

*Supplementary Information*

## **An efficient CoS<sub>2</sub>/CoSe<sub>2</sub> hybrid catalyst for electrocatalytic hydrogen evolution**

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## Experimental Section

### Materials and Reagents

Co(OAc)<sub>2</sub> · H<sub>2</sub>O, Na<sub>2</sub>SeO<sub>3</sub>, L-cysteine, Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, Diethylenetriamine (DETA, 99.0%), nafion solution (5 wt%) and graphite rod (99.9995%) were purchased from Sigma-Aldrich. Absolute ethanol and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 95.0-98.0%) were obtained from Beijing Chemical Co. (China). The ultra-pure water was prepared by the Millipore Milli-Q water purification system (18.2 MΩ). All reagents were used directly without further purification.

### Materials Synthesis

CoSe<sub>2</sub>/DETA Nanobelts were made according to the literature with some modifications.<sup>[1]</sup> Briefly, 0.249 g Co(OAc)<sub>2</sub> · H<sub>2</sub>O and 0.173 g Na<sub>2</sub>SeO<sub>3</sub> were added into a mixed solution (40 ml) with a volume ratio of V<sub>DETA</sub>/V<sub>DI</sub>=2:1 (DI, deionized water). The obtained wine solution was then transferred into a 50 ml Teflon-lined autoclave, which was sealed and maintained at 180 °C for 16 h. The black floccules were collected by centrifugation at 5000 rpm for 10 min, and washed with the mixed solution of water and absolute ethanol for several times. Finally, the final product was frozen by liquid nitrogen and lyophilized for 24 h.

CoS<sub>2</sub>/CoSe<sub>2</sub> hybrid was prepared by the following method. Firstly, 24 mg freshly made CoSe<sub>2</sub>/DETA nanobelts were dispersed in 24 ml DI (1 mg/ml) and sonicated for 15 min. After a homogeneous solution was achieved by stirring at room temperature, L-cysteine (0.072696g, 0.6 mM) was dissolved into and then stirred for 30 minutes. Finally, Co precursor (0.029105g, 0.1 mM, S:Co=6:1) were dissolved into. The mixture was stirred at room temperature until a homogeneous solution was achieved before transferred to a 30 mL Teflon-lined autoclave. It was heated in an oven at 200°C for 12 h with no intentional control of ramping or cooling rate. The final product was collected by centrifugation at 8000 rpm for 8 min, and washed with the mixed solution of water and absolute ethanol for several times to remove any possible ions. Finally, product was frozen by liquid nitrogen and lyophilized for 24 h. CoS<sub>2</sub> was prepared with the same

procedure in the absence of CoSe<sub>2</sub>/DETA nanobelts.

### **Characterizations**

The scanning electron microscopy (SEM) images were obtained using a PHILIPS XL-30 ESEM with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), Fast Fourier transform (FFT), high-angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM), and STEM-energy dispersive X-ray (EDX) mapping were taken by using a JEM-2010 (HR) microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250 with Al K $\alpha$  radiation (pass energy, 20.0 eV; energy step size, 1.0 eV; total acq. time: 1 min 0.1 s). X-ray diffraction (XRD) spectra were obtained using a Bruker D8 ADVANCE instrument with Cu K $\alpha$  radiation (40 kV, 40 mA). Raman spectroscopy was performed on a customized LabRAM HR Evolution Raman system (HORIBA Scientific) with an excitation wavelength of 532nm. Fourier transform infrared spectroscopy (FT-IR) was carried out on a Nicolet 6700 spectrometer. Inductively coupled plasma optical emission spectrometry (ICP -OES) was performed on X Series 2 (Thermo Scientific, USA). The Nyquist plots (EIS) were performed on Zahner Zennium. GC analysis was carried out on GC-2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second. All electrochemical measurements were performed on CHI 620a.

