

Supporting Information for
A novel CoP/MoS₂-CNTs hybrid catalyst with Pt-like activity for
hydrogen evolution

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Experimental

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Materials

Molybdenum sulfide (MoS_2 , 99.5%), cobalt(II) acetylacetonate ($\text{Co}(\text{acac})_2$, 97%), trioctylphosphine (TOP, 90%), oleylamine (OAm, 95%), carbon nanotubes (CNTs, 95%, inside diameter: 3-5 nm, outside diameter: 8-15 nm, length: 50 μm), ethanol ($\geq 99.7\%$), hexane ($\geq 99.5\%$), Nafion solution (5% in a mixture of lower aliphatic alcohols and water) and 20% Pt/C catalyst were purchased from Aladdin Chemistry Co. Ltd.

Synthesis of CoP/MoS₂-CNTs hybrid catalyst

In a typical synthesis, $\text{Co}(\text{acac})_2$ (0.257 g, 1 mmol), MoS_2 (50 mg, 0.312 mmol), CNTs (40mg), ODE (5 mL, 15.6 mmol) and OAm (10 mL, 30.4 mmol) were placed in a four-neck flask under a flow of argon. The mixture was stirred and heated to 120 °C. Then TOP (5 mL, 11 mmol) was added to the above mixture solution and heated to 330 °C and kept at this temperature for 1 h. The product was washed with a mixture solvent of hexane and ethanol ($V_{\text{hexane}}: V_{\text{ethanol}} = 1 : 3$) by centrifugation after cooling to room temperature. Finally, CoP/MoS₂-CNTs hybrid catalyst can be synthesized by drying in vacuum at 60 °C for 24 h. Without changing other reaction conditions, no CNTs were added into the above reaction system before heating, the product was CoP/MoS₂ hybrid catalyst. In addition, pure CoP nanorods can be obtained in the above system without the addition of CNTs and MoS₂.

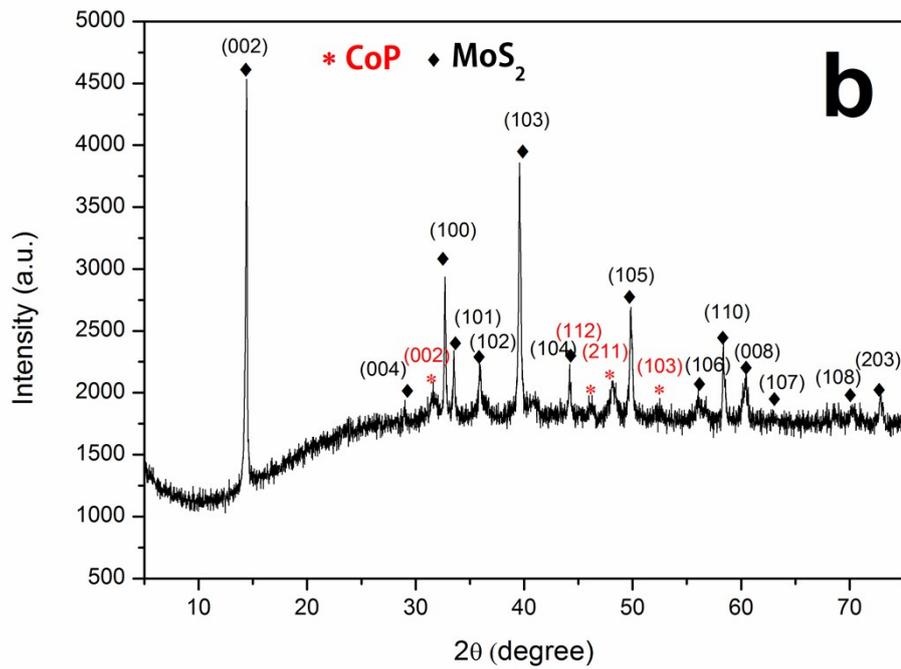
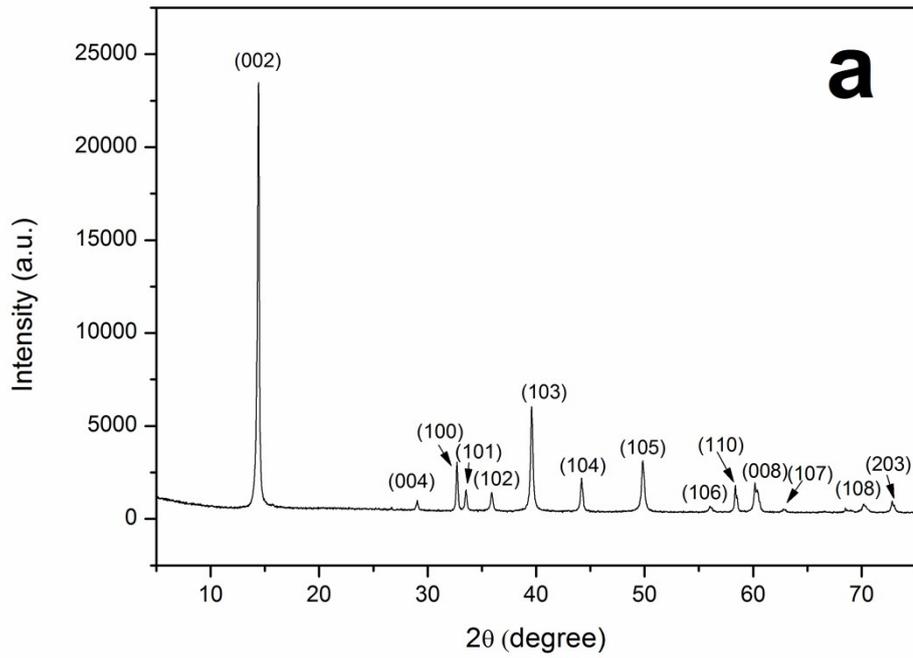
Characterization

X-ray diffraction (XRD) was measured on a panalytical X'pert PRO X-ray diffractometer with $\text{Cu K}\alpha$ monochromatized radiation ($\lambda = 1.54 \text{ \AA}$) and operated at 45 kV and 40 mA. Scanning electron microscope (SEM) were carried out in Hitachi S-4800 at 5 kV. Transmission electron microscopy (TEM) and energy dispersive X-Ray spectroscopy (EDX) were carried out on a Tecnai-G20

microscope (FEI, USA) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was operated on a VG ESCALABMK II spectrometer with a monochromatic Al K α source. N₂ sorption experiments were performed on a ChemBET 3000 (Quantachrome, USA) instrument.

