

Supporting Information

Mo-doped cobaltous sulfide nanosheet arrays as efficient catalysts for sulfion oxidation reaction promoting hydrogen production with ultra-low electric energy consumption

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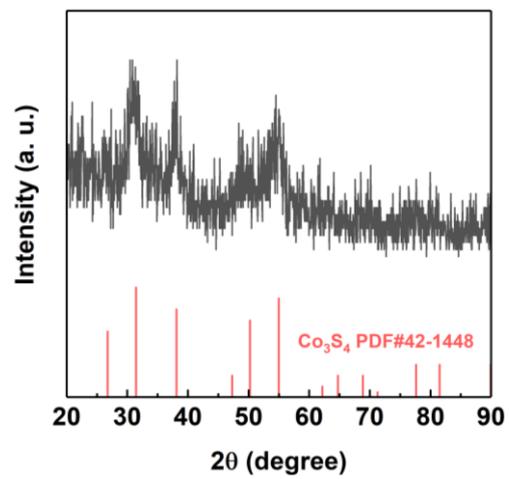


Fig. S1 XRD pattern of a scraped powder sample from Mo-Co-S/NF

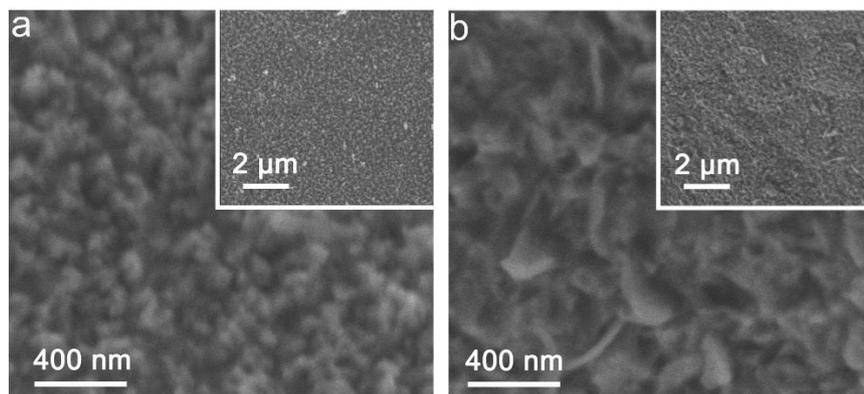


Fig. S2 SEM images of (a) Co-S/NF and (b) Mo-S/NF.

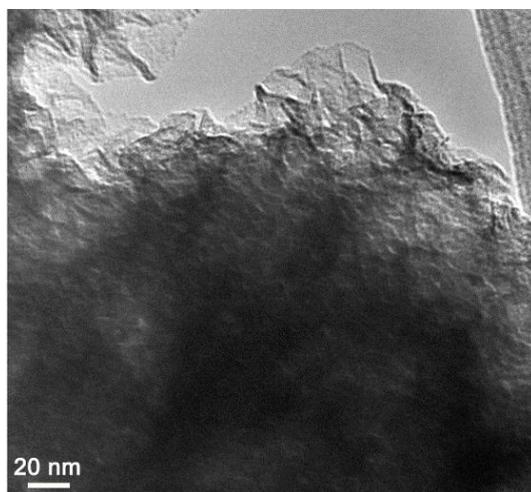


Fig. S3 TEM image of Co-Mo-S/NF.

Table. S1 The binding energy of Co 2p and Mo 3d XPS peaks.

	Mo-Co-S/NF	Co-S/NF	Mo-S/NF
Co ²⁺ 2p _{3/2}	781.6	781.4	/
Co ³⁺ 2p _{3/2}	778.6	778.4	/
Co ²⁺ 2p _{1/2}	797.8	797.5	/
Co ³⁺ 2p _{1/2}	795.8	795.5	/
Mo ⁴⁺ 3d _{5/2}	227.9	/	228.3
Mo ⁶⁺ 3d _{5/2}	231.8	/	232.2
Mo ⁴⁺ 3d _{3/2}	233.0	/	233.4
Mo ⁶⁺ 3d _{3/2}	235.1	/	235.4

