## **Supporting Information**

## **Experimental Section**

*Materials and Chemicals:* 2-methylimidazole ( $C_4H_6N_2$ , 99% purity), ammonium tetrathiomolybdate (( $NH_4$ )<sub>2</sub>MoS<sub>4</sub>, 99.97% purity), cobalt nitrate hexahydrate ( $Co(NO_3)_2 \cdot 6H_2O$ ,  $\geq$ 98% purity) and thioacetamide ( $CH_3CSNH_2$ ,  $\geq$ 99.0%) were supplied by Sigma-Aldrich. All materials were used without further purification.

Synthesis of 1D Co-MOF Nanorod Arrays (Co-MOF NRs): Firstly, a precursor solution for growing ZIF-67 was prepared by dissolving 2-methylimidazole (0.4 M) and cobalt nitrate hexahydrate ( $25 \times 10^{-3}$  M), respectively, in 40 mL deionized water (DI water), and then mixing the two solutions together. Immediately, a piece of acid-treated CC substrate (2.5 cm  $\times$  7 cm) was immersed into the solution. After reaction for 4 h, the sample was taken out, washed with DI water. Another precursor solution was prepared following the above procedure, after which the sample was immersed again for another 4 hours. Then, the sample was washed with DI water and dried overnight in vacuum.

Synthesis of  $MoS_2/CoS_2$  NRs: 0.02 g (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> was added into 30 mL DI water to form a transparent solution. A piece of Co-MOF/CC ( $^{2.5}$  cm ×  $^{2.5}$  cm) was immersed into the above solution and then transferred into a Teflon-lined stainless steel autoclave. After that, hydrothermal synthesis was carried out at 200 °C for 18 h, and then naturally cooled down to room temperature. The obtained sample was washed with DI water and dried at 60 °C in vacuum. To increase the crystallinity and remove the residual organic polymer in MOF, post annealing was conducted at 500 °C in Ar atmosphere for 2h.

*Synthesis of MoS<sub>2</sub>/CoS<sub>2</sub> NTs:* A piece of MoS<sub>2</sub>/CoS<sub>2</sub> nanorods on CC was immersed into an ethanol solution (30 mL) containing 0.18 g thioacetamide. After stirring for 15 min, the solution together with the sample was transferred into a Teflon-lined stainless steel autoclave for hydrothermal synthesis at 90 °C for 3 h. After the reaction, the samples were taken out, washed with ethanol and dried in vacuum overnight, followed by a 500 °C annealing in Ar for 2 h.

Synthesis of CoS<sub>2</sub> NRs: The synthesis of CoS<sub>2</sub> was performed by following the previously reported procedure.<sup>1</sup> Specifically, 0.18 g thioacetamide was added into 30 mL ethanol to form a transparent solution. A piece of Co-MOF NRs (2.5 cm×2.5 cm) was immersed into the above solution and transferred into a Teflon-lined stainless autoclave. The reaction was carried out at 90 °C for 3 h. The obtained sample was washed with DI water and dried at 60 °C in vacuum. After that, the sample was further annealed at 350 °C in Ar atmosphere for 2h.

*Synthesis of MoS*<sub>2</sub> *Nanosheets:* A piece of clean CC was immersed into an aqueous solution (30 mL) containing 0.02 g ( $NH_4$ )<sub>2</sub>MoS<sub>4</sub>. After hydrothermal reaction at 200 °C for 18 h, the sample was taken out, washed with DI water and dried at 60 °C in vacuum.

Synthesis of Pt/C Electrode: Commercial Pt/C (10wt.%, Sigma-Aldrich, 5mg) was well-dispersed in dilute Nafion alcohol solution (1750  $\mu$ L of ethanol, 200 mL of water and 50  $\mu$ L of Nafion) to form a homogenous ink. Then the ink (10  $\mu$ L) was drop casted onto glassy carbon electrode with a diameter of 3 mm (catalyst loading weight ~0.35 mg cm<sup>-2</sup>).

*Materials Characterization:* Scanning electron microscopy (SEM) imaging was performed using a SUPRA 40 ZEISS. Transmission electron microscopy (TEM) carried out using Titan 80/300 S/TEM operated at 200 kV. The diffraction patterns were collected using Bruker AXS XRD (Cu K $\alpha$ , I = 0.154 nm). X-ray photoelectron spectroscopy (XPS) measurements were performed using Thermo Scientific Thetaprobe XPS system (monochromatic Al K $_{\alpha}$  source, 40 eV pass energy). The carbon C 1s peak at 284.5 eV was used for charge correction. Raman measurements with excitation laser line of 514 nm were performed using LABRAM-HR Raman spectrometer (Horiba Jobin Yvon). The Si peak at 520.7 cm<sup>-1</sup> was used for calibration. Zeta potential was measured using Malvern Zetasizer Nano-ZS (Worcestershire, UK). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was carried out on an aberration-corrected JOEL ARM-200F equipped with a cold field emission gun, operating at 200 kV, and an Advanced STEM Corrector (ASCOR) probe corrector. Induced coupled plasma-optical emission spectrometer (ICP-OES) were conducted using Perkin Elmer Optima 5300DV.

