Supplementary Information

P doped Co_2Mo_3Se nanosheets grown on carbon fiber cloth as an efficient hybrid catalyst for hydrogen evolution

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Experimental Section

Materials and Reagents

Carbon fiber cloth (CFC, WOS 1002) was provided by Ce Tech Co., Ltd. $Co(OAc)_2{\cdot}H_2O$ (≥98%), Na_2SeO_3 (99%), phosphomolybdic acid hydrate ($H_3PO_4{\cdot}12MoO_3{\cdot}xH_2O$, PMA, ≥99.99%), Molybdosilicic acid hydrate ($H_4SiO_4{\cdot}12MoO_3{\cdot}xH_2O$, MSA, ≥99.99%) and Nafion solution (5 wt%) and graphite rod (99.9995%) were purchased from Sigma-Aldrich. Absolute ethanol (≥99.7%), hydrazine hydrateand ($N_2H_4{\cdot}H_2O$, 80%) and sulphuric acid (H_2SO_4, 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

A piece of CFC (2 cm × 2 cm) was carefully pre-treated with concentrated HNO_3 to remove impurity of surface, and then acetone, ethanol and deionized water were used for several times to ensure the surface of the CFC was well cleaned. After drying at 60 °C for 5 h, the weight of each treated CFC was recorded. P-Co_2Mo_3Se/CFC was synthesized as following. 0.4 mmol $Co(OAc)_2{\cdot}H_2O$ (0.09963 g), 0.05 mmol PMA (0.09126 g) and 1 mmol of Na_2SeO_3 (0.17294 g) were dissolved in 20 mL mixed solution of 12 mL deionized water (DI) and 8 mL $N_2H_4.H_2O$ ($V_{DI}/V_{N2H4.H2O}$ =3:2). After stirring for 30 minutes, the homogeneous solution was transferred into a 30 mL polytetrafluoro-ethylene Teflon-lined stainless steel autoclave with the pre-treated CFC, which was sealed and maintained at 180 °C for 16 h. The CFC was immersed in the mixed solution of water and absolute ethanol and with shaking table for an hour. Finally, the final product was frozen by liquid nitrogen and lyophilized for 24 h. $CoSe_2$/CFC and P-$MoSe_2$/CFC was prepared with the same procedure in the absence of Mo and Co precursor, respectively. Molybdosilicic acid hydrate

($H_4SiO_4 \cdot 12MoO_3 \cdot xH_2O$, MSA) was used to replace phosphomolybdic acid hydrate ($H_3PO_4 \cdot 12MoO_3 \cdot xH_2O$, PMA) to prepare $MoSe_2$/CFC. Different P-CoMoSe/CFC were synthesized with the same procedure by change the ratios of Co and Mo precursor. The different P-CoMoSe/CFC were named according to the atomic percentage (at.%) of Co and Mo obtained from ICP-OES. Details are listed in table S1.

The average weight of seven piece of treated CFC (2 cm × 2 cm) is 0.0550 g. The loading mass of $CoSe_2$/CFC, P-$MoSe_2$/CFC and P-$Co_2Mo_3Se_2$/CFC is 0.0090 g (1.13 mg/cm^2), 0.0092 g (1.15 mg/cm^2) and 0.0086 g (1.08 mg/cm^2), respectively. The mass of precipitate for $CoSe_2$/CFC, P-$MoSe_2$/CFC and P-$Co_2Mo_3Se_2$/CFC is 0.0884 g, 0.0916 g and 0.0985 g, respectively. So the yield for the products is 89.8%, 92.1% and 89.6%.

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 Kα 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 Kα radiation (40 kV, 40 mA). Raman spectroscopy was performed on a customized LabRAM HR Evolution Raman system (HORIBA Scientific) with an excitation wavelength of 514.5 nm. 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

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 mV s^{-1} was conducted in 0.5 M H_2SO_4 (sparged with pure N_2) using a Ag/AgCl (saturated KCl) electrode as the reference electrode, a graphite rod as the counter electrode, and a piece of P-CoMoSe/CFC (0.5 cm × 1 cm) as the working electrode, respectively. 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.[1] In 0.5 M H_2SO_4, $E_{RHE} = E_{Ag/AgCl} + 0.211\ V$. All the potentials reported in our manuscript were against RHE.

