

## **In-Plane Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub> Heterostructure for Hydrogen Evolution Reaction in Alkaline Media**

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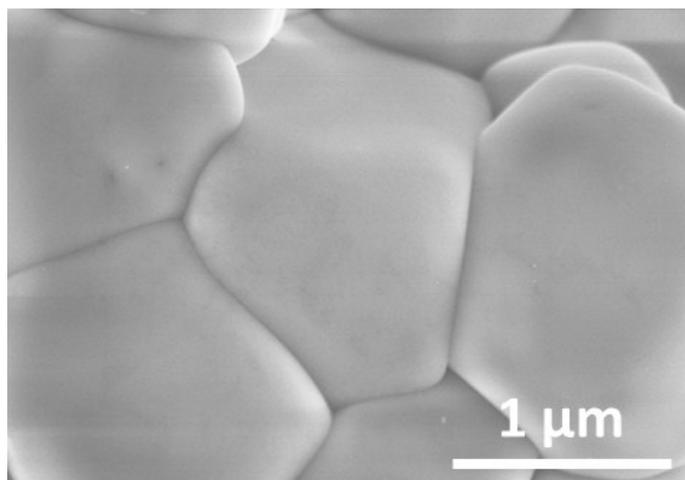


Figure S1.  $C_6H_8O_7-Co(NO_3)_2-NH_2CSNH_2-(NH_4)_6Mo_7O_{24}$  complex wrap on the surface of the NaCl crystals.

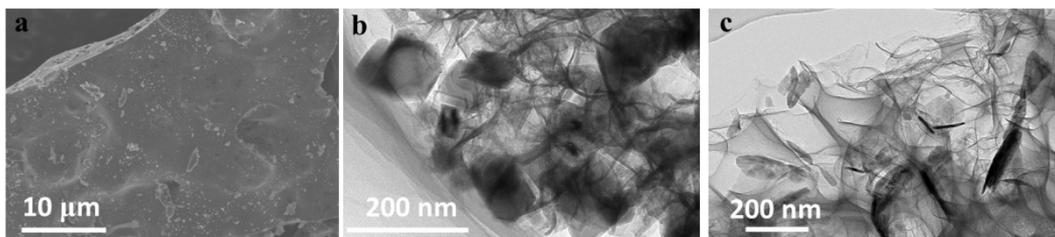


Figure S2. TEM of (a)  $\text{Co}_9\text{S}_8\text{-MoS}_2\text{@C}$ , (b)  $\text{Co}_9\text{S}_8\text{@3DC}$  and (c)  $\text{MoS}_2\text{@3DC}$ .

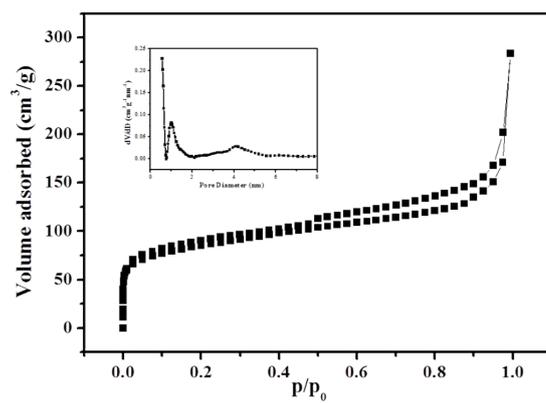


Figure S3. BET surface area of Co<sub>9</sub>S<sub>8</sub>-MoS<sub>2</sub>@3DC. Insert is the BJH pore size distribution.

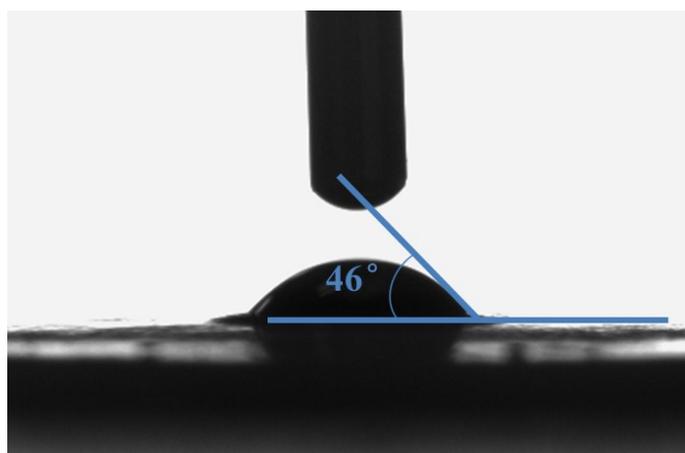


Figure S4. Static contact angle of  $\text{Co}_9\text{S}_8\text{-MoS}_2@3\text{DC}$ .