*Electrochemical Measurements*: All the electrochemical measurements were conducted on electrochemical workstation (PARSTAT MC) in a three-electrode mode. In 1 M KOH and PBS solution, as-fabricated samples, Hg/HgO (1M KOH) and graphite paper were used as the working electrode, reference electrode and counter electrode, respectively. In 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, saturated calomel electrode (SCE) was used as reference electrode. Potentials *vs.* RHE were calculated via the equation of  $E_{vsRHE} = E_{vsHg/HgO} + 0.059 \times PH + 0.098$  or  $E_{vsRHE} = E_{vsSCE} + 0.059 \times PH + 0.241$ . All HER polarization curves were recorded at a low scan rate of 5 mV s<sup>-1</sup>. Before recording, the potentials of all materials were scanned for 50 cycles in the range of -0.6 to 0 V *vs.* REH until a stable polarization curve was obtained. All polarization curves were corrected using 85% iR compensation unless otherwise noted. Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range of  $10^{5}$ -0.1 mHz with an AC amplitude of 10 mV at open circuit potential. Stability of the catalyst was evaluated by linear sweep voltammetry scanning 5000 cycles (LSV, sweep rate, 50 mV s<sup>-1</sup>) and chronopotentiometric measurements under the same configuration with 85% iR compensation. During the chronopotentiometric measurement, the electrolyte was replaced every 24 h. Cyclic

voltammetry method was used to determine the electrochemical double-layer capacitance ( $C_{dl}$ ). Electrochemically active surface area (ECSA) could be evaluated from the slope of the plot of the charging current versus scan rate, which was proportional to  $C_{dl}$ . To get the Tafel plot, the polarization curves were plotted as overpotential vs. log current density.

*Calculation Method*: All the calculations were carried out using DFT with the generalized Perdew-Burke-Ernzerhof (PBE)<sup>2</sup> and the projector augmented-wave (PAW) pseudopotential plane-wave method<sup>3</sup> as implemented in the VASP code.<sup>4</sup> For the PAW pseudopotential, a 10×10×1 Monkhorst-Pack (MP) *k*-point grid was used for CoS<sub>2</sub> (200) surface optimization calculations with a vacuum separation of ~15 Å and a plane-wave basis set with an energy cut-off of 500 eV with considering the spin polarization. Good convergence was obtained with these parameters and the total energy was converged to  $1.0 \times 10^{-6}$  eV per atom. The optimized (200) surface unit cell model was extended to  $2 \times 2 \times 1$  supercells for H adsorption and water dissociation studies. We carried out calculations with the van der Waals (vdW) correction by employing optPBE-vdW functional<sup>5</sup> using a  $2 \times 2 \times 1$  MP *k*-point grid. The nudged elastic band (NEB)<sup>6</sup> was used to analyse the energy barrier of water dissociation at the MoS<sub>2</sub>/CoS<sub>2</sub> hybrid catalysts.



Figure S1. SEM images of (a-c) Co-MOF NRs on CC, and (d-f) MoS<sub>2</sub>/CoS<sub>2</sub> NRs on CC.



**Figure S2.** XRD pattern of 1D Co-MOF NRs. All the labeled peaks match well with the pattern of ZIF-L reported in literature.<sup>7</sup>



**Figure S3.** The XRD patterns of the  $MoS_2/CoS_2$  NTs,  $CoS_2$ , and  $MoS_2$ . To be noted, no diffraction peak of  $MoS_2$  in  $CoS_2/MoS_2$  NTs is observed due to the small amount of  $MoS_2$  nanosheets anchored on the  $CoS_2$  nanotubes and poorly crystallized  $MoS_2$  nanosheets.



**Figure S4.** (a,b) Low-resolution and (c) high-resolution TEM images of the  $MoS_2/CoS_2$  NRs, showing the interlayer space of 0.72 nm between  $MoS_2$  layers.



**Figure S5.** (a,b) SEM images of bare  $MoS_2$  nanosheets grown on CC, (c) TEM image of  $MoS_2$  nanosheets, and (d) high-resolution TEM images of  $MoS_2$  nanosheets. The inset shows the interlayer space of 0.68 nm.