Electrochemical measurements

The electrochemical measurements of the samples were performed in nitrogen-purged 0.5 M H₂SO₄ using a Gamry Instruments Reference 600 potentiostat in a standard three-electrode cell at room temperature. Ag/AgCl electrode as the reference electrode, a Pt wire as the counter electrode and the glassy carbon electrode (GCE) modifying samples as the working electrode. The preparation of working electrode was described as follows. 5 mg of sample catalyst was added into 1 mL of ethanol containing 20 μ L of 5 wt% Nafion, the mixture was dispersed by sonicating for 30 min to form a homogeneous ink. Then 5 μ L catalyst ink was loaded onto a GCE surface. All the potentials were referenced to reversible hydrogen electrode (RHE) using the following equation: E (V vs. RHE) = E (V vs. Ag/AgCl) + 0.222 V + 0.059 pH. In 0.5 M H₂SO₄, E (V vs. RHE) = E (V vs. Ag/AgCl) + 0.222 V. Linear Sweep Voltammetry (LSV) measurements were carried out from -0.6 to 0 V vs. RHE with a scan rate of 5 mV \cdot s⁻¹ at room temperature and the data is presented with iR compensation. The double layer capacitance (C_{dl}) was conducted with cyclic voltammetry (CV) scanning from 0.1 to 0.2 V vs. RHE with different scan rates from 20 to 260 mV \cdot s⁻¹. The cycling stability test was performed by CV scanning 1000 cycles from -0.2 to 0.2 V (vs. RHE) with a scan rate of 100 mV \cdot s⁻¹. Electrochemical impedance spectroscopy (EIS) experiments were performed with frequencies ranging from 100 kHz to 0.1 Hz with an AC voltage of 5 mV at potential of 200 mV.



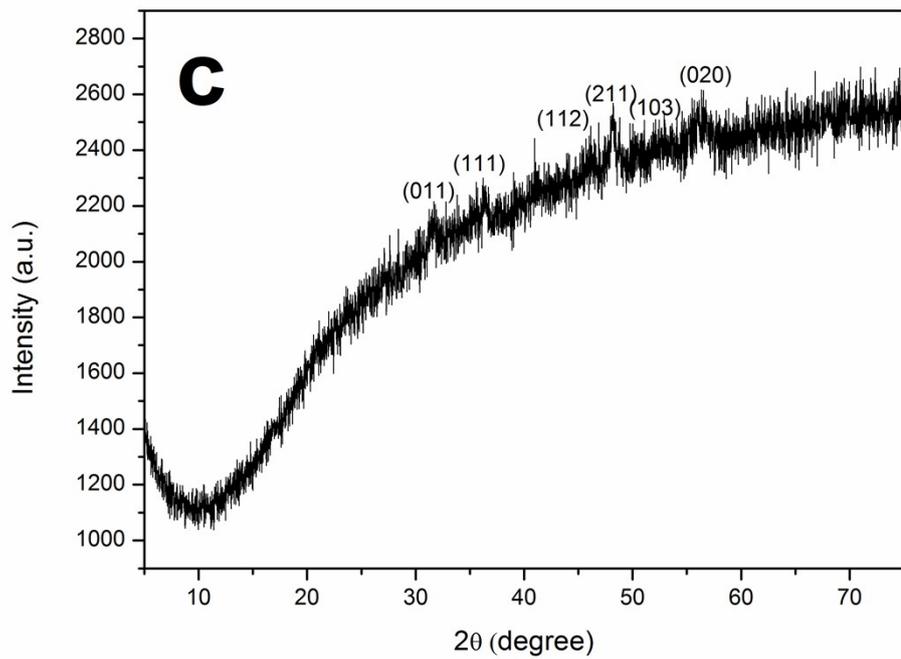
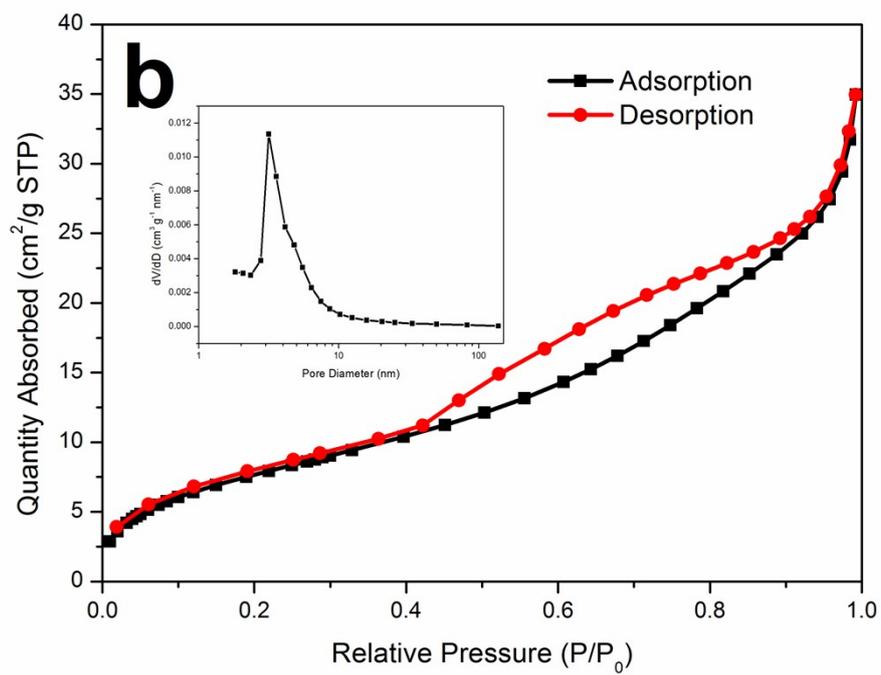
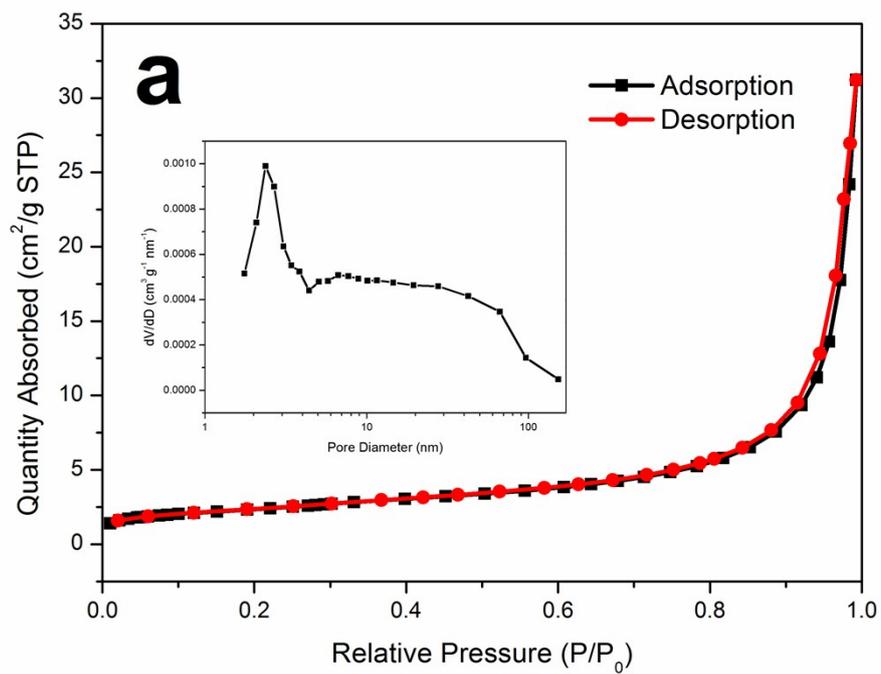


