# Supporting Information

# One Dimensional CoS<sub>2</sub>-MoS<sub>2</sub> Nano-flakes Decorated MoO<sub>2</sub> Sub-micro-wires for Synergistically Enhanced Hydrogen Evolution

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**Chemicals and synthesis:** Chemicals including commercial MoO<sub>2</sub>, NaMoO<sub>4</sub>·2H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, S powder, CS(NH<sub>2</sub>)<sub>2</sub>, CO(NH<sub>2</sub>)<sub>2</sub> and Nafion 117 solution were purchased from Sigma Aldrich. KOH pellets were purchased from Merck KGaA. MilliQ water with a resistivity  $\geq$  18 MQ was used to prepare all aqueous solutions. All the reagents were used without further purification.

## Synthesis of CoMoOS

CoMoO<sub>4</sub> sub-micron wires were prepared by a modified hydrothermal method. Firstly, 0.242 g of NaMoO<sub>4</sub>·2H<sub>2</sub>O (1.0 mmol) and 0.291 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.0 mmol) were mixed together with 33 ml of MilliQ water and stirred for 20 minutes to obtain a precursor solution. Then the solution was transferred to the Teflon lined autoclave which was further placed in an oven at 120 °C for 4 h. After reaction, the purple powder was collected by centrifuge, rinsed 3 times with distilled water and ethanol and then oven dried at 80 °C.

In the process of sulfuration step, three quartz boats, with 1.5 g of sulfur in the left boat, 0.1 g of CoMoO<sub>4</sub> in the right one and the empty middle one acting as a spacer, were placed in a stream of nitrogen in the furnace. The spacer could facilitate the mixing between the sulfur and CoMoO<sub>4</sub> during sulfuration process according to Computational Fluid Dynamics (CFD) calculations (**Fig. s9, ESI**). The temperature was programmed from room temperature to 500 °C with a gradient of 5 °C·min<sup>-1</sup> and kept at 500 °C for 0.5 h. The samples produced were denoted as CoMoOS. The optimal sulfuration condition was obtained by studying different factors during the sulfuration of CoMoO<sub>4</sub> (**Fig. s8**).

#### Synthesis of MoS<sub>2</sub>

 $MoS_2$  were prepared by a modified hydrothermal method. Firstly, 1.694 g of  $NaMoO_4 \cdot 2H_2O$  (7.0 mmol) and 2.283 g of  $CS(NH_2)_2$  (30.0 mmol) were mixed together with 35 mL of MilliQ water and stirred for 30 minutes to obtain a clear precursor solution. Then the solution was transferred to the Teflon lined autoclave which was further placed in an oven at 180 °C for 24 h. After reaction, the black powder was collected by centrifuge, rinsed 3 times with distilled water and ethanol and then oven dried at 70 °C. The obtained black powder was characterized by XRD and its XRD spectrum was consistent with that of  $MoS_2$  reported in the previous literature. <sup>1</sup>

## Synthesis of CoS<sub>2</sub>

 $CoS_2$  were synthesized by two-step process: firstly, Co-precursor was prepared by a hydrothermal reaction and then experienced a sulfuration process to obtain the  $CoS_2$ . In details, 0.438 g of  $Co(NO_3)$ · $6H_2O$  (1.5 mmol) and 0.451 g of  $CO(NH_2)_2$  (30.0 mmol) were mixed together with 30 mL of MilliQ water and stirred for 30 minutes. Then the solution was transferred to the Teflon lined autoclave which was further placed in an oven at 120 °C for 6 h. After reaction, the pink powder was collected by centrifuge, rinsed 3 times with distilled water and ethanol and then oven dried at 70 °C. In the process of sulfuration step, three quartz boats, with 1.5 g of sulfur in the left boat, 50 mg of Co-precursor in the right one and the empty middle one acting as a spacer, were placed in a stream of nitrogen in the furnace. The temperature was programmed from room temperature to 500 °C with a gradient of 5 °C·min<sup>-1</sup> and kept at 500 °C for 1.0 h. The obtained black powder was confirmed to be  $CoS_2$  by XRD.

