

Hierarchical amorphous carbon-coated Co/Co₉S₈ nanoparticles on MoS₂ toward synergistic electrocatalytic water splitting

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Experimental methods

Synthesis of amorphous carbon-coated Co nanoparticles: In a typical synthesis, firstly, 0.291 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.224 g triethylene diamine (TEDA), and 0.166 g p-phthalic acid (PTA) were dissolved in 50 mL N,N-dimethylformamide solution to obtain a homogeneous solution. Then the mixture was evaporated at 80 °C to remove the solvent with stirred vigorously. The as-prepared dry powders were heated at 900 °C for 1 h under the protection of N_2 , and the furnace was cooled to room temperature.

Synthesis of carbon-coated $\text{Co}/\text{Co}_9\text{S}_8$ combined MoS_2 : 50 mg ammonium tetrathiomolybdate (ATTM) was dissolved in 20 ml deionized water, sonicated 15 min for homogeneous mixing. Then 30 mg carbon coated Co nanoparticles was slowly added to the beaker and sonicated for 15 min. Then, the mixture was freeze-dried in lyophilization. The product was heated in 400 °C under H_2/Ar (5%/95%) with a rate of 5 °C/min and maintained for 1 h; typical sample was denoted as $\text{Co}/\text{CoS}_x\text{--MoS}_2$.

Synthesis pure MoS_2 : 50 mg ammonium tetrathiomolybdate (ATTM) was dissolved in 20 ml deionized water and sonicated 15 min, then the mixture was freeze-dried in lyophilization. The product was heated in 400 °C under H_2/Ar (5%/95%) with a rate of 5 °C/min and maintained for 1 h.

Electrode preparation and electrochemical measurements: All the electrochemical measurements were performed at ambient temperature in a typical three-electrode electrochemical cell with an electrochemical station (CHI 660D electrochemical station) in 1M KOH. An Ag/AgCl (saturated KCl-filled) electrode was used as reference electrode. A glassy carbon electrode (3mm in diameter) was served as the support for the working electrode. A graphite rod was used as counter electrode. Typically, homogeneous catalyst ink was prepared by dispersing 5 mg of catalysts in 1 ml water-ethanol solution with volume ratio of 4:1 containing 50 μL 0.5 wt.% Nafion solution and sonicated for 1 h. In short, 5 μL well-dispersed catalysts was dropped on the glassy carbon electrode surface and air-dried at room temperature for measurements. Linear sweep voltammetry was carried out with a scan rate of 5 $\text{mV} \cdot \text{s}^{-1}$

¹ for the polarization curves. The long-term electrochemical stability tests were obtained through CV scanning with continuous cycling at 100 mV·s⁻¹. Electrochemical impedance spectroscopy was studied were evaluated with the frequency range from 100 kHz to 0.1 Hz. Time-dependent current density curves were operated by chronoamperometric measurements. All the potentials used in the paper here was converted to the reversible hydrogen electrode (RHE), based on the Nernst equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E^{\theta}_{\text{Ag/AgCl}}$. All polarization curves were iR corrected.

Calculation of Turnover Frequency (TOF): The active site density and per-site TOF for the as-prepared Co/CoS_x-MoS₂ were experimentally determined by an electrochemical approach¹, using the following equation. Here it is assumed that all of the surface-active sites are fully exposed in the electrolyte.

$$\text{TOF} = I / (2NF)$$

I: current (A) during the linear sweep measurement.

The factor 1/2 is associated with the fact that producing one hydrogen molecule from two protons requires two electrons.

F: Faraday constant (96485 C/mol).

N: number of active sites (mol): cyclic voltammetry measurements (Figure S8) were acquired with a three-electrode configuration at various scan rates of 100 mV s⁻¹ in 1 M KOH solution. The surface-active sites were regarded to have a linear relationship with the integrated voltammetry charges because no obvious redox peak was observed in the entire potential window. If an electron is assumed to undergo both reduction and oxidation reactions, the upper limit of active number (N) can be estimated as:

$$N=Q/2F$$

Q is the total charge of the CV curve

For the Co/CoS_x-MoS₂ electrode: the number of active sites was about $9.742 \times 10^{-6} \text{ mol cm}^{-2}$, and the TOF values at various overpotentials were obtained from the polarization curve (Figure S10, Supporting Information).