### **Electrochemical Measurements**

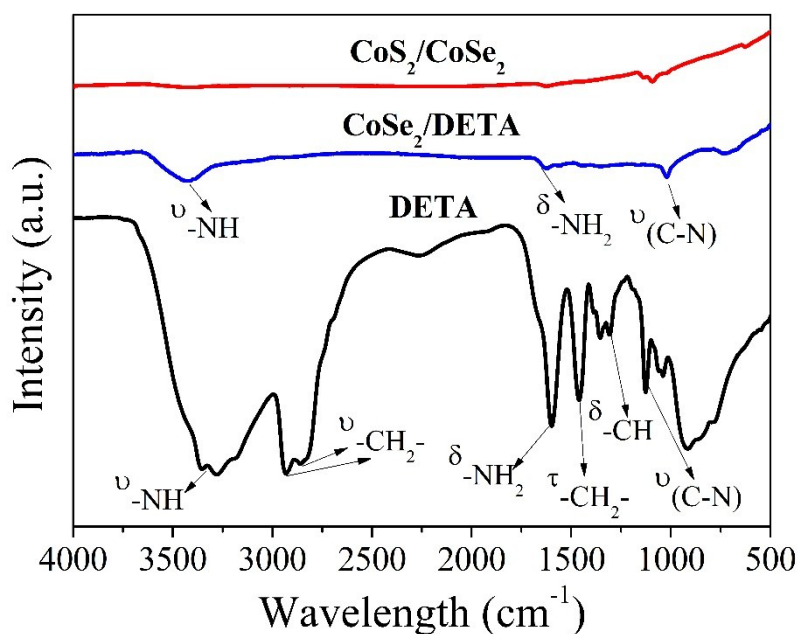
The electrode modification process is as following. Typically, 4 mg of sample were dispersed in 1 mL water-ethanol solution with volume ratio of 3:1 by sonicating to form a homogeneous ink. Then 5  $\mu$ L of the dispersion (loading ca. 0.285 mg cm<sup>-2</sup>) and 0.5  $\mu$ L Nafion solution (0.5 wt%) were loaded onto a glassy carbon electrode of 3 mm diameter and then dried in air at room temperature. All other electrochemical measurements were performed similar to our previous works [21, 22] and details are in the supporting information.

Electrochemical measurements were performed in a three-electrode system at an electrochemical workstation (CHI 620a). Linear sweep voltammetry (LSV) at a scan rate of  $5 \text{ mV s}^{-1}$  was conducted in  $0.5 \text{ M H}_2\text{SO}_4$  (sparged with pure  $\text{N}_2$ ) using a Ag/AgCl (saturated KCl) electrode as the reference electrode, a graphite rod as the counter electrode, and the glassy carbon electrode with various samples as the working electrode, respectively. Current density was normalized to the geometrical area of the working electrode ( $0.07 \text{ cm}^2$ ). All the data were recorded after applying a number of potential sweeps until the electrodes were stable. All of the potentials were calibrated with respect to a reversible hydrogen electrode (RHE) according to the literature.<sup>[2]</sup> In  $0.5 \text{ M H}_2\text{SO}_4$ ,  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.217 \text{ V}$ . All the potentials reported in our manuscript were against RHE.