Fig. S1 XRD patterns of (a) pure MoS₂, (b) CoP/MoS₂ and (c) pure CoP.



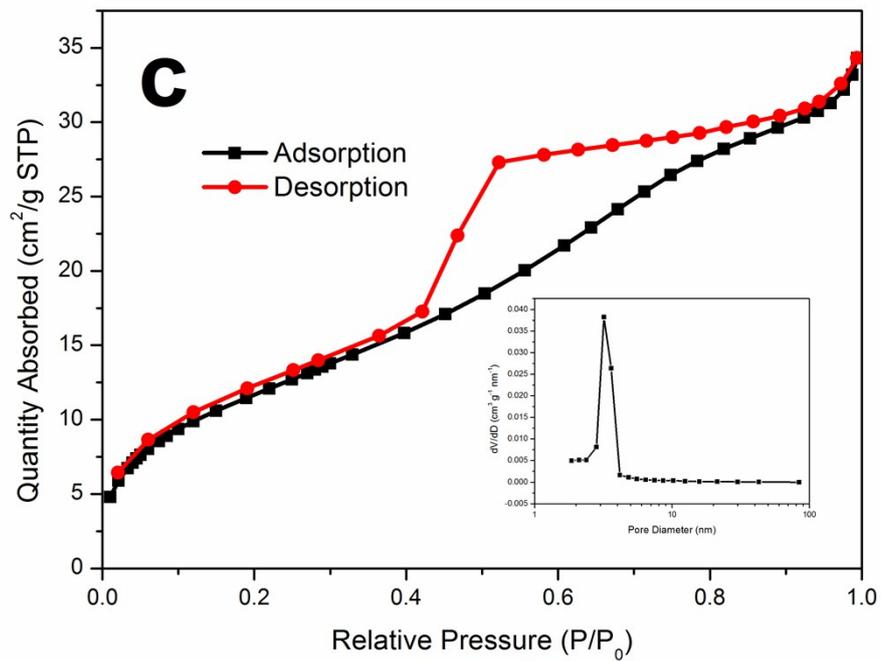


Fig. S2 N₂ sorption isotherm of the (a) pure MoS₂, (b) CoP/MoS₂ catalyst and pure CoP (Insets show the corresponding pore-size distribution curve).

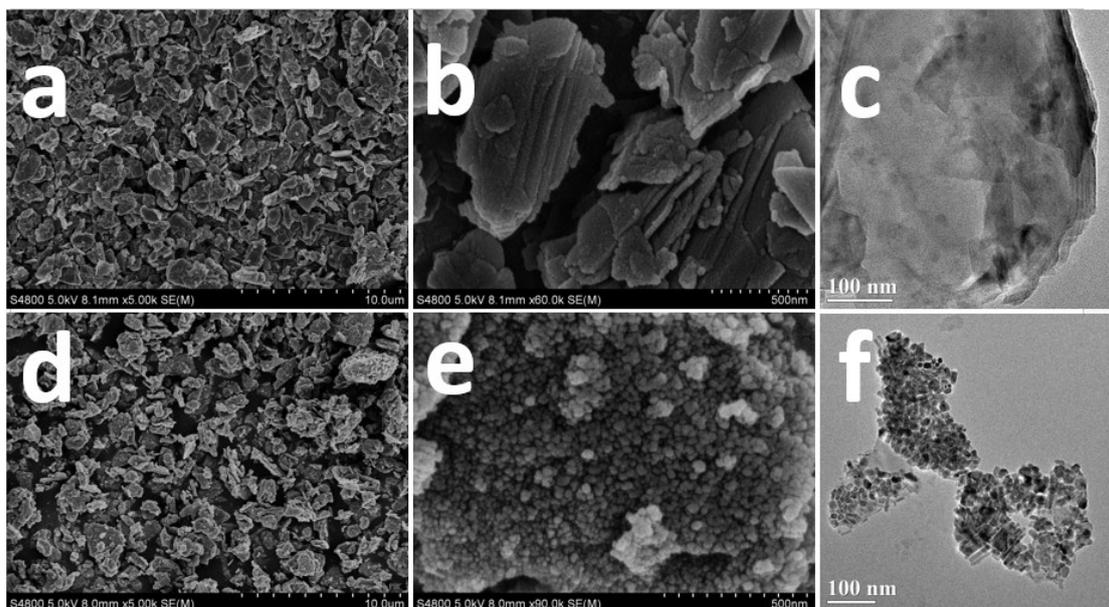


Fig. S3 SEM and TEM images of (a-c) pure MoS₂ and (d-f) CoP/MoS₂.