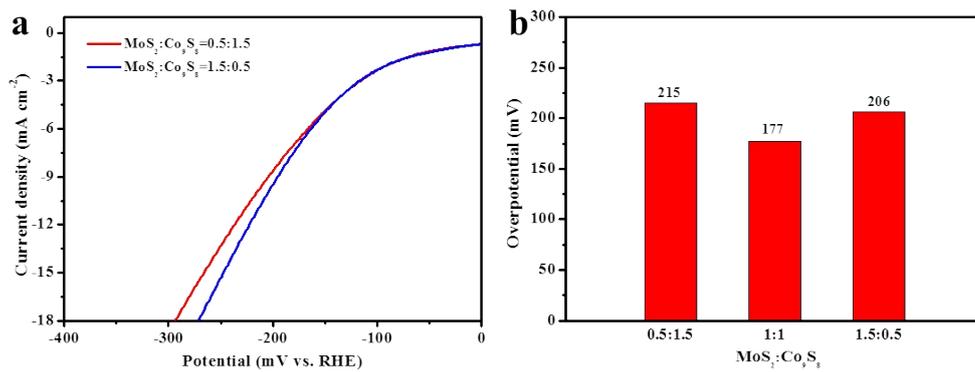


Figure S5. HER performance of MoS<sub>2</sub>-Co<sub>9</sub>S<sub>8</sub>@3DG with different ratio of MoS<sub>2</sub> to Co<sub>9</sub>S<sub>8</sub> (0.5:1.5, 1:1, 1.5:0.5)

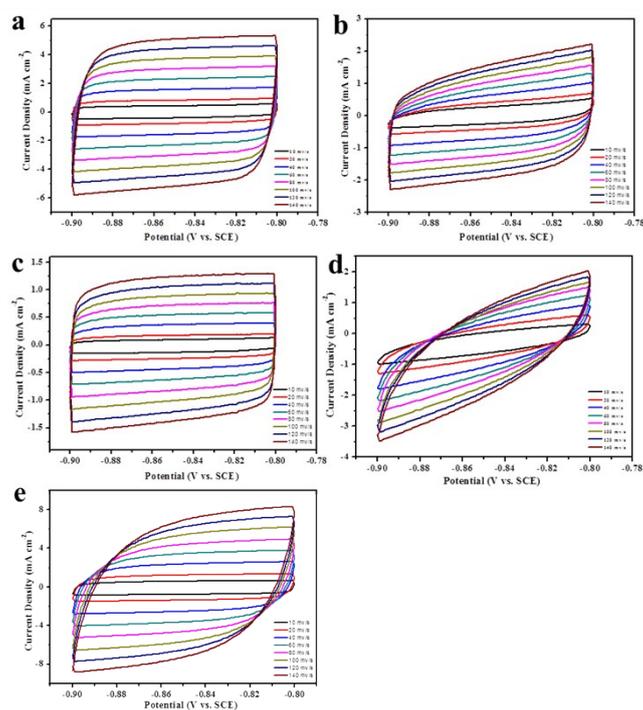


Figure S6. Cyclic voltammograms in the region of -0.9 — -0.8 V vs. SCE. (a)  $\text{Co}_9\text{S}_8\text{-MoS}_2@3\text{DC}$ , (b)  $\text{Co}_9\text{S}_8@3\text{DC}$ , (c)  $\text{MoS}_2@3\text{DC}$ , (d)  $\text{Co}_9\text{S}_8\text{-MoS}_2@3\text{DC}$ , and (e) N S doped C.