**Physical characterization**: Phase fractions were determined using X-ray diffraction (XRD) and the data of all the materials except  $MoO_2$  and  $MoS_2$  were collected with Co K $\alpha$  radiation on a Bruker D8 Advance eco diffractometer with a Lynxeye XE energy discrimination position sensitive detector. The data of  $MoO_2$  and  $MoS_2$  were collected with Cu K $\alpha$  radiation on a Bruker Phase D2 and the Cu K $\alpha$  radiation source were pointed in the XRD spectra image.

The morphologies of as-prepared samples were characterized by Scanning electron microscopy (SEM) images using an FEI Nova NanoSEM at 5 kV. Conventional transmission electron microscopy (TEM) was carried out using a Tecnai T20 Twin operated at 200 kV with samples made by evaporating a drop of dispersions of the submicron wires in butanol onto holey-carbon-coated Cu grids. A Tecnai F20 SuperTwin operating at 200 kV was used to obtain scanning transmission electron microscopy (STEM) images and energy dispersive spectral (EDS) maps. STEM and TEM employed the same sample preparation process. X-ray photoelectron spectroscopy (XPS) analysis was performed using either an AXIS Nova or an AXIS Ultra spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K $\alpha$  source using the standard aperture (analysis area: 0.3 mm  $\times$  0.7 mm).

Nitrogen sorption isotherms were measured at 77 K with a Micromeritic Tri Flex surface characterization analyzer and the specific surface areas were calculated by using the Brunauer-Emmett-Teller (BET) method.

*Electrochemical measurements*: 10.0 mg of CoMoOS, 50 µl of Nafion (5 wt%) and 1.0 ml of ethanol were mixed in a 1.5 ml vial, followed by sonicating for 10 minutes to obtain a uniform dispersed suspension. To obtain the working electrode, 80 µl of suspension (~0.8 mg of catalysts) was dropped onto 1.0 X 1.0 cm<sup>2</sup> copper foam ("CoMoOS/CF") and dried at room temperature in the fume cupboard. CoMoO<sub>4</sub>/CF, MoO<sub>2</sub>/CF, MoS<sub>2</sub>/CF, CoS<sub>2</sub>/CF and MoO<sub>2</sub>/MoS<sub>2</sub>/CoS<sub>2</sub>/CF were obtained by the same procedure. The glassy carbon substrate (connected to RDE) was also used and 5 µL aliquot of as-prepared catalyst ink was dropped on the surface of the GC substrate. SP150 (Bio-Logic Science Instruments) was used for the electrochemical tests. A three-electrode system was set up with CoMoOS/CF (or materials for control experiments) clipped by a platinum clip as the working electrode, a graphite rod and Hg/HgO as the

counter electrode and the reference electrode, respectively, in 1.0 M KOH. All the potentials in linear sweep voltammetry (LSV) plots were scanned at a scan rate of 5 mV/s and then were corrected with ohmic potential drop (iR) losses ( $C_{correction} = E_{measure} - iR$ ) to avoid the impact of electrolyte resistance. The Frequency range for Electrochemical Impedance Spectroscopy (EIS) is from 100 kHz to 10 mHz on SP 150 (BioLogic).

Component	Phase name	Percentage (%)	$\mathbf{R}_p$	
MoO <sub>2</sub>	Cattierite, syn	1.6 %	-	
$MoS_2$	Molybdenite-2H, syn)	72.5 %	4.80	
$CoS_2$	Cattierite, syn	25.9 %		

Table s1. XRD	Quantitative Ana	alysis – Rietveld
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The XRD data was analysed using whole-pattern profile fitting method as embodied in the software package TOPAS (version 5, Bruker AXS).<sup>2</sup>



Fig. s1 (a)  $N_2$  adsorption-desorption isotherms and (b) corresponding pore size distribution plots of CoMoOS composite.