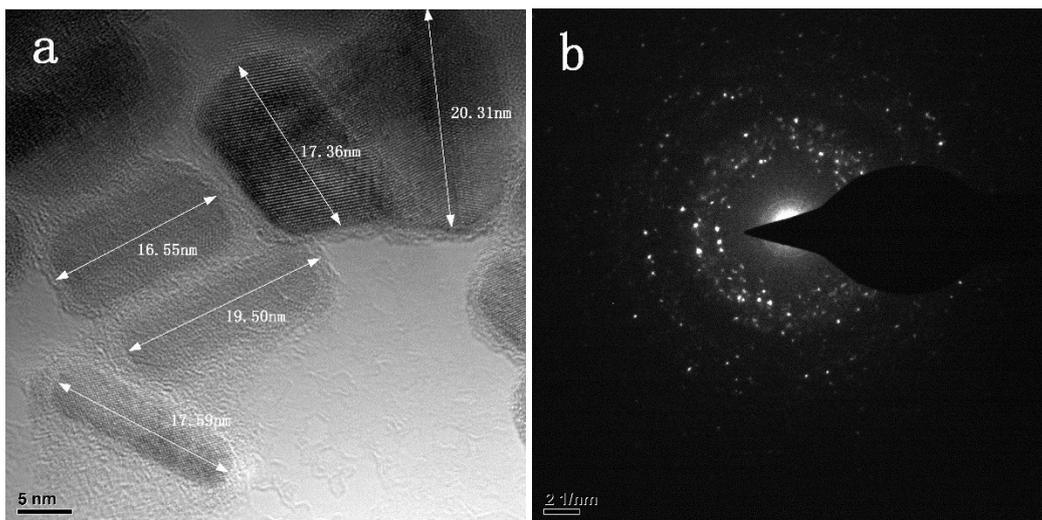
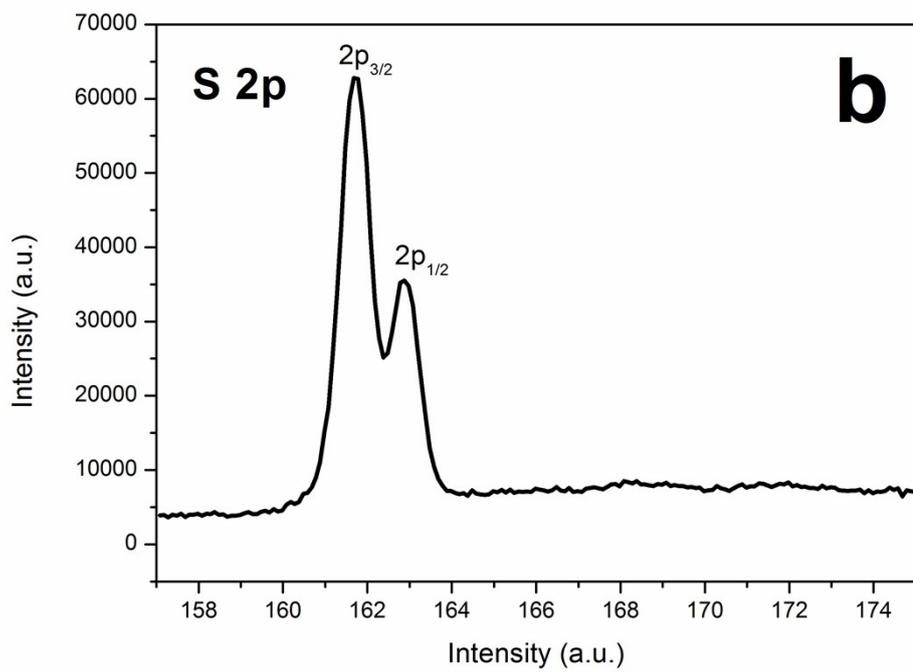
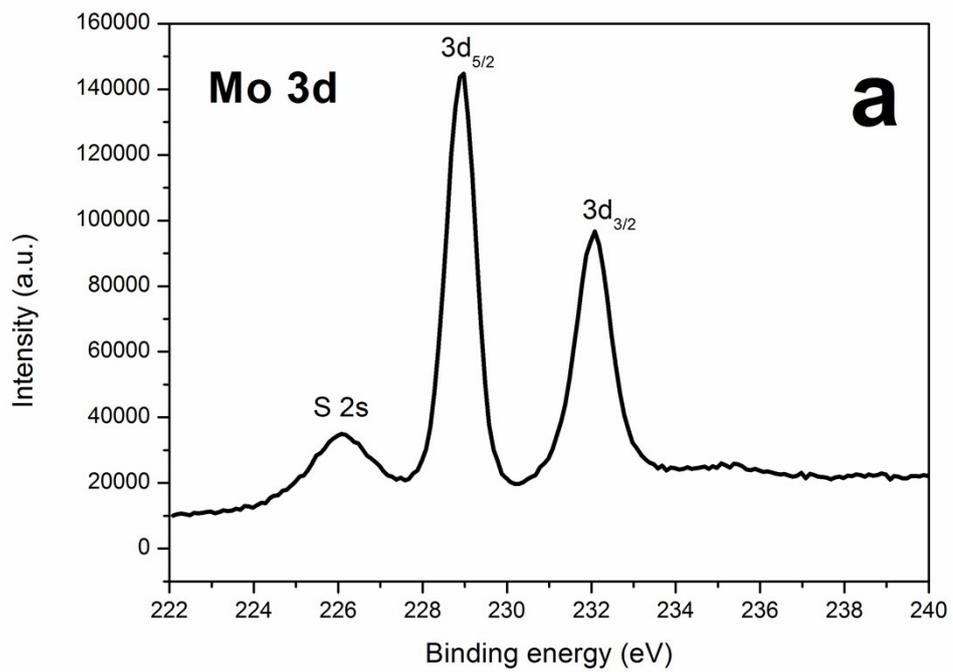
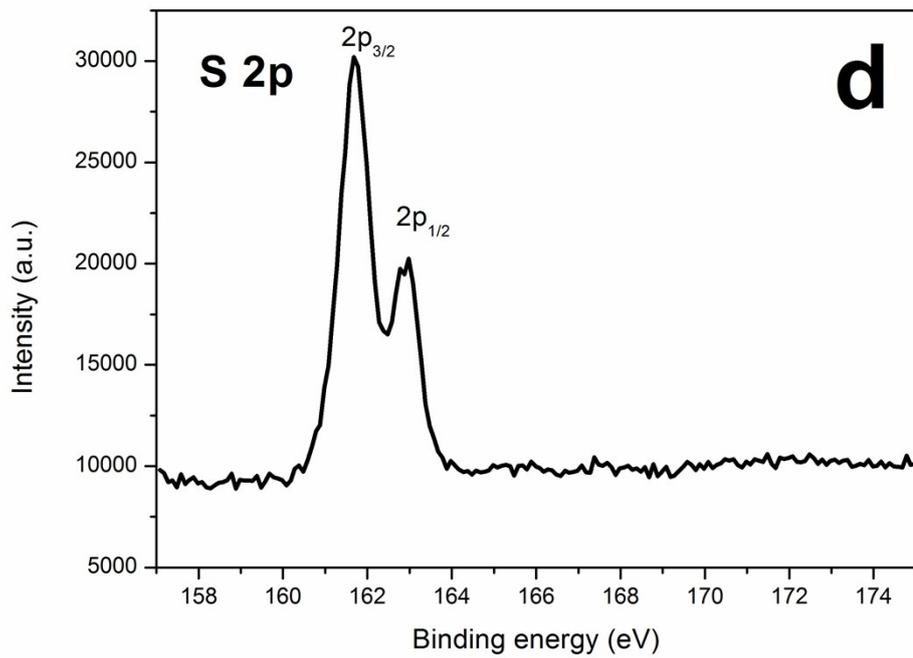