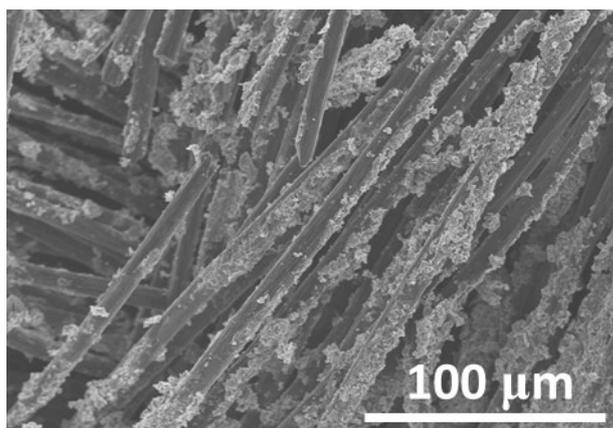


Figure S7. SEM image of catalysts on the carbon clothes after i-t test at  $50 \text{ mA cm}^{-2}$ .

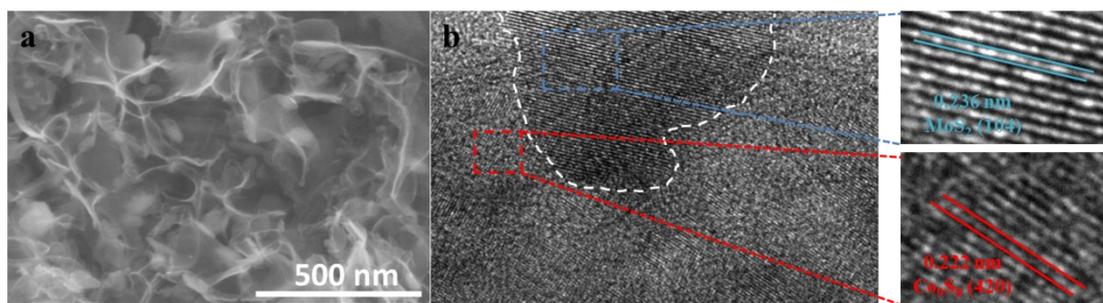


Figure S8. (a) SEM and (b) HRTEM images of catalysts after i-t test.

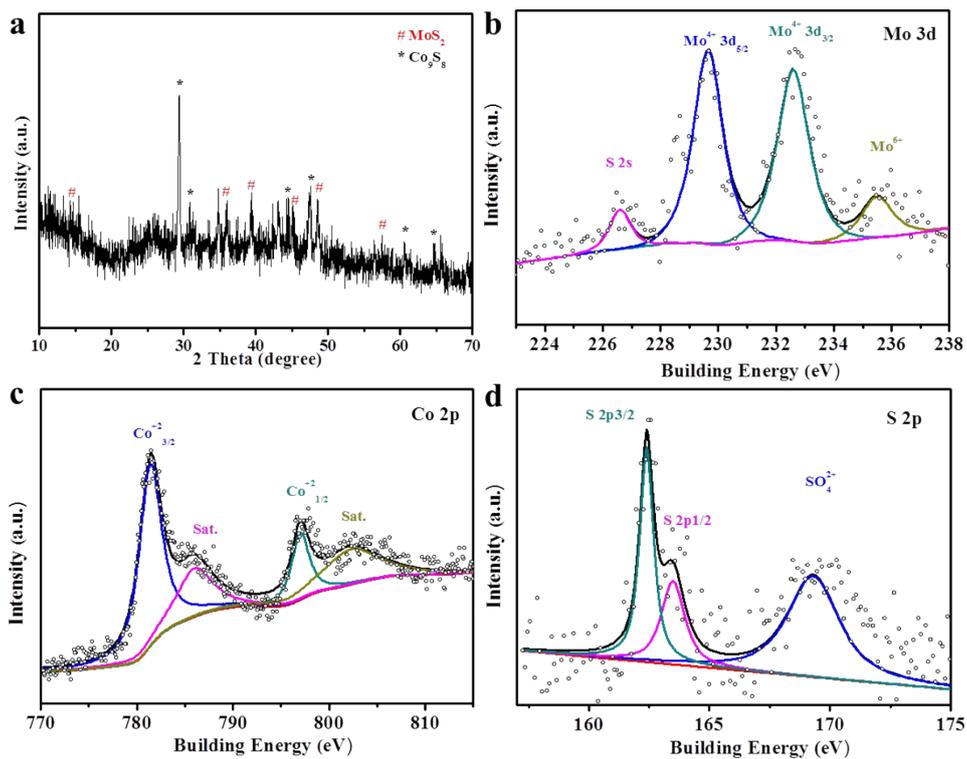


Figure S9. (a) XRD and (b-c) XPS images of catalysts after i-t test.