**Figure S6.** Zeta potential intensity distributions of  $MoS_2$ ,  $CoS_2$ ,  $MoS_2/CoS_2$  NRs,  $MoS_2/CoS_2$  NTs and MOF nanoparticles with particle concentration of 100 µg mL<sup>-1</sup> in distilled water.



**Figure S7**. EDS and ICP-OES results of (a) Co-MOF and (b) MoS<sub>2</sub>/CoS<sub>2</sub> NTs. Note that the Mo signal overlaps with S. The ICP-OES shows that the nitrogen concentration is reduced from 25.55 wt.% in Co-MOF to 0.81 wt.% in MoS<sub>2</sub>/CoS<sub>2</sub> NTs, indicating the almost negligible content of the Co-MOF residues.



Figure S8. (a)  $N_2$  adsorption/desorption isotherms and (b) corresponding pore-size distribution of Co-MOF,  $MoS_2/CoS_2 NRs$  and  $MoS_2/CoS_2 NTs$ .



**Figure S9.** (a) HAADF-STEM images of  $MoS_2/CoS_2$  NTs and (b,c) corresponding intensity profiles along the a-a line (b) and b-b line (c).



Figure S10. Benchmark of MoS<sub>2</sub>-based catalysts for HER (a) in alkaline and (b) acid media.



**Figure S11.** Electrocatalytic performance tested in 1M PBS. (a) LSV polarization curves of  $MoS_2/CoS_2$  NTs,  $MoS_2/CoS_2$  NRs,  $CoS_2$ ,  $MoS_2$ , Pt/C and CC. (b) The corresponding Tafel plots. (c) LSV polarization curves of  $MoS_2/CoS_2$  NTs recorded initially and after 2000 sweeps. (d) The chronopotentiometric curves of  $MoS_2/CoS_2$  NTs recorded at current density of 10 mA cm<sup>-2</sup> for 24 hours.



**Figure S12.** EIS spectra of the  $MoS_2/CoS_2 NTs$ ,  $MoS_2/CoS_2 NRs$ ,  $MoS_2$  and  $CoS_2$  in (a) 0.5 M H<sub>2</sub>SO<sub>4</sub> and (b) 1 M KOH electrolytes.



**Figure S13.** Cyclic voltammetry of (a)  $MoS_2/CoS_2$  NTs, (b)  $MoS_2/CoS_2$  NRs, (c)  $CoS_2$ , and (d)  $MoS_2$  at different scan rate: 4, 8, 12, 16, 20 and 50 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (e) Corresponding capacitive currents at 0.8 V vs. SCE as a function of scan rates for  $MoS_2/CoS_2$  NTs,  $MoS_2/CoS_2$  NRs,  $CoS_2$  and  $MoS_2$  in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

![](_page_11_Figure_0.jpeg)

Figure S14. XPS survey spectra of the MoS<sub>2</sub>/CoS<sub>2</sub> NTs.

![](_page_11_Figure_2.jpeg)

Figure S15. Raman spectra of MoS<sub>2</sub> and MoS<sub>2</sub>/CoS<sub>2</sub> NTs.

![](_page_12_Figure_0.jpeg)

**Figure S16.** The optimized hybrid MoS<sub>2</sub>/CoS<sub>2</sub> models. (a) MoS<sub>2</sub> nanoribbon with S atoms terminal along y-direction. (b) MoS<sub>2</sub> nanoribbon with S atoms terminal along x-direction. (c) MoS<sub>2</sub> nanoribbon with Mo atoms terminal along y-direction. (d) MoS<sub>2</sub> nanoribbon with Mo atoms terminal along x-direction. The dark blue, yellow and grey balls denote Co, S and Mo atoms, respectively.

![](_page_13_Figure_0.jpeg)

**Figure S17.** Calculated charge density difference between CoS<sub>2</sub> and MoS<sub>2</sub>. Here, the green and the light red represent electrons depletion and accumulation, respectively. The dark blue, yellow and grey balls denote Co, S and Mo atoms, respectively.

![](_page_13_Figure_2.jpeg)

**Figure S18.** (a) Water molecule adsorption at the most energetic state on the surface of MoS<sub>2</sub>/CoS<sub>2</sub>. (b) The most stable configuration of hydroxyl adsorbed at MoS<sub>2</sub>/CoS<sub>2</sub>. The dark blue, yellow and grey, red and cyan balls represent Co, S, Mo, O and H atoms, respectively.

![](_page_14_Picture_0.jpeg)

**Figure S19.** The optimized model of H adsorption at  $MoS_2/CoS_2$ . The dark blue, yellow and grey, cyan balls represent Co, S, Mo and H atoms, respectively.

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