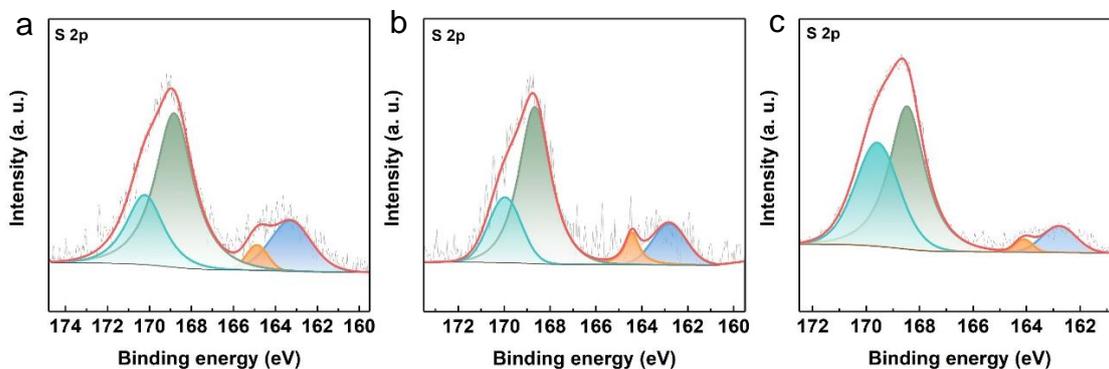


Fig. S4. The S 2p spectra of (a) Co-Mo-S/NF, (b) Co-S/NF and (c) Mo-S/NF.

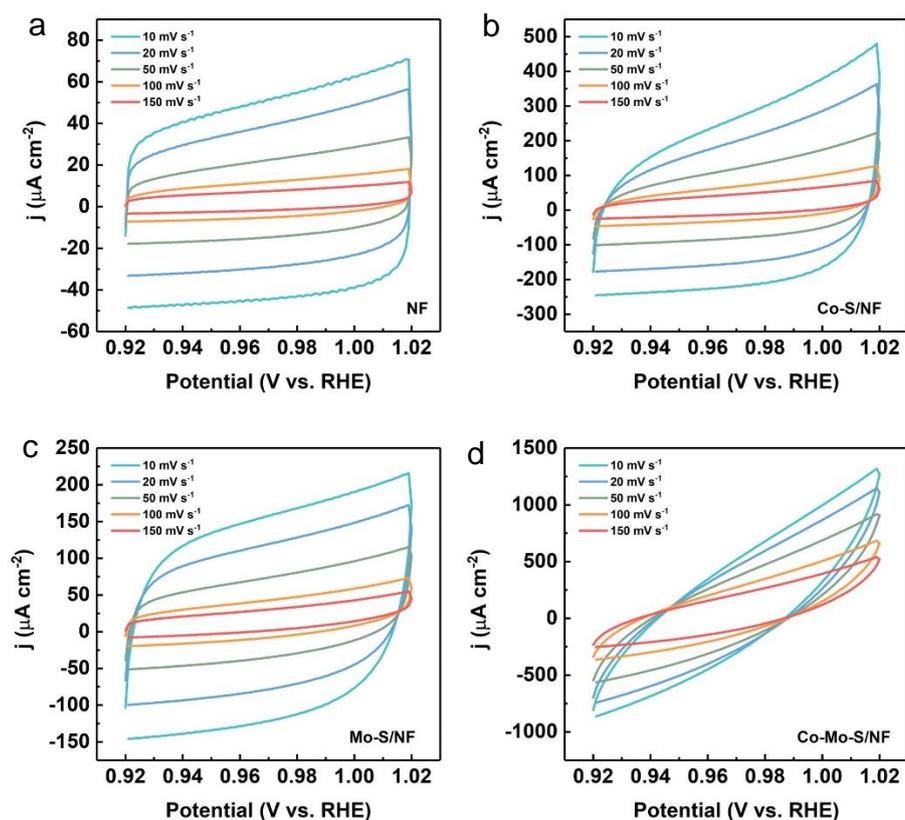


Fig. S5 The double-layer capacitance measurements of the electrodes; (a-d) the cyclic voltammograms of the catalysts at a series of scan rates of 10, 20, 50, 100, and 150 mV s^{-1} from 0.92 to 1.02 V vs. RHE in 1 M NaOH.

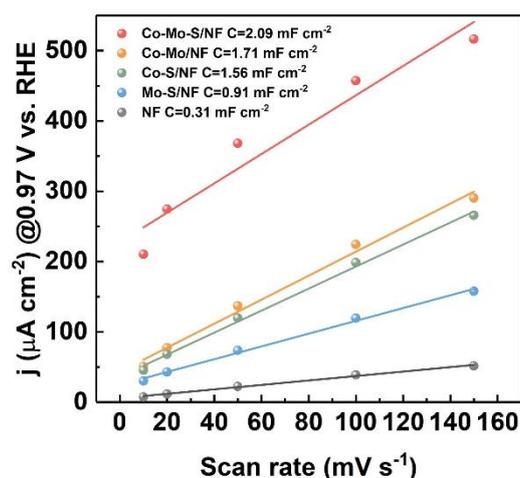


Fig. S6 The linear fitting of the oxidation currents of the catalysts at 0.97 V vs. RHE versus scan rates.