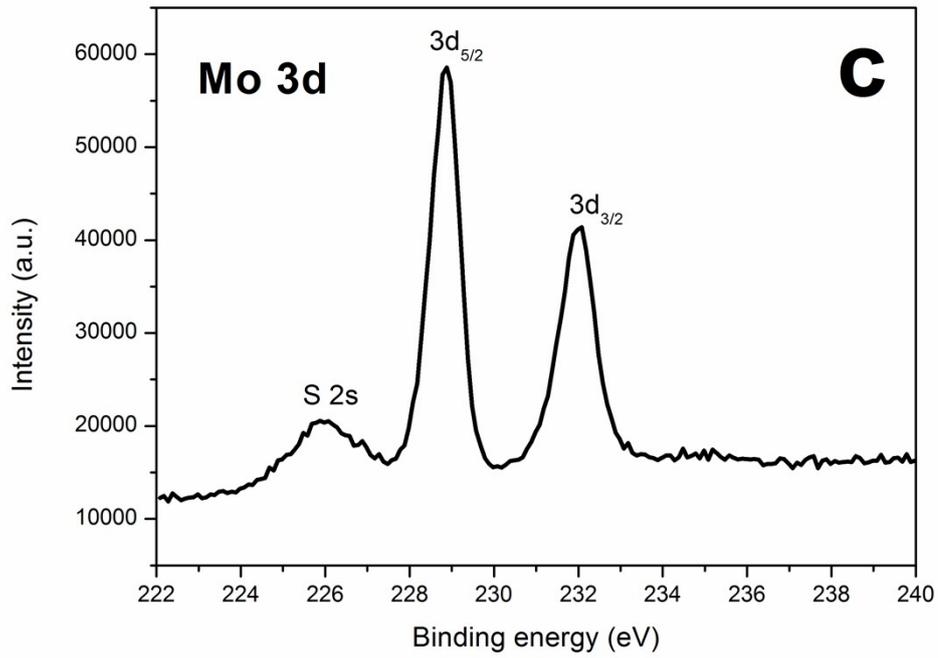
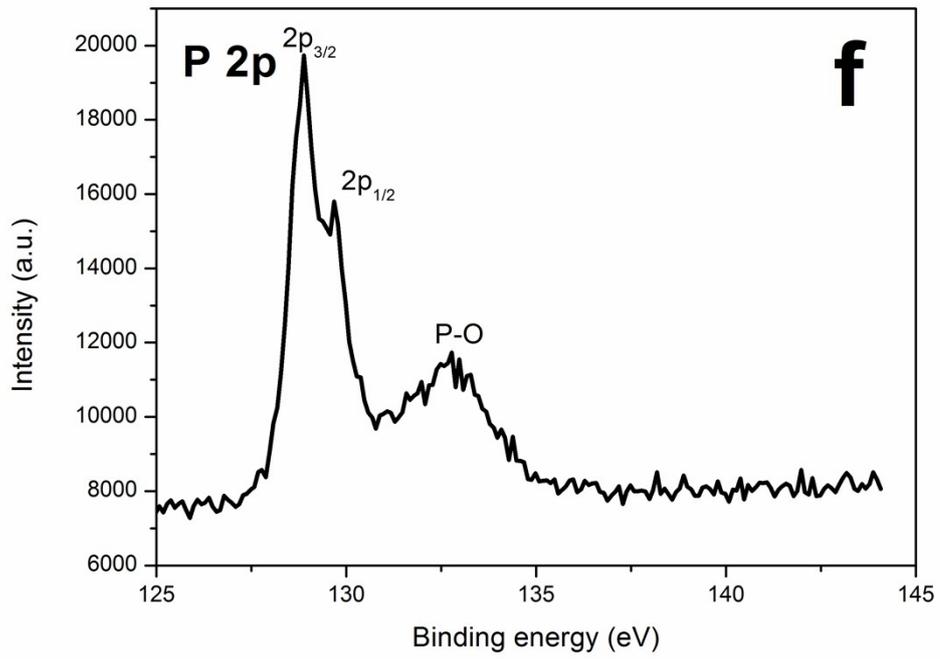
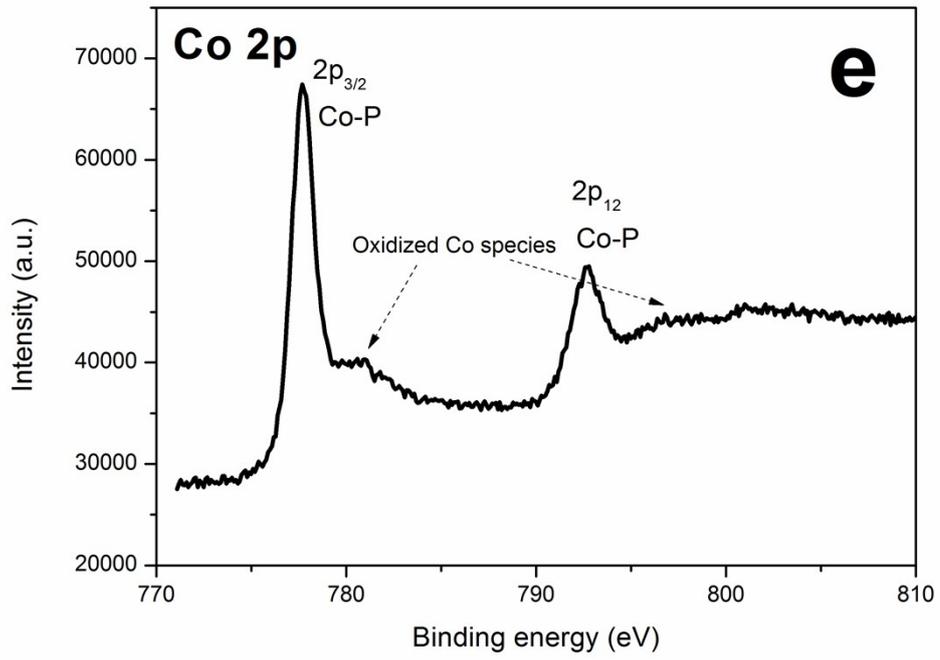