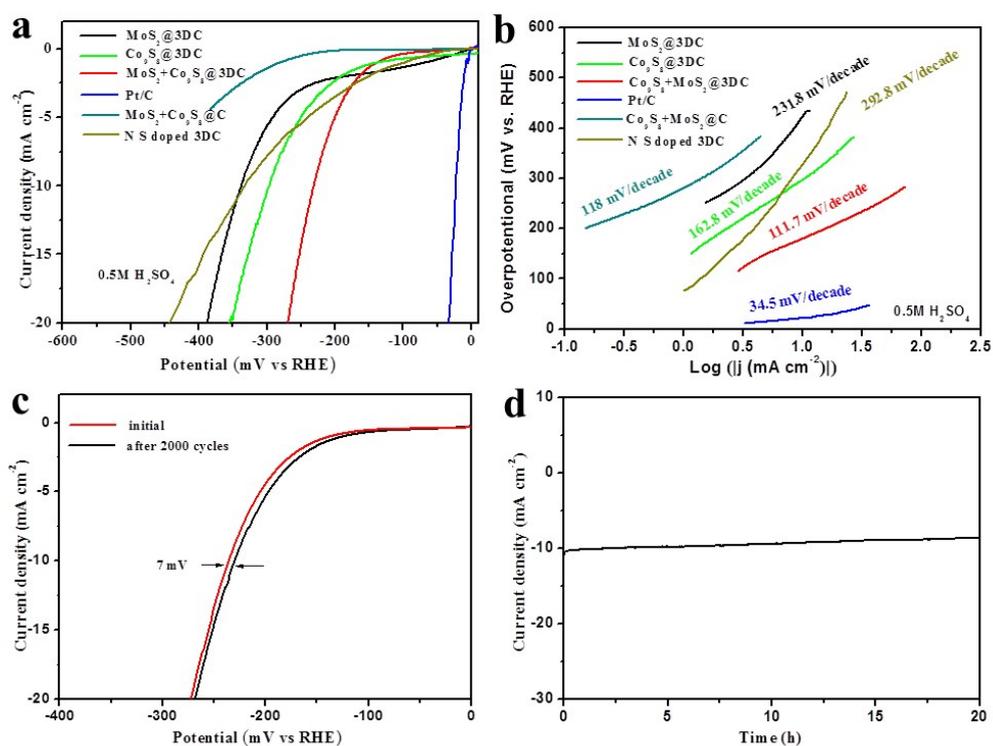


Figure S10. (a) polarization curves, (b) Tafel slope, of Co<sub>9</sub>S<sub>8</sub>-MoS<sub>2</sub>@3DC, Co<sub>9</sub>S<sub>8</sub>@3DC, MoS<sub>2</sub>@3DC, and Co<sub>9</sub>S<sub>8</sub>-MoS<sub>2</sub>@3DC in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (c) Cathodic linear sweep voltammograms of Co<sub>9</sub>S<sub>8</sub>-MoS<sub>2</sub>@3DC for the first and 2000th CV cycles in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (d) Long-term chronoamperometric test performed at overpotential of 230 mV in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