Electrical double-layer capacitance measurements were used to determine the electrochemical active surface area (ECSA) of the catalysts. According to Fig. S5, the electrical double-layer capacitance could be obtained based on the specific capacitance value of a smooth standard with a real surface area of 1 cm². 40 uF cm⁻² is considered as the value of specific capacitance for a smooth standard with a real surface area of 1 cm² based on previous studies.

The electrochemical active surface area could be obtained via the following equation:

$$A_{\text{ECSA}} = \frac{\text{The electrical double-layer capacitor}}{40}$$

For example:

$$\text{Co-S/NF: } A_{\text{ECSA}} = \frac{2090}{40} = 52.25 \text{ cm}^2_{\text{ECSA}}$$

Table S2 The calculated ECSA of the obtained electrodes

Catalysts	Mo-Co-S/NF	Co-S/NF	Mo-S/NF	NF
C _{dl} (mF cm ⁻²)	2.09	1.56	0.91	0.31
ECSA (cm ² _{ECSA})	52.25	39.00	22.75	7.75

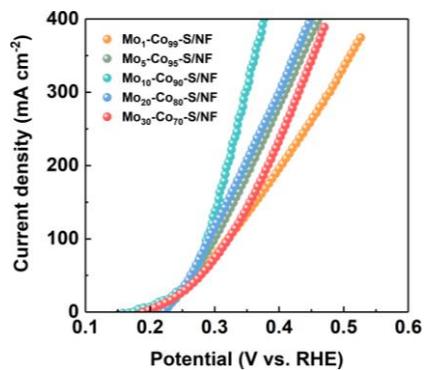


Fig. S7 LSV curves of Mo-Co-S/NF with different atomic ratios between Co and Mo species.

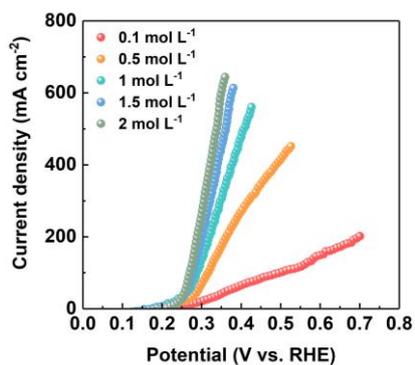


Fig. S8 LSV curves of the Mo-Co-S/NF in the electrolytes with different concentrations of Na₂S.

Table S3. Comparison of SOR catalytic activity.

Catalysts	Electrolytes	Potential (V vs. RHE) @ 100 mA cm ⁻²	References
Co-Ni ₃ S ₂	1 M NaOH+1M Na ₂ S	0.59	1
Cu ₂ S/NF	1 M NaOH+1M Na ₂ S	0.44	2
WS ₂ NSs	1 M NaOH+1M Na ₂ S	~0.75	3
CoS ₂ @C/MXene/NF	1 M NaOH+1M Na ₂ S	0.389	4
VSe ₂	1 M NaOH+1M Na ₂ S	0.45	5
Graphite electrode	1 M NaOH+1M NaHS+2 M NaClb	0.51	6
Pt disk	1M Na ₂ S	1.0 (vs. SCE)	7
CoNi@NGs	1 M NaOH+1M Na ₂ S	0.52	8
Mo-Co-S/NF	1 M NaOH+1M Na ₂ S	0.294	This work
Co-S/NF	1 M NaOH+1M Na ₂ S	0.467	This work
Mo-S/NF	1 M NaOH+1M Na ₂ S	0.582	This work

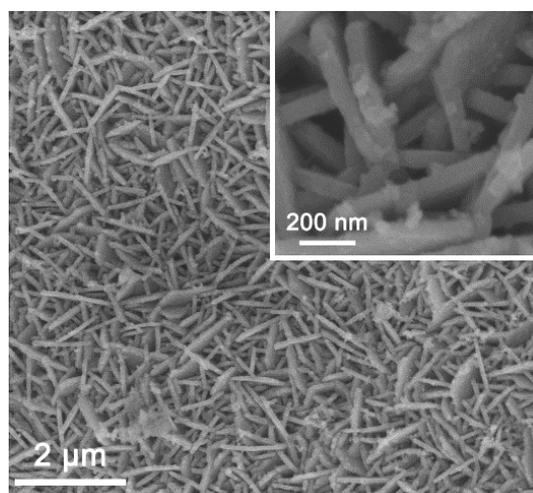


Fig. S9. The SEM images of Co-Mo-S/NF after electrocatalytic SOR for 40 hours.