Fig. s2 Raman spectroscopy of CoMoOS, MoO<sub>2</sub>, MoS<sub>2</sub> and CoS<sub>2</sub>.

The Raman measurements with the excitation laser line of 488 nm were performed using a Renishaw Raman microscope. The power of the excitation laser line was approximately 0.5 mW with a spectral range from 100 cm<sup>-1</sup> to 1800 cm<sup>-1</sup>. The Raman emission was collected by an Olympus  $50 \times$  objective. Each extended range scans at 30 seconds rate with a spectral binning of 2 pixels.

From the Raman spectrum of MoS<sub>2</sub>, peaks at 286, 378 and 406 cm<sup>-1</sup> correspond to the  $E_{1g}$ ,  $E_{2g}^{-1}$  (the in-plane vibration of the S atoms) and  $A_{1g}$  (the out-of-plane vibration of the S atoms) modes of MoS<sub>2</sub>, respectively (*Adv. Funct. Mater.* 2012, 22, 1385-1390). In the spectrum of CoS<sub>2</sub>, the peaks at 286 and 387 cm<sup>-1</sup> ascribe to  $E_g$  and  $A_g$  (*Nanoscale*, 2016, 8, 6435), respectively. The peaks at 201, 227, 346, 362, 456, 496, 566 and 738 cm<sup>-1</sup> in MoO<sub>2</sub> are consistent with those shown in the literature (*J. Mater. Chem. A*, 2015, 3, 20080-20085). Regarding to the Raman spectrum of CoMoOS, the peak at 406 cm<sup>-1</sup> comes from  $A_{1g}$  in MoS<sub>2</sub> while the peak at 286 cm<sup>-1</sup> might originate from  $E_{1g}$  in MoS<sub>2</sub> or  $E_g$  in CoS<sub>2</sub>. The peak at 378 cm<sup>-1</sup> in CoMoOS is wider than that in MoS<sub>2</sub> which might be due to the effect of  $A_g$  mode in CoS<sub>2</sub>, while new peaks at 816, 874, and 933 cm<sup>-1</sup> might derive from the multiphonon bands involving LA(M) and other phonons at M point (*Tribol Lett.*, 2011, 42, 301-310). There are no peaks from MoO<sub>2</sub> overlap with those from CoMoOS due to the low content of MoO<sub>2</sub> in CoMoOS hybrid.



Fig. s3 Representative relevant XP spectra of CoMoOS before and after HER electrolysis.

X-ray photoelectron spectroscopy (XPS) analysis was performed using either an AXIS Nova or an AXIS Ultra spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K $\alpha$  source using the standard aperture (analysis area: 0.3 mm × 0.7 mm).

XPS was used to obtain information about the surface chemistry of fresh CoMoOS and CoMoOS after HER electrolysis. Relevant high resolution spectra are displayed in **Fig. s3**. XPS was used to obtain information about the surface chemistry of fresh CoMoOS and CoMoOS after HER electrolysis. Relevant high resolution spectra are displayed in **Fig. s3**. In the case of the Mo 3d we also present the results of curve-fitting since this provides useful information about contributions from chemically different Mo species. In the other three cases this is not the case: 2p spectra of first-row transition metals such as Co are notoriously difficult to fit and simple peak assignments are not possible (see e.g. http://www.xpsfitting.com/search/label/Cobalt and references therein). Instead, a qualitative interpretation based on the spectral shape is provided below. The measured S 2p spectra are complex and a detailed, meaningful and reliable interpretation is beyond the scope of this report. As in the case of the Co 2p, a qualitative interpretation of S 2p spectra also provides useful information. The O 1s spectrum is generally broad and featureless. It is difficult to fit reliably and

correctly because it is comprised of many different contributions separated by only small chemical shifts.

