Supporting Information

Experimental Section

**Materials and Chemicals:** 2-methylimidazole (C₄H₆N₂, 99% purity), ammonium tetrathiomolybdate ((NH₄)₂MoS₄, 99.97% purity), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, ≥98% purity) and thioacetamide (CH₃CSNH₂, ≥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 × 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 × 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 MoS₂/CoS₂ NRs:** 0.02 g (NH₄)₂MoS₄ 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 MoS₂/CoS₂ NTs:** A piece of MoS₂/CoS₂ 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 CoS₂ NRs:** The synthesis of CoS₂ was performed by following the previously reported procedure. 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$_2$ Nanosheets:** A piece of clean CC was immersed into an aqueous solution (30 mL) containing 0.02 g (NH$_4$)$_2$MoS$_4$. After hydrothermal reaction at 200 ºC for 18 h, the sample was taken out, washed with DI water and dried at 60 ºC in vacuum.

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

**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 Kα, l = 0.154 nm). X-ray photoelectron spectroscopy (XPS) measurements were performed using Thermo Scientific Thetaprobe XPS system (monochromatic Al Kα 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$^{-1}$ 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$_2$SO$_4$ 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$^{-1}$. 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$^{-1}$) and chronopotentiometric measurements under the same configuration with 85% iR compensation. During the chronopotentiometric measurement, the electrolyte was replaced every 24 h. Cyclic
voltaammetry method was used to determine the electrochemical double-layer capacitance \( (C_d) \). 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 \( C_d \). 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)\(^2\) and the projector augmented-wave (PAW) pseudopotential plane-wave method\(^3\) as implemented in the VASP code.\(^4\) For the PAW pseudopotential, a 10×10×1 Monkhorst-Pack (MP) \( k \)-point grid was used for CoS\(_2\) (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 2×2×1 supercells for H adsorption and water dissociation studies. We carried out calculations with the van der Waals (vdW) correction by employing optPBE-vdW functional\(^5\) using a 2×2×1 MP \( k \)-point grid. The nudged elastic band (NEB)\(^6\) was used to analyse the energy barrier of water dissociation at the MoS\(_2/\)CoS\(_2\) hybrid catalysts.
**Figure S1.** SEM images of (a-c) Co-MOF NRs on CC, and (d-f) MoS$_2$/CoS$_2$ 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.$^7$
**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$^{-1}$ in distilled water.

Figure S7. EDS and ICP-OES results of (a) Co-MOF and (b) MoS$_2$/CoS$_2$ 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$_2$/CoS$_2$ NTs, indicating the almost negligible content of the Co-MOF residues.
Figure S8. (a) N₂ adsorption/desorption isotherms and (b) corresponding pore-size distribution of Co-MOF, MoS₂/CoS₂ NRs and MoS₂/CoS₂ NTs.

Figure S9. (a) HAADF-STEM images of MoS₂/CoS₂ NTs and (b,c) corresponding intensity profiles along the a-a line (b) and b-b line (c).
Figure S10. Benchmark of MoS$_2$-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$^{-2}$ 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$_2$SO$_4$ 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$^{-1}$ in 0.5 M H$_2$SO$_4$. (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$_2$SO$_4$. 
Figure S14. XPS survey spectra of the MoS$_2$/CoS$_2$ NTs.

Figure S15. Raman spectra of MoS$_2$ and MoS$_2$/CoS$_2$ NTs.
Figure S16. The optimized hybrid MoS$_2$/CoS$_2$ models. (a) MoS$_2$ nanoribbon with S atoms terminal along y-direction. (b) MoS$_2$ nanoribbon with S atoms terminal along x-direction. (c) MoS$_2$ nanoribbon with Mo atoms terminal along y-direction. (d) MoS$_2$ nanoribbon with Mo atoms terminal along x-direction. The dark blue, yellow and grey balls denote Co, S and Mo atoms, respectively.
Figure S17. Calculated charge density difference between CoS$_2$ and MoS$_2$. 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.

Figure S18. (a) Water molecule adsorption at the most energetic state on the surface of MoS$_2$/CoS$_2$. (b) The most stable configuration of hydroxyl adsorbed at MoS$_2$/CoS$_2$. The dark blue, yellow and grey, red and cyan balls represent Co, S, Mo, O and H atoms, respectively.
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.
References