Table S4. Comparison of the electrochemical hydrogen production performance of the two-electrode electrolytic system.

Catalysts	Electrolyte	Potential (V) @100 mA cm ⁻²	References
Co-Ni ₃ S ₂	1 M NaOH+1M Na ₂ S 1 M NaOH+1M Na ₂ S	0.950	1
Cu ₂ S/NF	1 M NaOH+1M Na ₂ S 1 M NaOH	0.640	2
WS ₂ NSs	1 M NaOH+2 M Na ₂ S 2.5 M H ₂ SO ₄	~1.24	3
CoS ₂ @C/MXene/NF	1 M NaOH+1M Na ₂ S Sea water	~0.61	4
CoNiCuMnMo-NPs/CC	0.1M KOH+0.1 M MGLY 0.5 M H ₂ SO ₄	0.550/-/-	9
CC@N-CoP	0.96 M FeSO ₄ /0.74 M Fe ₃ (SO ₄) ₂ in 0.5 M H ₂ SO ₄ 0.5 M H ₂ SO ₄	1.18	10
Mo-Co-S/NF Pt-C/CP	1 M NaOH+1M Na ₂ S 0.5 M H ₂ SO ₄	-0.257	This work
Mo-Co-S/NF Pt-C/CP	1 M NaOH+1M Na ₂ S 1 M NaOH	0.515	This work
Mo-Co-S/NF Pt-C/CP	1 M NaOH 0.5 M H ₂ SO ₄	0.840	This work
Mo-Co-S/NF Pt-C/CP	1 M NaOH 1 M NaOH	1.653	This work

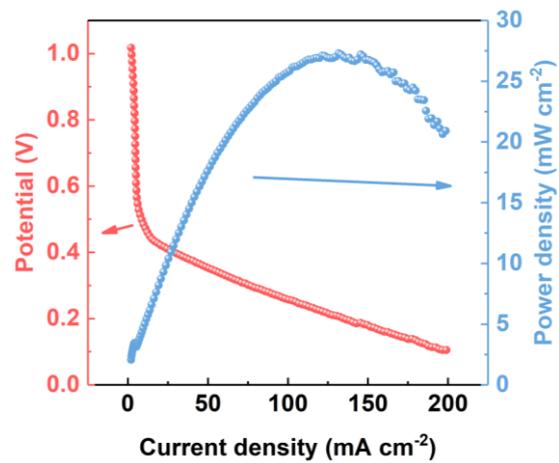


Fig. S10 The polarization curve and corresponding power density of the two-electrode system in a dissymmetrical acid (Pt-C/CP for HER)-base (Co-S/NF for SOR) coupled electrolyzer (this electrolyzer is used as the galvanic cell at the low current density).