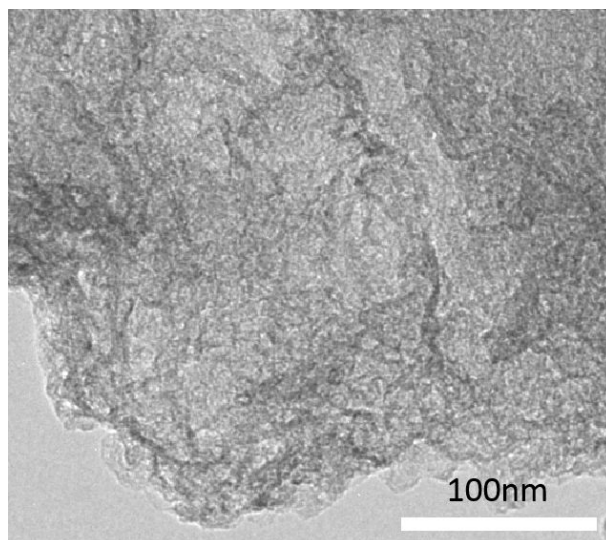


Figure S1 TEM image of pristine MoS₂

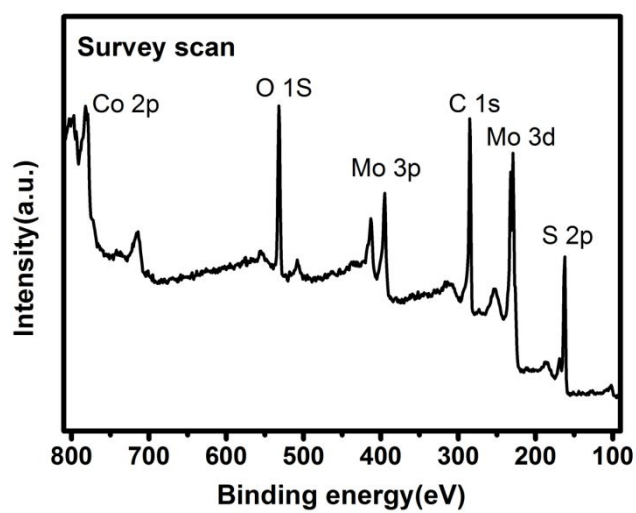


Figure S2 XPS survey spectrum of the Co/CoS_x-MoS₂

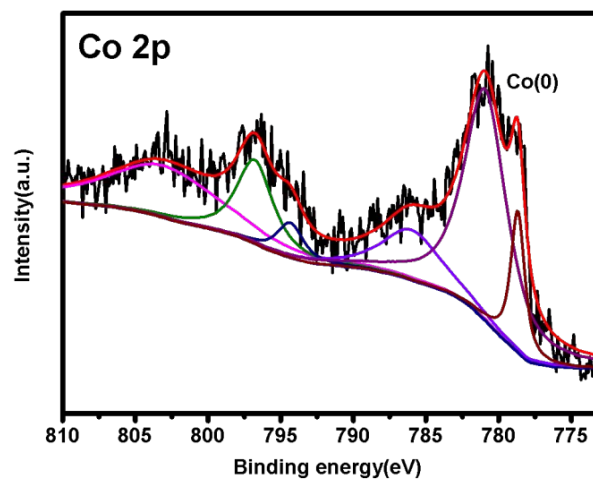


Figure S3 high-resolution spectra of Co 2p for the carbon coated Co nanoparticles