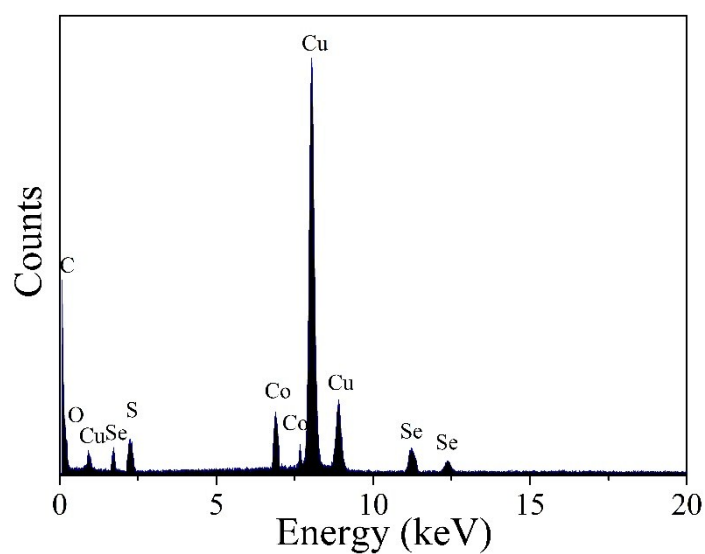
The electrochemical stability of different catalysts was evaluated by CV from  $+0.10 \text{ V}$  to  $-0.4 \text{ V}$  vs. RHE with a scan rate of  $50 \text{ mV s}^{-1}$ , cycling the electrode 3000 times. Amperometric  $i$ - $t$  curve was also obtained at a constant potential of  $-0.13 \text{ V}$  to evaluate the stability. The double-layer capacitances ( $C_{\text{dl}}$ ) were estimated by CV in the  $0.1$ - $0.2 \text{ V}$  vs. RHE region at various scan rates ( $20$ - $200 \text{ mV s}^{-1}$ ) to evaluate the effective surface area of various catalysts.

The Faradaic efficiency was calculated by comparing the amount of measured hydrogen generated by potentiostatic cathodic electrolysis with calculated hydrogen.

The ohmic resistance used for  $iR$ -correction was obtained from electrochemical impedance spectroscopy (EIS) measurements with frequencies ranging from  $100 \text{ mHz}$  to  $1 \text{ M Hz}$  with an AC voltage of  $5 \text{ mV}$ . The impedance data were fitted to a simplified Randles circuit to extract the series resistances ( $R_s$ ) and charge-transfer resistances ( $R_{\text{ct}}$ ).



**Figure S1.** Fourier transform infrared (FT-IR) spectra of DETA,  $\text{CoSe}_2/\text{DETA}$  nanobelts and the  $\text{CoS}_2/\text{CoSe}_2$  hybrid.



**Figure S2.** Energy dispersive X-ray (EDX) spectra of  $\text{CoS}_2/\text{CoSe}_2$ .

**Table S1.** Elements percentage of  $\text{CoSe}_2/\text{DETA}$ ,  $\text{CoS}_2$ , and  $\text{CoSe}_2/\text{CoS}_2$  obtained from ICP-OES.

Elements	$\text{CoSe}_2/\text{DETA}$		$\text{CoS}_2$		$\text{CoSe}_2/\text{CoS}_2$	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
Co	2.377	1	1.847	1	1.818	1
Se	6.175	1.94	---	---	2.350	0.96
S	---	---	2.119	2.11	1.247	1.26

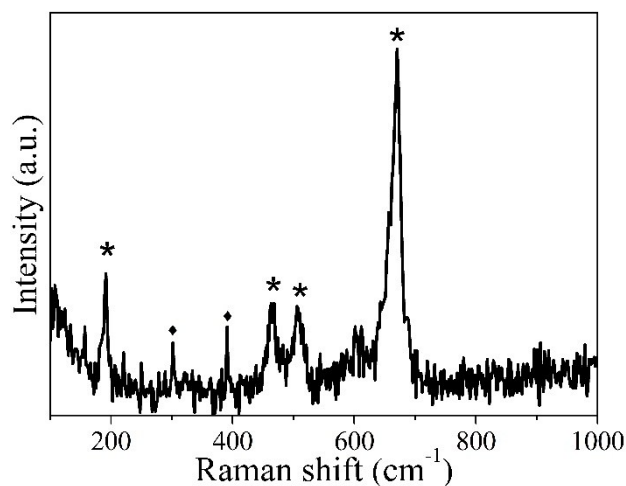
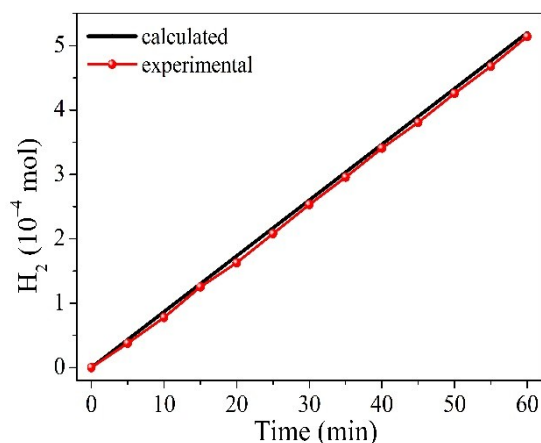