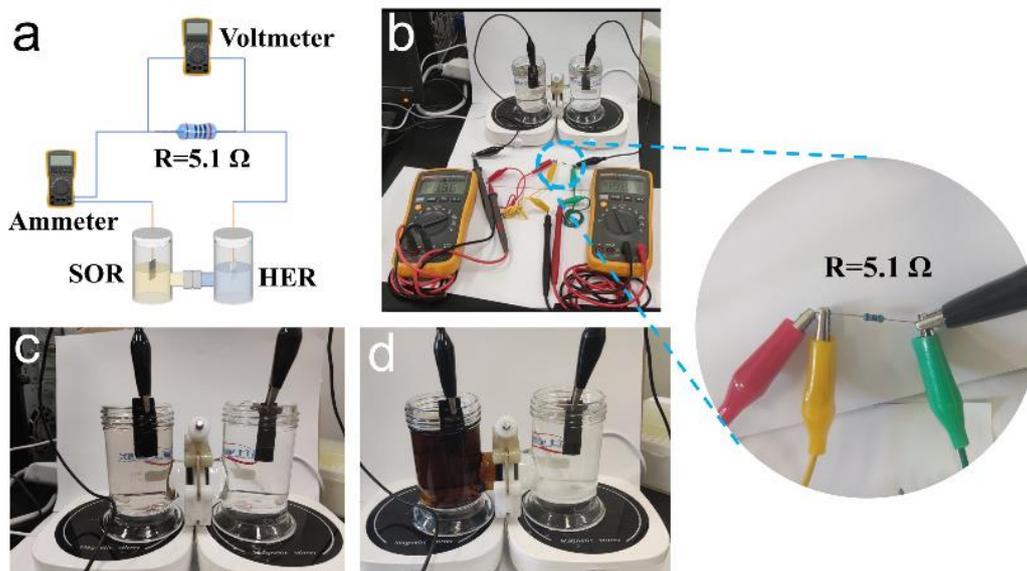


Fig. S11 (a) Schematic of the circuit, (b) the picture of the actual circuit connection for the acid-base coupling system (positive electrode: Pt-C/CP (0.5 M H₂SO₄), negative electrode: Mo-Co-S/NF (1 M NaOH containing 1 M Na₂S)) using a resistor (5.1 Ω) as the load. (c) The picture of the asymmetric acid-base coupling system before driving the load. (d) The picture of the asymmetric acid-base coupling system after working for 12 h.

The calculation formula is as follows:

1 Kg H₂ is generated, and the required amount of charge (Q) is:

$$Q = (1000g \times N_A \times 2e) / M_{H_2} = (1000 \times 2 \times 6.022 \times 10^{23} \times 1.602 \times 10^{-19}) / 2.016 = 95706785.7 \text{ C}$$

Where N_A is the Avogadro constant, e is the charge of an electron and M_{H_2} is the relative molecular mass of hydrogen (H₂).

For the HER (pH=14) + OER (pH=14) system, the applied voltages (U1) at a current density of 100 mA cm⁻² is 1.822 V. The amount of electricity (W1) required to obtain 1 Kg H₂ is:

$$W1 = QU1 = 95706785.7 \times 1.653 = 158203316.762 \text{ J} \approx 43.945 \text{ KW}\cdot\text{h}$$

For HER (pH=14) + SOR (pH=14) system, the applied voltages (U2) at the current density of 100 mA cm⁻² is 0.515 V.

The amount of electricity (W2) required to obtain 1 Kg H₂ is:

$$W2 = QU2 = 95706785.7 \times 0.515 = 49288994.636 \text{ J} \approx 13.691 \text{ KW}\cdot\text{h}$$

For HER (pH=0) + OER (pH=14) system, the applied voltages (U3) at the current density of 100 mA cm⁻² is 0.840 V.

The amount of electricity (W3) required to obtain 1 Kg H₂ is:

$$W3 = QU3 = 95706785.7 \times 0.840 = 8039369.988 \text{ J} \approx 22.332 \text{ KW}\cdot\text{h}$$

For HER (pH=0) + SOR (pH=14) system, the applied voltages (U4) at the current density of 100 mA cm⁻² is -0.257 V.

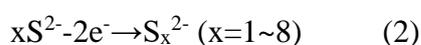
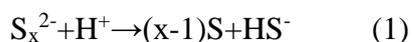
The amount of electricity (W3) required to obtain 1 Kg H₂ is:

$$W4 = QU4 = 95706785.7 \times (-0.257) = -24596643.925 \text{ J} \approx -6.832 \text{ KW}\cdot\text{h}$$

Table S5. The energy consumption of different systems to obtain 1 Kg H₂ of different systems to obtain 1 Kg H₂ of different electrolytes in this work.

Catalytic electrodes	Voltage (V) @100 mA cm ⁻²	The amount of electricity (KW·h) @ 100 mA cm ⁻²
HER (pH=14) + OER (pH=14)	1.653	43.945
HER (pH=14) + SOR (pH=14)	0.515	13.691
HER (pH=0) + OER (pH=14)	0.840	22.332
HER (pH=0) + SOR (pH=14)	-0.257	-6.832

Calculation of Faradic efficiency for sulfur: The electrolyte after the electrolysis process is acidified by adding sulfuric acid (the pH value of the electrolyte was adjusted to about 1 to form colloidal sulfur based on equation (1)), centrifuged, washed, dried, and weighed to obtain the weight of the sulfur product. According to equations (1) and (2), S^{2-} is converted into polysulfide (S_x^{2-}) and finally sulfur is formed. No matter what the value of x, the number of transferred electrons (n) in the whole SOR process from S^{2-} to S is 2.



