Eq8.5 \end{array}$ 

![](_page_8_Figure_0.jpeg)

Figure S7. Compared the change of the linear sweep voltammetry (LSV) curves of pristine  $CoMoO_4$  and plasma treated  $CoMoO_4$  with 60s at 10 cycles to 1000 cycles at scan rate of 5 mV s<sup>-1</sup> in 1 M KOH solution electrolyte.

![](_page_8_Figure_2.jpeg)

Figure S8. (a, b) The XPS survey of  $CoMoO_4$  and plasma treated  $CoMoO_4$ , and the changing of XPS after 2 hours OER. The ICP tests show the Mo element's concentrations of plasma-treated  $CoMoO_4$  sample before and after OER are 16.9175 and 3.1001 ppm, respectively.

Catalysts	Electrolyte	Overpotential at 10 mA cm <sup>-2</sup>	Tafel (mV dec <sup>-1</sup> )	Ref.
Plasma-treated CoMoO <sub>4</sub>	1M KOH	314 mV	51	This work
CoMoO <sub>4</sub> nanosheets	1M KOH	376 mV	79	This work
CoMoO <sub>4</sub> nanospheres	1M KOH	410 mV	84	s5
CoMoO <sub>4</sub> porous flower	1M KOH	312 mV	56	s6
CoMoO <sub>4</sub> nanoneedle	1M KOH	235 mV	66	s7
Co <sub>3</sub> O <sub>4</sub> nanosheets	0.1M KOH	500 mV	234	s8
plasma-engraved Co <sub>3</sub> O <sub>4</sub>	0.1M KOH	300 mV	68	s8
nanosheets				
Co <sub>3</sub> O <sub>4</sub> Nano-meshes	1M KOH	307 mV	76	s9

Table S1. OER activities of the same works electrocatalysts in KOH electrolyte

#### **Supplementary References**

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