Fig. S4 (a) TEM and (b) SAED images of pure CoP NRs.







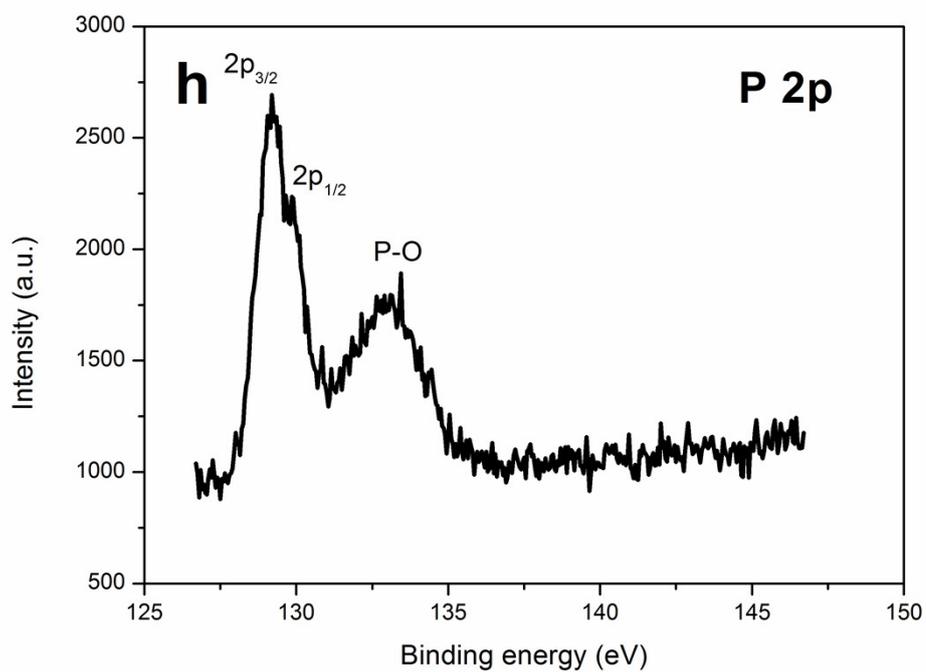
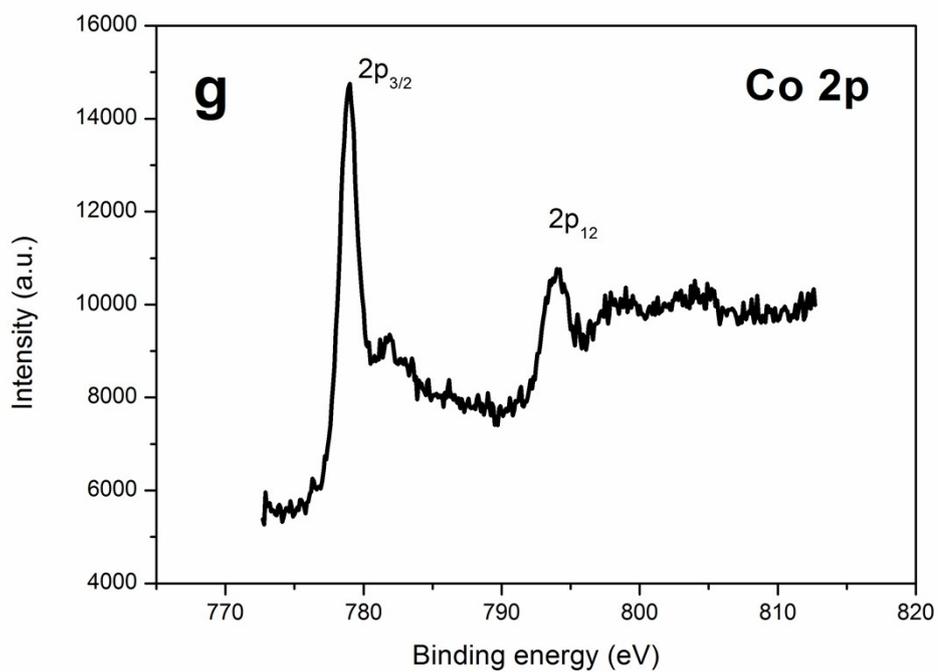