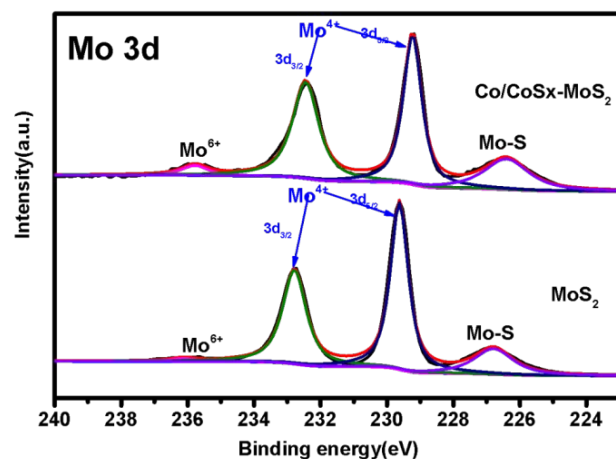


Figure S4 high-resolution spectra of Mo 3d for the pristine MoS₂ and Co/CoS_x-MoS₂

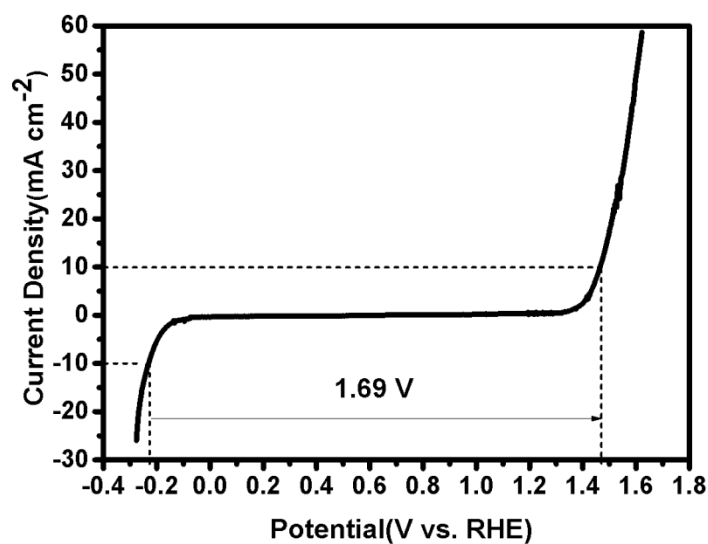


Figure S5 Water splitting polarization of the Co/CoS_x-MoS₂ in 1 M KOH

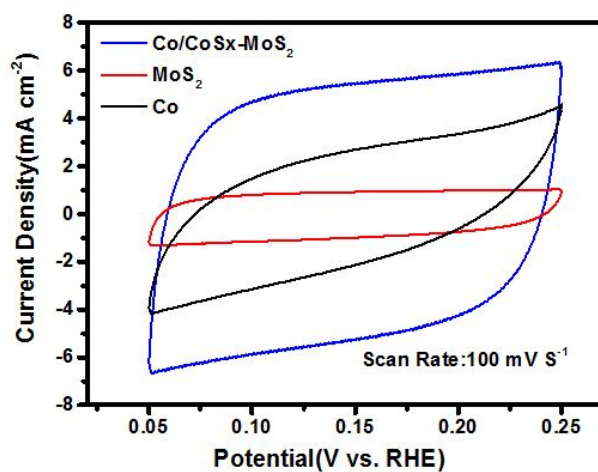


Figure S6. CV curve of the carbon-coated Co/Co₉S₈-MoS₂ obtained in 1M KOH electrolyte with a scan rate of 100 mV/s.