The surface of fresh CoMoOS is confirmed to consist mainly of the metal sulfides: The Co 2p spectrum displays the characteristic  $2p_{3/2}-2p_{1/2}$  doublet with the  $2p_{3/2}$  component just below 780 eV, consistent with sulphide (Co<sup>2+</sup>). A shoulder observed at approx. 781 eV is probably due to some oxide and/or hydroxide. The Mo 3d spectral region shows a dominant doublet with the main  $3d_{5/2}$  peak at 229.5, again consistent with the Mo in the sulphide form (Mo<sup>4+</sup>). In addition, the broad S 2s peak is noticeable at 227 eV and some intensity around 236 eV, due to the Mo  $3d_{3/2}$  component of an oxide (Mo<sup>6+</sup>), the  $3d_{5/2}$  component contributing to the peak at around 233 eV. The S 2p region is dominated by doublets at lower binding energy, typical for sulphides, with some intensity at up to 169 - 170 eV (oxidised sulfur). <sup>3</sup>,<sup>4</sup>

After HER for 40 h, all spectra present evidence for significant oxidation at the surface: the Co 2p doublet has broadened and shifted to a higher BE, the oxide component in the Mo 3d spectrum has increased relative to the sulphide doublet, and the S 2p spectrum is now dominated by the high BE peak due to oxidised S. In the O 1s spectrum, the peak at 532 cm<sup>-1</sup> can be ascribed to H<sub>2</sub>O molecules adsorbed on the surface of the CoMoOS, demonstrating a good hydrophilic property which is favourable to Volmer step during HER in alkaline solutions.



Fig. s4 SEM images of commercial  $MoO_2$  (a, d), prepared  $MoS_2$  (b, e) and  $CoS_2$  (c, f). XRD patterns of commercial  $MoO_2$  (g), prepared  $MoS_2$  (h) and  $CoS_2$  (i). The scale bar is 4  $\mu$ m for a, b and c and 1  $\mu$ m for d, e and f.



**Fig. s5** HER performances of CoMoOS on glassy carbon in alkaline solutions (scan rate: 5 mV/s; RDE rotating speed: 1600 rpm) which is consistent with the performance on copper foam shown in **Fig. 2a**.



**Fig. s6** EIS Nyquist plots of CoMoOS; inset: the corresponding equivalent circuit diagram.

 $R_s$  is the uncompensated solution resistance,  $CPE_c$  and  $R_c$  are the constant element and resistance reflecting electron transport at CoMoOS/CF interface, respectively.  $CPE_{ct}$  and  $R_{ct}$  are the constant phase element and charge transfer resistance at the CoMoOS/electrolyte interface, respectively.

**Table s2.** Values of elements circuit (Fig. s6) resulted from fitting the EIS data at -0.2V vs RHE

R <sub>s</sub>	Qc	a <sub>c</sub>	R <sub>c</sub>	Q <sub>ct</sub>	n <sub>ct</sub>	R <sub>ct</sub>
$(\Omega)$	$(F \cdot s^{(a-1)})$			$(F \cdot s^{(a-1)})$		$(\Omega)$
0.8653	0.0654	0.5088	0.3537	0.04913	0.8828	2.081



**Fig. s7** OER performances of CoMoOS in alkaline solutions with different mass loading on 1X1 cm<sup>2</sup> copper foam: LSV plots (**a**) and Tafel slopes (**b**) of CoMoOS



**Fig. s8** HER performance (in alkaline solutions) of catalysts prepared at different sulfuration conditions: (a) different sulfuration temperature; (b) different sulfuration duration; (c) different mass of sulfur; (d) whether using a spacer boat in sulfuration process.

#### **Computational Fluid Dynamics (CFD) simulations**

CFD simulations were used to elucidate how the addition spacer boat used in the experiments contributed to enhance mixing, leading to the experimental results observed in this work. **Fig. s9 (1)** illustrates the two-dimensional geometry of the model used in the simulation. The final mesh, after mesh independence testing, of 13602 and 13812 elements were used for the case with three and two boats, respectively.