Fig. S5 XPS spectra of (a) Mo 3d and (b) S 2p regions of the pure MoS₂. (c) Mo 3d, (d) S 2p, (e) Co 2p and (f) P 2p regions of the as-synthesized CoP/MoS₂ hybrid catalyst. (g) Co 2p and (h) P 2p regions of the pure CoP.

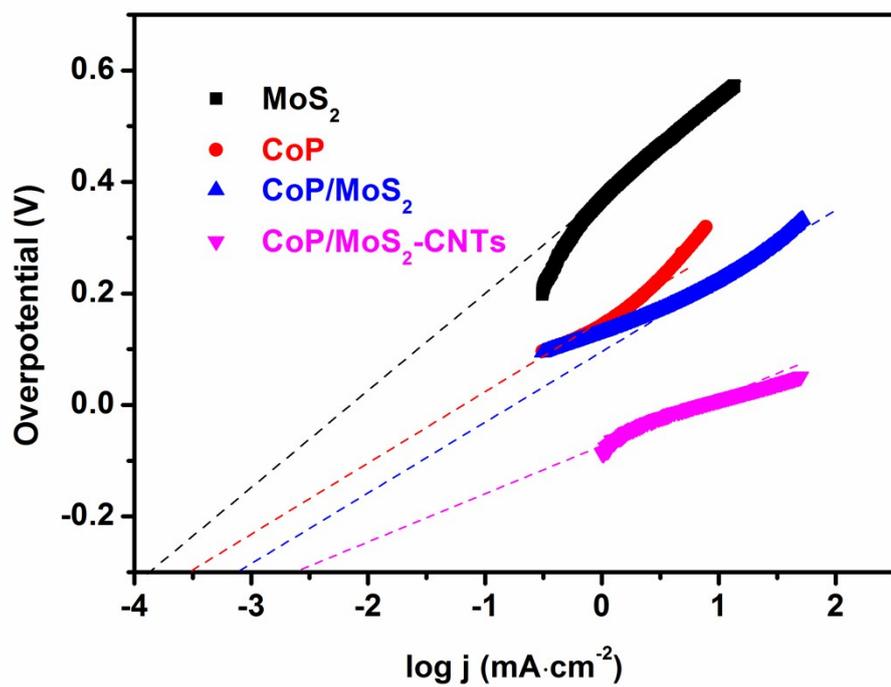
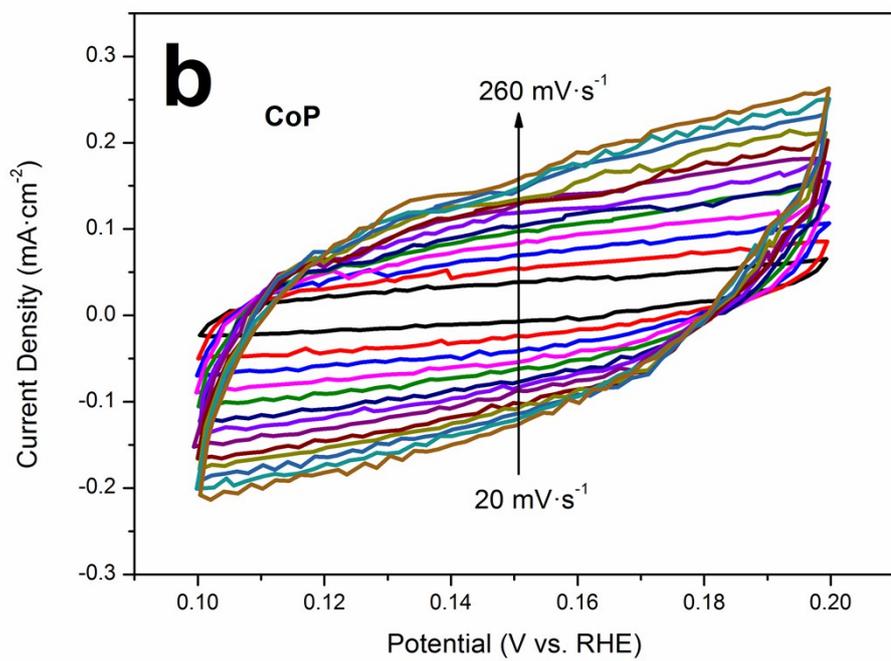
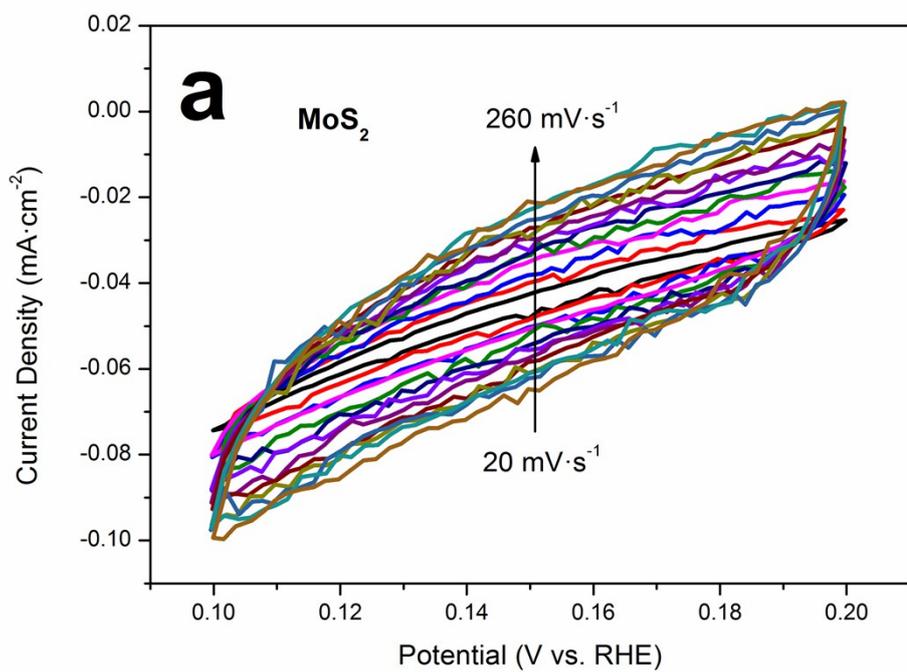


Fig. S6 Calculation of exchange current density of pure MoS₂, pure CoP, CoP/MoS₂ and CoP/MoS₂-CNTs.