The electrochemical stability of different catalysts was evaluated by CV from +0.10 V to −0.4V vs. RHE with a scan rate of 50 mV s^{-1}, cycling the electrode 3000 times. Amperometric i-t curve was also obtained at a constant potential of -0.11 V to evaluate the stability. The double-layer capacitances (C_{dl}) were estimated by CV in the 0.1-0.2 V vs. RHE region at various scan rates (20-200 mV s^{-1}) to evaluate the effective surface area of various catalysts.

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

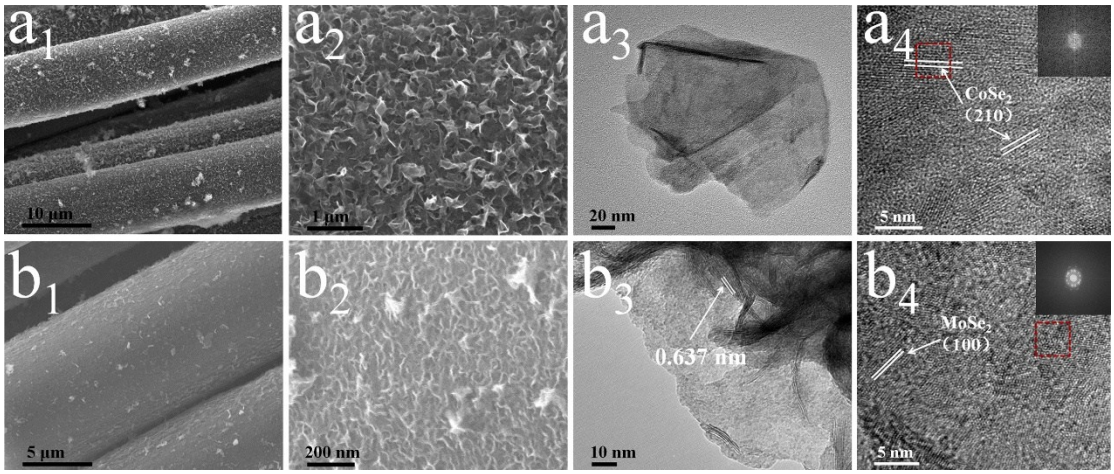

Fig. S1 (a_1) Low-magnification and (a_2) high-magnification SEM image of $CoSe_2$/CFC. (a_3) TEM image and (a_4) HRTEM image of $CoSe_2$. (b_1) Low-magnification and (b_2) high-magnification SEM image of P-$MoSe_2$/CFC. (b_3) TEM image and (b_4) HRTEM image of P-$MoSe_2$. FFT images were selected from the red box part in Fig. a_4 and b_4.

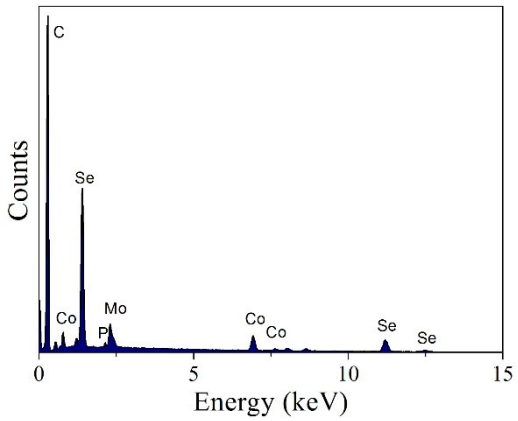

Fig. S2 Energy dispersive X-ray (EDX) spectra of P-Co_2Mo_3Se/CFC.

Table S1. The atomic percentage (at.%) of Co, Mo, Se and P elements in different catalysts obtained from ICP-OES.