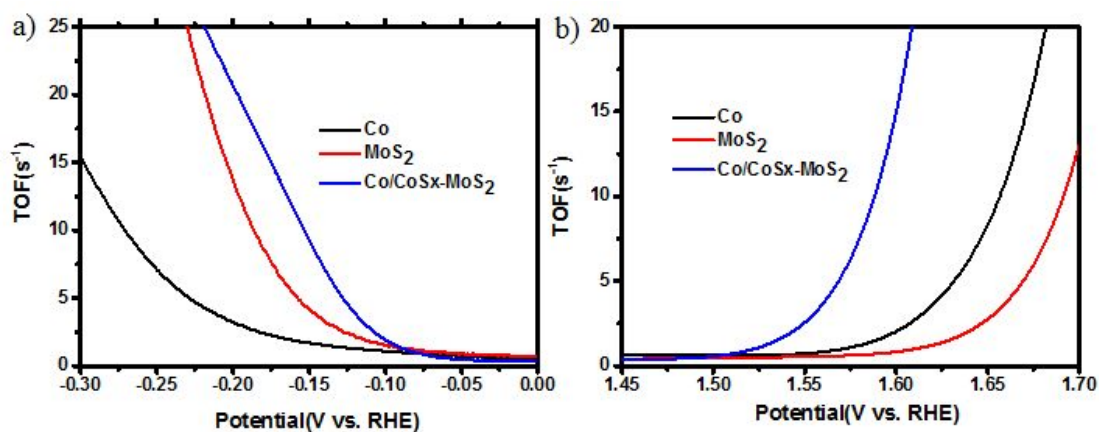


Figure S7. TOFs at various overpotentials in 1M KOH solution for HER a) for OER b).

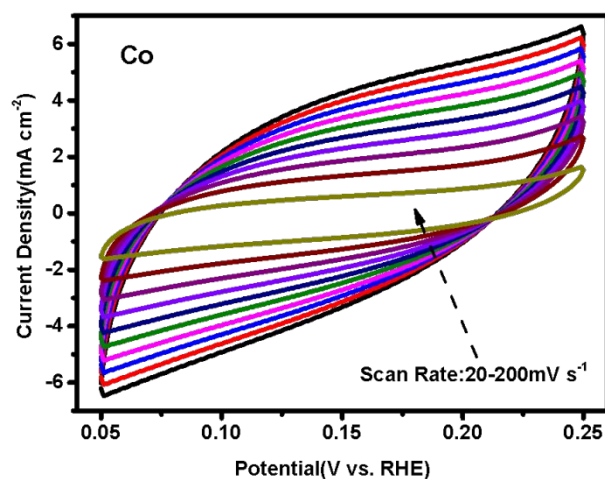


Figure S8 Cyclic voltammograms (CV) of Co is taken in a potential window (0.05-0.25 V vs. Ag/AgCl) at various scan rates of 20 to 200 mV s^{-1} in 1.0 M KOH solution

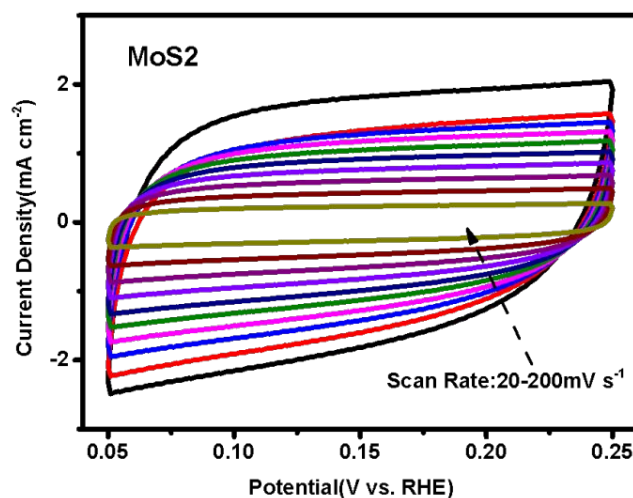


Figure S9 Cyclic voltammograms (CV) of MoS_2 is taken in a potential window (0.05-0.25 V vs. Ag/AgCl) at various scan rates of 20 to 200 mV s^{-1} in 1.0 M KOH solution