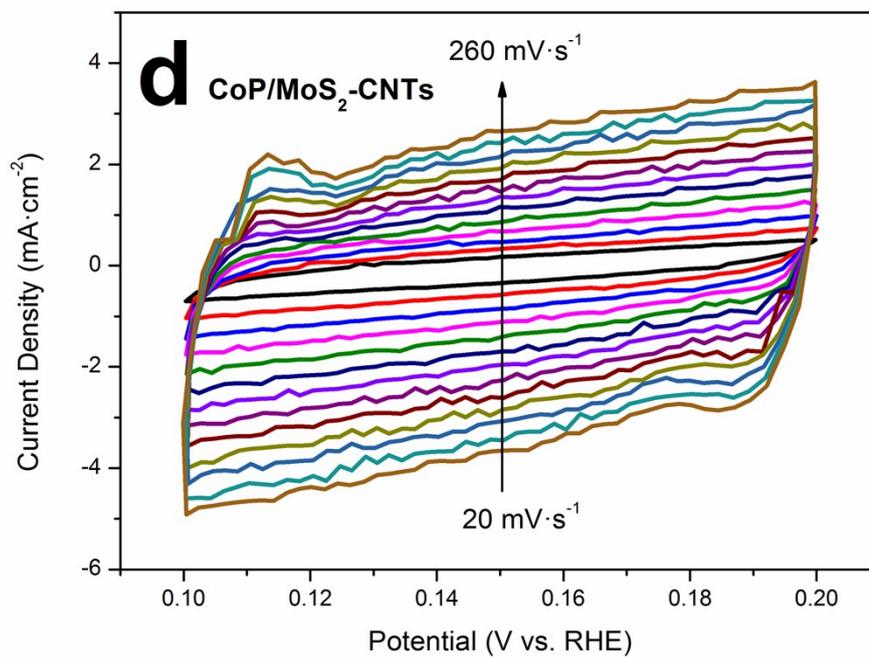
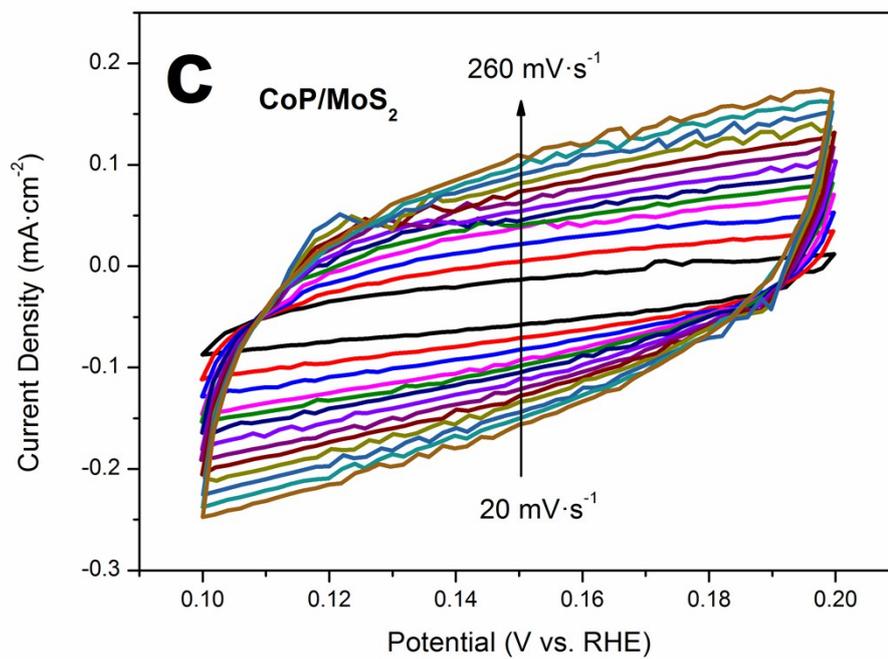


Fig. S7 CV curves of the pure MoS₂, pure CoP, CoP/MoS₂ and CoP/MoS₂-CNTs catalysts in 0.5 M H₂SO₄ solution in the region of 0.1-0.2 V vs. RHE with different scan rates from 20 mV·s⁻¹ to 260 mV·s⁻¹.

Catalyst	BET surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore size (nm)
MoS ₂	8.6	0.048	22.1
CoP	44.2	0.047	3.9
CoP/MoS ₂	29.2	0.05	6.25
CoP/MoS ₂ -CNTs	62.6	0.47	26.8

Table S1 Textural properties of the pure MoS₂, pure CoP, CoP/MoS₂ and CoP/MoS₂-CNTs catalysts.

Table S2 Calculations of the exchange current density of the pure MoS₂, pure CoP, CoP/MoS₂, and CoP/MoS₂-CNTs catalyst by using extrapolation methods.

Catalyst	$\log(j \text{ (mA} \cdot \text{cm}^{-2}))$ at $\eta=0 \text{ V}$	Exchange current density j_0 [$\mu\text{A} \cdot \text{cm}^{-2}$]
MoS ₂	-3.8	0.158
CoP	-3.5	0.216
CoP/MoS ₂	-3.1	0.794
CoP/MoS ₂ -CNTs	-2.5	3.16