Catalyst	Co	Mo	Se	P	Co:Mo
$CoSe_2$/CFC	0.47	---	1	---	---
P-Co_4Mo_1Se/CFC	0.41	0.11	1	0.0082	3.72:1
P-Co_3Mo_2Se/CFC	0.29	0.19	1	0.014	1.53:1
P-Co_1Mo_1Se/CFC	0.24	0.25	1	0.019	1:1
P-Co_2Mo_3Se/CFC	0.19	0.30	1	0.023	1:1.58
P-Co_1Mo_4Se/CFC	0.094	0.39	1	0.031	1:4.15
P-$MoSe_2$/CFC	---	0.49	1	0.040	---

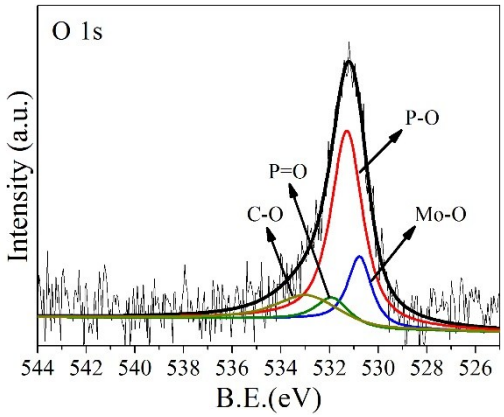

Fig. S3 O1s XPS spectra in P-CoMoSe/CFC.

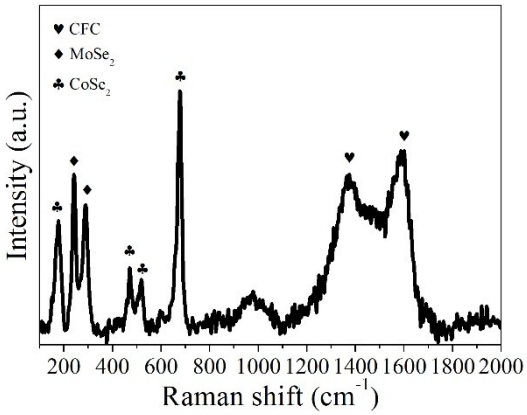

Fig. S4. Raman spectra of P-CoMoSe/CFC.

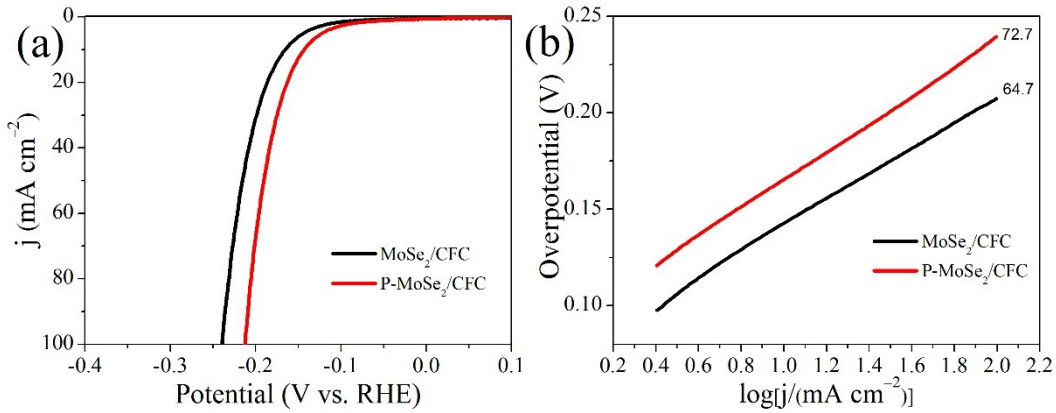

Fig. S5 (a) Polarization curves, (b) Tafel plots of $MoSe_2$/CFC and P-$MoSe_2$/CFC.