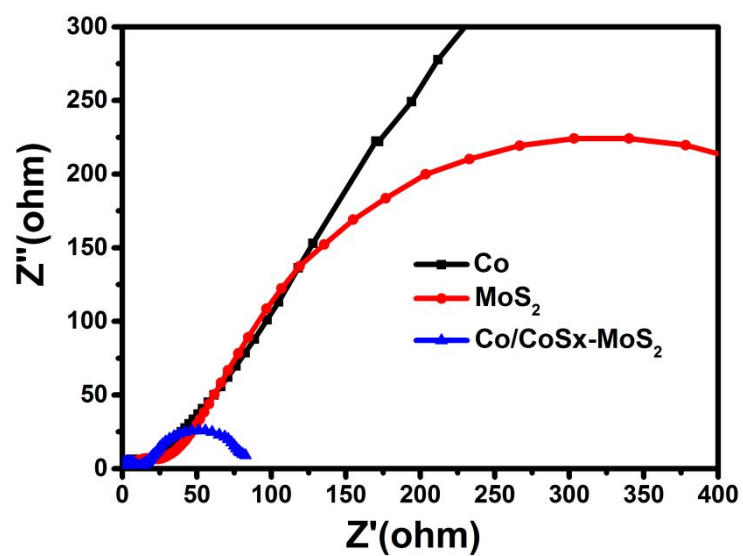


Figure S10 Nyquist plots of carbon coated Co, MoS₂ and Co/CoS_x-MoS₂ in 1 M KOH with an overpotential of 200 mV over the frequency range from 1000 kHz to 0.1 Hz.