The Faradaic efficiency can be obtained based on the following equations (3) - (5).

$$Q = j \times t \quad (3)$$

$$m_{\text{theory}} = \frac{Q \times M_S}{n \times F} \quad (4)$$

$$\text{Faradaic efficiency}(\%) = \frac{m_s}{m_{\text{theory}}} \times 100\% \quad (5)$$

Where Q is the total quantity of electric charge consumed; M_S is the relative molecular weight of S (32); n is the number of transferred electrons in the whole SOR process from S^{2-} to S; F, j and t are the Faraday constant (96485 C mol^{-1}), the current density and reaction time, respectively; m_s and m_{theory} are the practice and theory weight of generated sulfur.

Table S6 Yield of sulfur powder and the faradaic efficiency of SOR.

Time (h)	Practical sulfur powder yield (g)	Theoretical sulfur powder yield (g)	Faradaic efficiency of SOR (%)
0	0	0	-
12	0.344	0.358	96.09
24	0.692	0.717	96.51
36	1.051	1.075	97.77
48	1.399	1.433	97.63
60	1.753	1.792	97.82

References

1. Li, Y.; Duan, Y.; Zhang, K.; Yu, W., Efficient anodic chemical conversion to boost hydrogen evolution with low energy consumption over cobalt-doped nickel sulfide electrocatalyst. *Chemical Engineering Journal* 2022, 433, 134472.
2. Pei, Y.; Cheng, J.; Zhong, H.; Pi, Z.; Zhao, Y.; Jin, F., Sulfide-oxidation-assisted electrochemical water splitting for H₂ production on a bifunctional Cu₂S/nickel foam catalyst. *Green Chemistry* 2021, 23 (18), 6975-6983.
3. Yi, L.; Ji, Y.; Shao, P.; Chen, J.; Li, J.; Li, H.; Chen, K.; Peng, X.; Wen, Z., Scalable Synthesis of Tungsten Disulfide Nanosheets for Alkali-Acid Electrocatalytic Sulfion Recycling and H₂ Generation. *Angewandte Chemie International Edition* 2021, 60 (39), 21550-21557.
4. Zhang, L.; Wang, Z.; Qiu, J., Energy-Saving Hydrogen Production by Seawater Electrolysis Coupling Sulfion Degradation. *Advanced Materials* 2022, 34 (16), 2109321.
5. Feng, W.; Cheng, M.; Du, R.; Wang, Y.; Wang, P.; Li, H.; Song, L.; Wen, X.; Yang, J.; Li, X.; He, J.; Shi, J., Gram-Scale Synthesized Two-Dimensional VSe₂ and SnSe₂ for Ultrahigh Electrocatalytic Sulfion Recycling. *Advanced Materials Interfaces* 2022, 9 (13), 2200060.
6. Petrov, K.; Srinivasan, S., Low temperature removal of hydrogen sulfide from sour gas and its utilization for hydrogen and sulfur production. *International Journal of Hydrogen Energy* 1996, 21 (3), 163-169.
7. Zhao, Y.; Wang, S.; Varela, H.; Gao, Q.; Hu, X.; Yang, J.; Epstein, I. R., Spatiotemporal Pattern Formation in the Oscillatory Electro-Oxidation of Sulfide on a Platinum Disk. *The Journal of Physical Chemistry C* 2011, 115 (26), 12965-12971.
8. Zhang, M.; Guan, J.; Tu, Y.; Chen, S.; Wang, Y.; Wang, S.; Yu, L.; Ma, C.; Deng, D.; Bao, X., Highly efficient H₂ production from H₂S via a robust graphene-encapsulated metal catalyst. *Energy & Environmental Science* 2020, 13 (1), 119-126.
9. Fan, L.; Ji, Y.; Wang, G.; Chen, J.; Chen, K.; Liu, X.; Wen, Z., High Entropy Alloy Electrocatalytic Electrode toward Alkaline Glycerol Valorization Coupling with Acidic Hydrogen Production. *Journal of the American Chemical Society* 2022, 144 (16), 7224-7235.
10. Zhou, Q.; Shen, Z.; Zhu, C.; Li, J.; Ding, Z.; Wang, P.; Pan, F.; Zhang, Z.; Ma, H.; Wang, S.; Zhang, H., Nitrogen-Doped CoP Electrocatalysts for Coupled Hydrogen Evolution and Sulfur Generation with Low Energy Consumption. *Advanced Materials* 2018, 30 (27), 1800140.