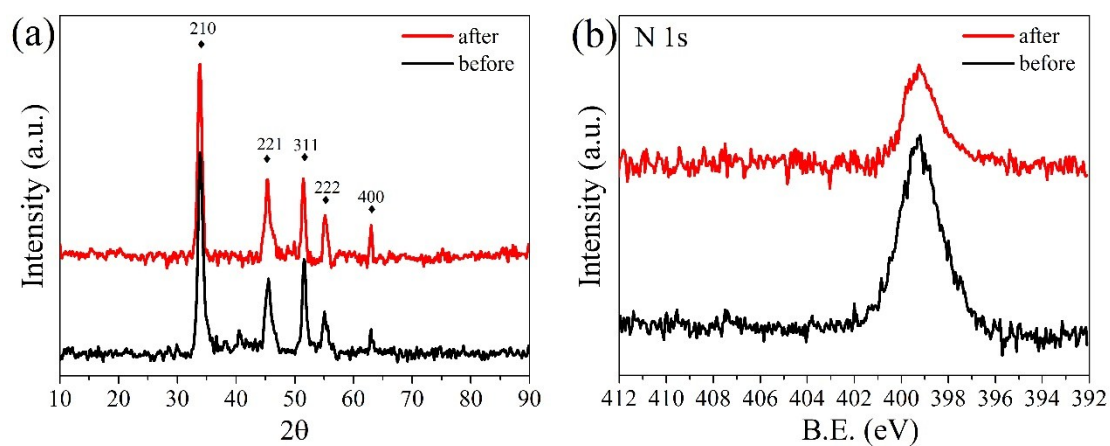
Figure S3. Raman spectra of CoS<sub>2</sub>/CoSe<sub>2</sub>.

Table S2. Electrochemical parameters of different catalysts.