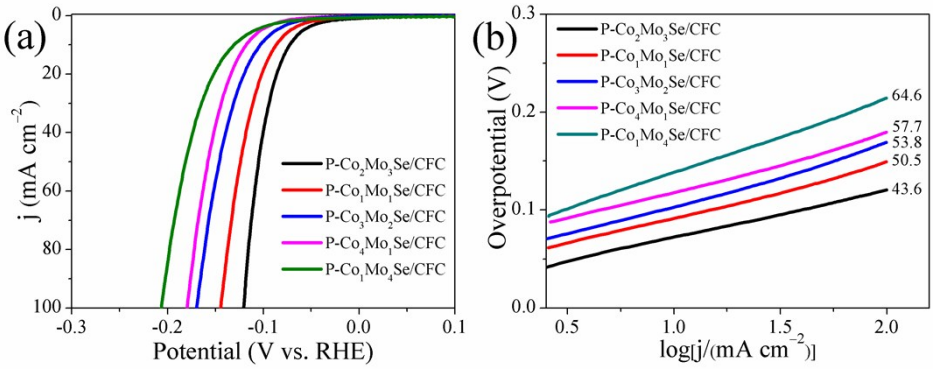

Fig. S6 (a) Polarization curves, (b) Tafel plots of P-CoMoSe/CFC at different Co:Mo ratios.

Table S2. Electrochemical parameters of different catalysts.

Catalyst	Tafel slopes [mV dec^{-1}]	$\eta_{j=10}$ [mV]	$\eta_{j=100}$ [mV]
$MoS_2/CoSe_2$[2]	36	68	Not given
Ni/NiO/$CoSe_2$[3]	39	Not given (~88 mV by estimating)	Not given
$CoSe_2$ NP/CP[4]	40	137	181
$Mn_{0.05}Co_{0.95}Se_2$[5]	36	195	Not given (233 mV~j_{80})
MoCN[6]	46	140	Not given
$CoS_2/CoSe_2$[7]	33.6	80	155
P-WN/rGO[8]	54	85	Not given (~280 mV by estimating)
$MoSe_2$/RGO[9]	69	115	Not given
SnO_2@$MoSe_2$[10]	51	174	Not given
$CoSe_2$[11]	40	160	Not given
P-Co_2Mo_3Se/CFC (current work)	43.6	71	120

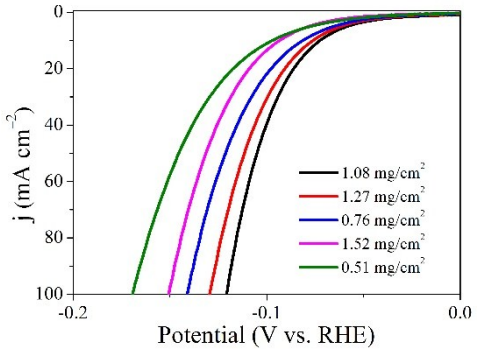

Fig. S7 Polarization curves of P-Co_2Mo_3Se/CFC with different loading mass.

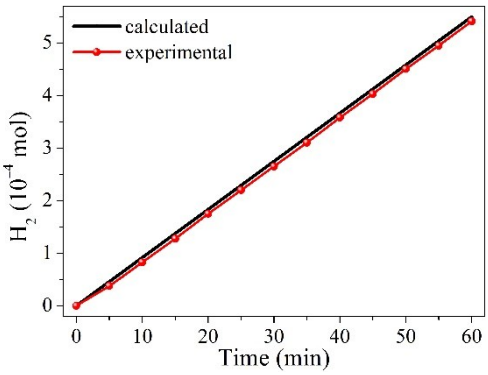

Fig. S8 The amount of H_2 theoretically calculated and experimentally measured versus time for P-Co_2Mo_3Se/CFC at overpotential of 200 mV for 60 min.