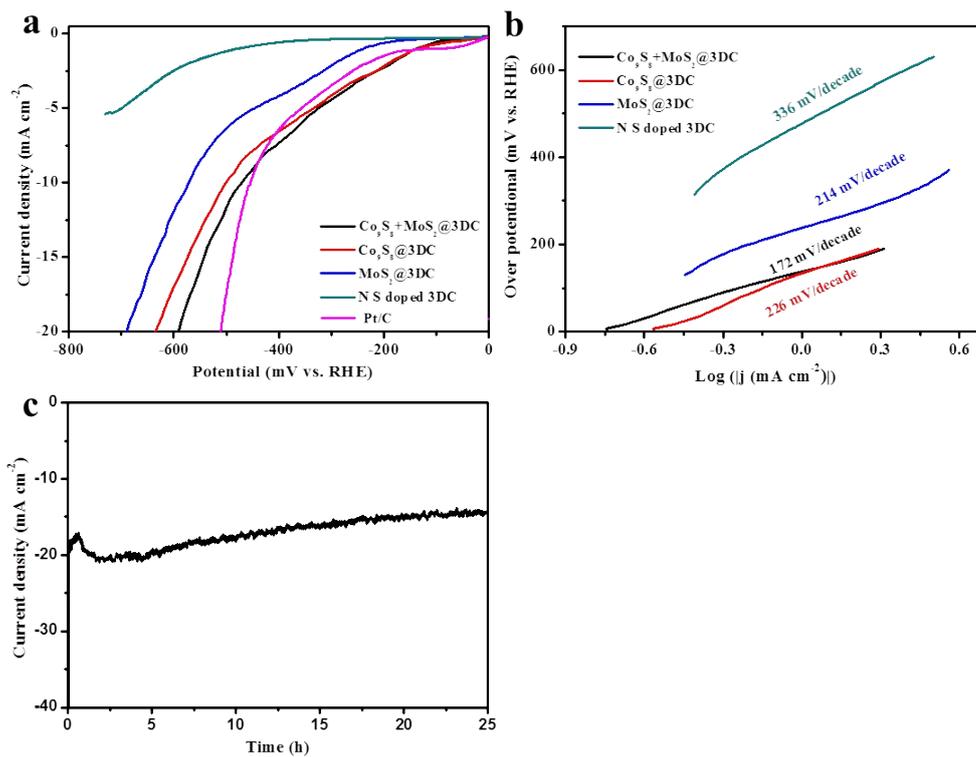


Figure. S11. (a) polarization curves and (b) Tafel slope of  $\text{Co}_9\text{S}_8\text{-MoS}_2@3\text{DC}$ ,  $\text{Co}_9\text{S}_8@3\text{DC}$ ,  $\text{MoS}_2@3\text{DC}$ ,  $\text{Co}_9\text{S}_8\text{-MoS}_2@3\text{DC}$ , and N, S doped C in 1 M PBS. (c) Long-term chronoamperometric test performed at overpotential of 470 mV in 1 M PBS.

Table S1. Performance comparison of the HER activity in alkaline electrolyte

<b>catalyst</b>	<b>Current density j=10mA cm<sup>-2</sup></b>	<b><math>\eta</math> at corresponding j (mV)</b>	<b>Tafel slope (mV•dec<sup>-1</sup>)</b>	<b>Reference</b>
<b>Co-WSe<sub>2</sub>/MWNTs</b>	10	241		J. Mater. Chem. A, 2018,6, 4793-4800
<b>MoS<sub>2</sub>/graphene/Ni foam</b>	10	> 600	98	Adv. Func. Mater., 2014, 24(39): 6123-6129.
<b>Co<sub>3</sub>S<sub>4</sub>@MoS<sub>2</sub></b>	10	310	59	Chem. Mater. 2017, 29, 5566–5573
<b>Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs</b>	10	361	61	Adv. Mater. 2015, 27, 4752-4759
<b>MoS<sub>2</sub>/Ni<sub>3</sub>S<sub>2</sub></b>	10	218	88	Angew. Chem. Int. Ed. 2016, 55, 6702-6707.
<b>Carbon Paper/Carbon Tubes/CobaltSulfide</b>	10	306	72	ACS Nano 2016, 10, 2342- 2348
<b>CoMoS<sub>x</sub></b>	10	190	124	ACS Appl. Mater. Interfaces2019112421634- 21644

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<b>Co<sub>9</sub>S<sub>8</sub>+Ni<sub>3</sub>S<sub>2</sub>/Ni</b>	10	278	-	Electrochimica Acta, 2019, 299: 152-162.
<b>Co<sub>3</sub>S<sub>4</sub>/MoS<sub>2</sub>/Ni<sub>2</sub>P</b>	10	178	98	J. Mater. Chem. A 2017, 5, 25410-25419
<b>CoSe<sub>2</sub>-MoSe<sub>2</sub>/rGO- C</b>	10	215	83.2	J. Mater. Chem. A 2018, 6, 12701-12707.
<b>Co<sub>9</sub>S<sub>8</sub>@MoS<sub>2</sub>/CNFs</b>	10	190	110	Adv. Mater. 2015, 27, 4752-4759

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