Corresponding to the experimental setup, **Fig. s9 (2)** illustrates the types boundary used in the simulation. Table s8 collates the boundary conditions employed. As a simplifying assumption, only the nitrogen flow was simulated without the presence of the evaporated sulphur; the nitrogen being the main bulk gaseous carrier in the system which determines the overall flow behaviour in the system.

Turbulent flow was in the system was captured using the Reynolds-time averaged Navier–Stokes model with standard k– $\epsilon$  two equation closure model. For pressure–velocity coupling, the SIMPLE algorithm was used. The transport and turbulence were discretised using a second-order upwind scheme. Pressure equation was discretised using the PRESTO scheme. Transient simulation was considered and a time step size of 0.01s with 10 iterations per time step was used. The CFD model was solved using ANSYS Fluent V17.1.

Boundary condition for Nitrogen inlet was mass flow inlet (mass flow rate=0.181kg/s). The pressure outlet was used for the outlet of the furnace. The temperature of furnace walls was set at 773.15K, and the remaining walls outside of the furnace was set at 298.15K.

Model equations are described in Equations (1-4):

$$\frac{\partial \rho}{\partial t} + \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \qquad (1)$$

$$\frac{\partial u}{\partial t} + \frac{\partial p}{\partial x} = \frac{1}{Re} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) - \frac{\partial (u^2)}{\partial x} - (2)$$

$$\frac{\partial (uv)}{\partial x}$$

$$\frac{\partial v}{\partial t} + \frac{\partial p}{\partial x} = \frac{1}{Re} \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) - \frac{\partial (uv)}{\partial x} - (3)$$

$$\frac{\partial (uv^2)}{\partial x} + g_y$$

where

$$Re = \frac{\rho_g d \left( \nu_g - \nu_s \right)}{\mu_g} \tag{4}$$



Fig. s9 (1) CFD model geometry





The mixing behaviour of the flow field can be compared via the macros- and microscale. Macro scale mixing can be denoted by the vector plots generated by the simulations, showing the airflow pattern within the furnace tube. Examining the vector plots between the two-boat and the three-boat system revealed the similar observation in flow field behaviour in the region of the bed in which the CoMoO<sub>4</sub> is placed. There was the typical and expected recirculation flow after the 'baffle' imposed by the boat wall. This was not included for brevity.

The micro scale mixing can be delineated by the turbulent kinetic energy of the flow field, which quantifies the microscale (scales smaller than the size of the mesh) fluctuation of the flow. Fig. s9 (3) the turbulent kinetic energy for the three-boat system is significantly higher at the region above where the  $CoMoO_4$  is placed. This will translate to more micro level mixing of any evaporated sulphur from the first boat leading to the higher interaction and reaction observed in the experiments. From the simulations, it appeared that the second 'constriction' in the flow field imposed by the third boat led to higher build-up of turbulence in the system.



Fig. s9 (3) Turbulent kinetic energy comparisons (a) two boats (b) three boats

- N. Liu, Y. Guo, X. Yang, H. Lin, L. Yang, Z. Shi, Z. Zhong, S. Wang, Y. Tang and Q. Gao, Microwave-Assisted Reactant-Protecting Strategy toward Efficient MoS2 Electrocatalysts in Hydrogen Evolution Reaction, ACS Applied Materials & Interfaces, 2015, 7, 23741-23749.
- Kern, A., Coelho, A.A. & Cheary, R.W. (2004): Convolution based profile fitting. -Diffraction Analysis of the Microstructure of Materials, edited by Mittemeijer, E.J. & Scardi, P. Materials Science, Springer, ISBN 3-540-40510-4, 17 - 50.
- 3. NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database Number 20, National Institute of Standards and Technology, Gaithersburg MD, 20899 (2000), doi:10.18434/T4T88K, (retrieved 10/09/2018).
- 4. M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.S. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni, Appl. Surf. Sci. 257 (2011) 2717-2730.