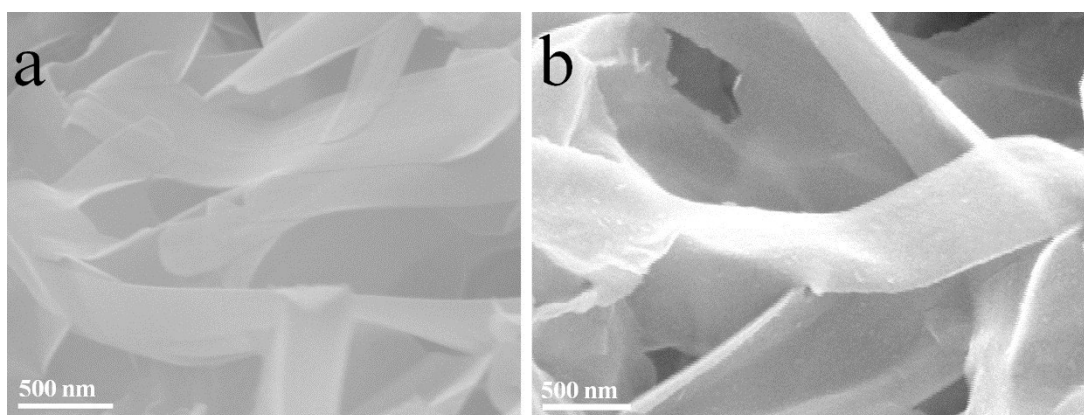
Catalyst	Mass loading [mg cm <sup>-2</sup> ]	Tafel slopes [mV dec <sup>-1</sup> ]	$\eta_{j=10}$ [mV]	$\eta_{j=100}$ [mV]
MoS <sub>2</sub> /CoSe <sub>2</sub> <sup>1b</sup>	0.28	36	68	Not given
MoS <sub>2</sub> /RGO <sup>2</sup>	0.280	41	Not given (~150 mV by estimating)	Not given
Defect-rich MoS <sub>2</sub> nanosheets <sup>3</sup>	0.285	50	Not given (~190 mV by estimating)	Not given
CoNi@NC <sup>4</sup>	0.32	104	224	Not given
Oxygen-incorporated MoS <sub>2</sub> nanosheets <sup>5</sup>	0.285	55	Not given (~180 mV by estimating)	Not given (~280 mV by estimating)
MoS <sub>2</sub> nanosheets within graphite <sup>6</sup>	0.200	41	Not given (~160 mV by estimating)	Not given (~280 mV by estimating)
MS <sub>2</sub> @MoS <sub>2</sub> /RGO (M=Fe, Co, Ni) <sup>7</sup>	0.285	38.4, 38.5, 37.4	123, 110, 98	224, 202, 175
Ni/NiO/CoSe <sub>2</sub> <sup>8</sup>	0.28	39	Not given (~88 mV by estimating)	Not given
CoSe <sub>2</sub> NP/CP <sup>9</sup>	0.26	40	137	181
Mn <sub>0.05</sub> Co <sub>0.95</sub> Se <sub>2</sub> <sup>10</sup>	0.28	36	195	Not given
MoCN <sup>11</sup>	0.4	46	140	Not given
CoS <sub>2</sub> /CoSe <sub>2</sub> (current work))	0.285	33.6	80	155



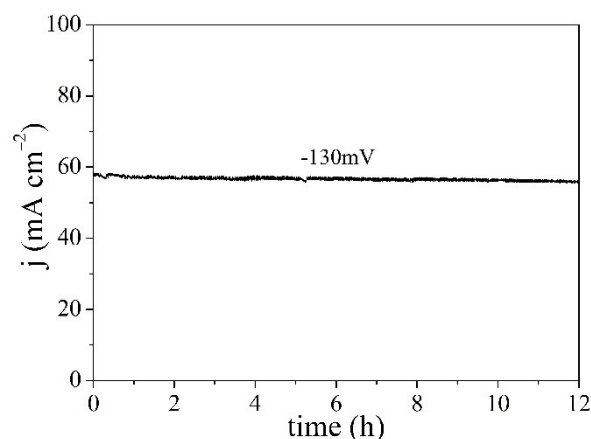
**Figure S4.** The amount of  $H_2$  theoretically calculated and experimentally measured versus time for  $CoS_2/CoSe_2$  at overpotential of 200 mV for 60 min.



**Figure S5.** (a) XRD pattern and (b) XPS spectra of  $CoSe_2$ -DETA nanobelts before and after immersed in pure acetic acid solution for 24h. The XRD pattern of  $CoSe_2$ -DETA nanobelts after the acid treat is similar to that of the before acid treat. The same as to the N1s spectra. These indicate that the  $CoSe_2$ -DETA nanobelts are stable in acid solution.



**Figure S6.** SEM images of (a) before and (b) after the  $CoSe_2$ -DETA nanobelts immersed in pure acetic acid solution for 24h. The products keep the belt-like morphology after the acid treatment. This confirmed that the  $CoSe_2$ -DETA nanobelts are stable in acid solution.



**Figure S7.** Current versus time during the long term (12 h) with a constant potential ( $-0.13$  V vs. RHE) of  $\text{CoS}_2/\text{CoSe}_2$ .

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