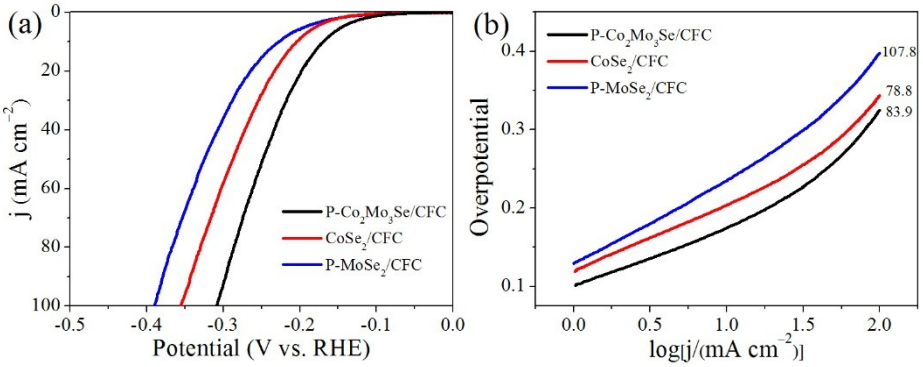

Fig. S9 (a) Polarization curves, (b) Tafel plots of P-$MoSe_2$/CFC, $CoSe_2$/CFC and P-Co_2Mo_3Se/CFC in 1M KOH.

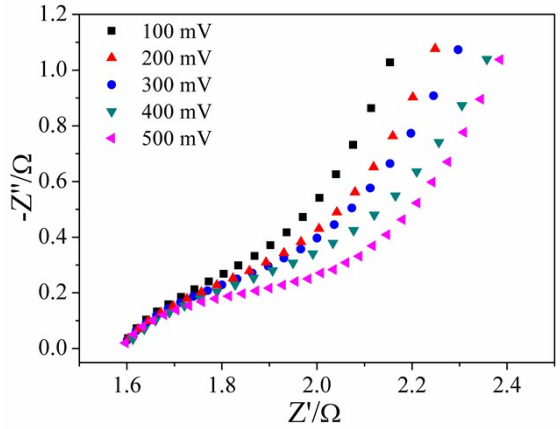

Fig. S10 Nyquist plots of P-Co_2Mo_3Se/CFC at various overpotentials.

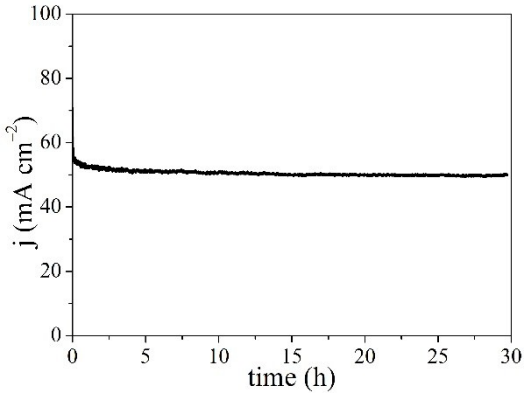

Fig. S11 Current versus time during the long term (30 h) with a constant potential (− 0.11 V vs. RHE) of P-Co_2Mo_3Se/CFC.

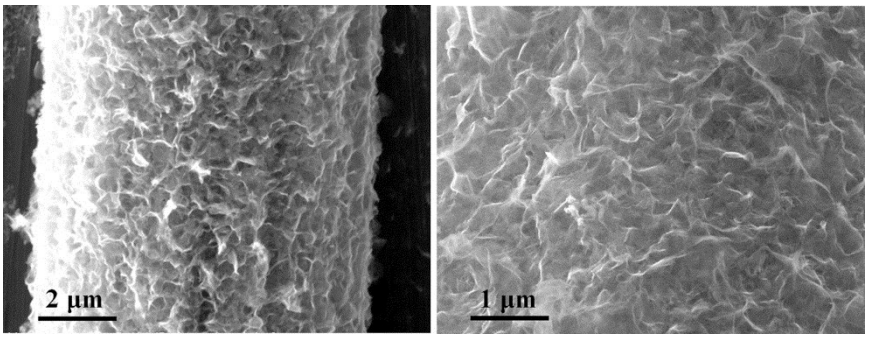

Fig. S12 SEM image of P-Co_2Mo_3Se/CFC after the stability test (30 h).

References

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