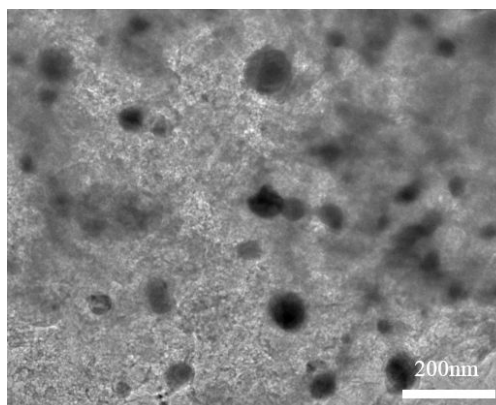


Figure S11 TEM image of the Co/CoS_x-MoS₂ after 1000 cycles CV test

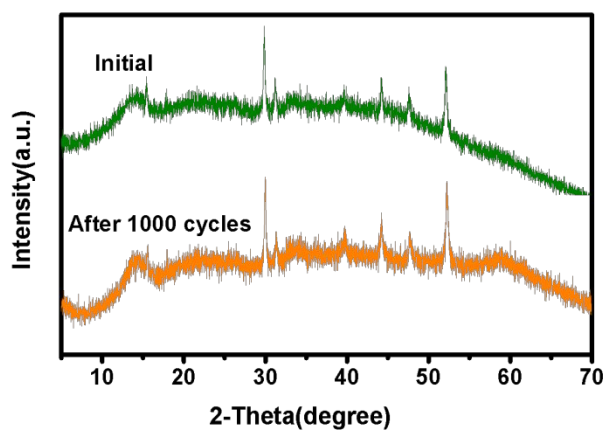


Figure S12 XRD of the Co/CoS_x-MoS₂ before and after 1000 cycles CV test

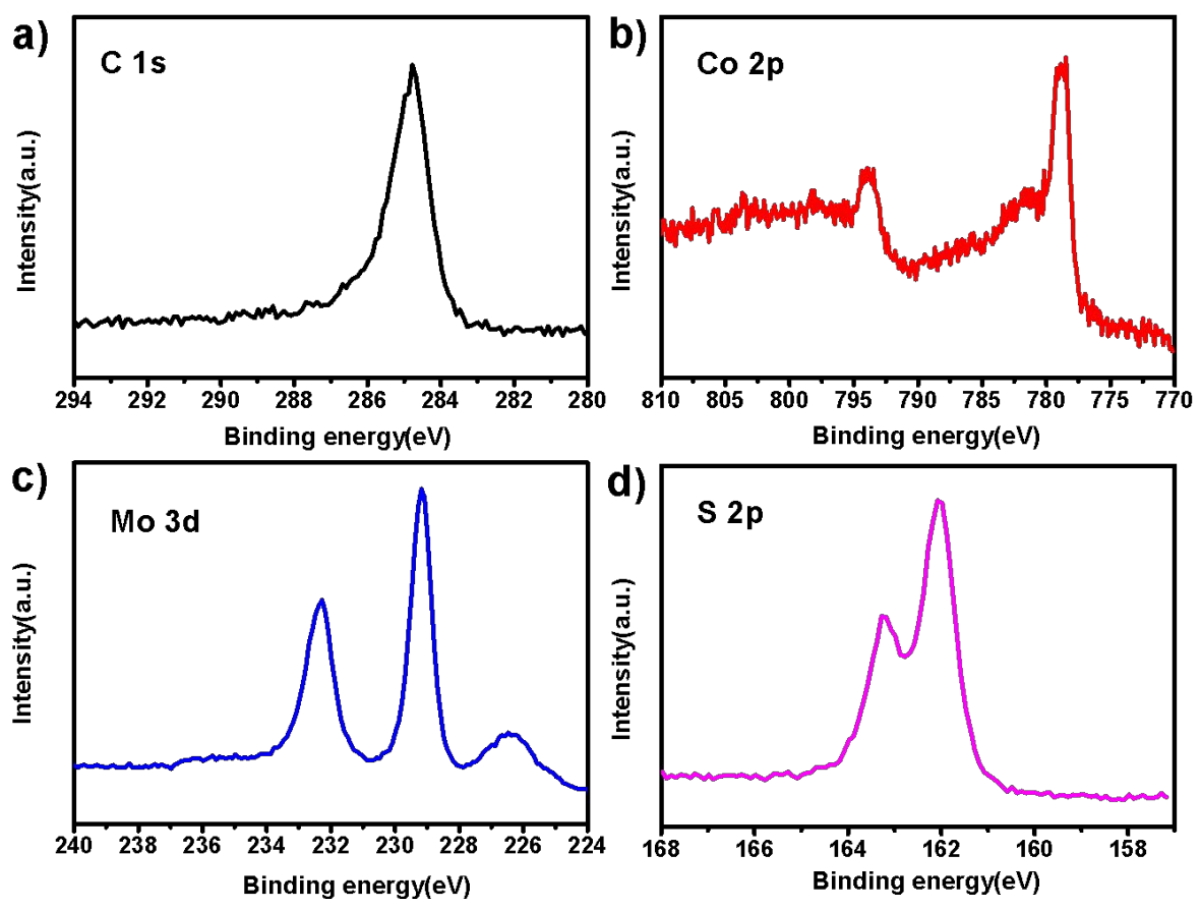


Figure S13 XPS high-resolution spectra of a) C 1s, b) Co 2p, c) Mo 3d, and d) S 2p XPS spectra of the Co/CoS_x-MoS₂ after 1000 cycles CV test

Table S1. Comparison of HER and OER activity data among various catalysts in 1 M KOH solution

Materials	Reaction	η [V]	Tafel slope [mV dec ⁻¹]	References
		10 mA cm ⁻²		
Co/CoS_x-MoS₂	HER	128	65	This work
	OER	325	74	
Co ₉ S ₈ @MoS ₂	HER	143	117	<i>ACS Appl Mater Interfaces</i> ²
	OER	340	79	
Co ₉ S ₈ @MoS ₂ /CNFs	HER	190	110	<i>Adv. Mater.</i> ³
	OER	430	61	
Co/CoP-5	HER	253	73.8	<i>Adv. Energy Mater.</i> ⁴
	OER	340	79.5	
Co-MoS ₂	HER	203	158	<i>Energy Environ.</i> ⁵
	OER	-	-	
Ni _{0.9} Fe _{0.1} PS ₃ @MXene	HER	196	140	<i>Adv. Energy Mater.</i> ⁶
	OER	312	48.9	
Co ₉ S ₈ HNSs	HER	267	139	<i>Nanoscale</i> ⁷
	OER	342	104	
CoxMoy@NC	HER	218	73.5	<i>J. Mater. Chem. A</i> ⁸
	OER	330	48.7	
Co ₉ S ₈ -NixSy/NF	HER	163	88	<i>J. Mater. Chem. A</i> ⁹
	OER	-	-	
Ni-Co-P HNBs	HER	107	46	<i>Energy & Environmental Science</i> ¹⁰
	OER	270	76	

Supplementary References

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