Supplementary Information

Potassium electrochemical optimization of MoS_2 catalytic hydrogen evolution reaction performance

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Experimental section

Synthesis of the MoS_2@pCNF films. Polyvinyl alcohol (PVA) was used as the carbon precursor and mixed with polytetrafluoroethylene (PTFE) to prepare primary fibers of PTFE/PVA through electrospinning. The procedure is as follows: First, 1.412 g of PVA was added to 10 mL of deionized water and stirred at 60°C for 5 hours. Then, 5.491 g of PTFE was added to the above mixture and stirred at 60 °C for 12 hours until a homogeneous solution was obtained. The primary PTFE/PVA fibers were then produced by electrospinning under an electric field of 18 kV. The primary fibers were heated to 260 °C at a rate of 5 °C/min and thermally treated for 2 hours to obtain pre-oxidized carbon nanofibers. Finally, the pCNF films were prepared by carbonizing the fibers in an argon atmosphere at a temperature of 800°C for 2 hours, with a heating rate of 5 °C/min. Ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) was used as the source of Mo, and thiourea ($CS(NH)_2$) was used as the source of S to grow MoS_2 in the pores of the pCNF films using a hydrothermal method. Initially, 30 mg of CNF film was added to 10 mL of an aqueous solution containing 60 mg of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 1.5 g of $CS(NH)_2$ until the solution became bright in color. Thiourea also played a role in reducing Mo (VI) to Mo (IV). The solution was then transferred to a stainless steel reactor lined with PTFE and subjected to hydrothermal treatment at 220°C for 24 hours to obtain the MoS_2@pCNF film.

Synthesis of the C@MoS_2@pCNF films. The MoS_2@pCNF composite material was immersed in 100 mL of Tris buffer (pH = 8.0), and 200 mg of dopamine hydrochloride was added to the solution. The mixture was stirred for 6 hours to obtain the PDA@MoS_2@pCNF precursor material. After washing the precursor material several times with deionized water, it was dried at 60 °C. The dried precursor was then heated in an argon atmosphere at a rate of 5 °C/min to 550 °C and thermally treated for 3.5 hours to obtain the C@MoS_2@pCNF film.

Synthesis of the C@MoS_x@pCNF films. A button-type potassium-ion battery was assembled for the electrochemical intercalation regulation of potassium. The prepared C@MoS_2@pCNF films were cut into small pieces with an average mass density of approximately 1.5 mg cm^{-2}, which served as the cathode. Potassium foil was used as the anode, and 1.0 M KFSI/EC:DMC (1:1, v/v) was used as the electrolyte. The cell was assembled in an argon-filled glove box (H_2O, O_2<0.01 ppm).

A constant current cycling charge-discharge process was performed in the potential range of 0.01 to 3 V (vs. K^+/K) at a current density of 100 mA g^{-1} to achieve the electrochemical regulation of potassium. After the charge-discharge process was completed, the cathode was removed from the battery and washed in acetone, anhydrous ethanol, and deionized water for 2 minutes each to remove residual electrolyte. Finally, the cathode was dried in a vacuum oven for 5 minutes, resulting in the C@MoS_x@pCNF film.

Physical characterization. XRD analysis is a characterization technique used for the qualitative and quantitative analysis of material phases. X-ray powder diffraction (XRD) studies of the sample were conducted using a D8 Advance A25 X-ray diffractometer with Cu Kα radiation, scanning in the range of $2\theta = 10 \sim 80°$. The scanning electron microscope (SEM, Hitachi S-4800) is an important tool for observing the microscopic morphology of surfaces of materials. The transmission electron microscope (TEM, FEI Talos F200X) is capable of characterizing the dimensions, crystallinity, phase structure, and growth direction of thin materials. Energy-dispersive X-ray spectroscopy (EDS) is obtained using a spectrometer in conjunction with the SEM and can analyze the composition and content of materials at micro-regions. X-ray photoelectron spectroscopy (XPS) was recorded using a spectrometer (Axis Supra) to characterize the surface composition. The type and content of elements can be determined based on the peak positions, intensities, and shifts in the X-ray photoelectron spectrum. The contact angle measurements were conducted using the DSA20 instrument from KRUSS, Germany.

Electrochemical measurements. The electrochemical activity for the hydrogen evolution reaction (HER) of C@MoS_2@pCNF films was evaluated using a three-electrode system on a CS310H electrochemical workstation. To ensure testing accuracy, the experiments were conducted at room temperature in H_2-saturated 0.5 M H_2SO_4 electrolyte. The self-supported electrodes, either C@MoS_2@pCNF or C@MoS_x@pCNF, were used as the working electrode and were clamped securely with a stainless steel electrode during testing. A mixture of 10 mg MoS_2 powder and 20 μL Nafion was uniformly dispersed in 1 mL of a water-ethanol mixed solution (v/v

= 1:1), and 40 μL of the precursor solution was drop-cast onto hydrophilic carbon cloth, which was then dried at 70 °C to obtain the MoS_2 catalytic electrode as a control. A platinum foil was used as the counter electrode, and an Ag/AgCl (1 M KCl) electrode was used as the reference electrode. All potentials were calibrated against the reversible hydrogen electrode (RHE), and according to the Nernst equation: $E_{Ag/AgCl\ (1\ M\ KCl)} = E_{RHE} + 0.22$ V. Linear sweep voltammetry (LSV) is a commonly used method for investigating electrochemical activity. The principle involves varying the voltage linearly with time at a certain rate, resulting in a curve that illustrates the relationship between current and voltage. When the voltage scan rate is fast, a polarization curve is obtained; when the rate is slower, a voltammogram is produced. In this study, the polarization curve was acquired by linear potential scanning at a rate of 10 mV s^{-1} from –1.1 to 0.1 V (vs. RHE) and is used to determine the overpotential required to initiate the hydrogen evolution reaction (HER). The Tafel curve can be derived from the polarization curve through mathematical conversion and is used to elucidate the kinetics of the catalytic reaction. Current-time stability tests are conducted by recording the variation of current with time at a fixed electrochemical potential. Electrochemical impedance spectroscopy (EIS) tests were conducted at a potential of −0.2 V (vs. RHE) with an alternating current signal amplitude of 10 mV. The frequency range was from 100 kHz to 0.1 Hz.

Catalysts	Overpotential (mV vs. RHE) at 10 mA cm $^{-2}$	Tafel slo pe (mV/ dec^{-1})	Reference
C@MoS$_x$@pCNF	51	77	This work
EG-MoS$_2$@CNTs	188	87	Int. J. Hydrogen Energy 46, 6419-6426 (2021)
1T/2H mixed-phase MoS$_2$	127	86	J. Electroanal. Chem. 925, 116905 (2022)
MoS$_2$-NTA/Ti$_3$C$_2$	216	105	Small 18, 2105129 (2022)
Ti$_3$C$_2$T$_X$/MoS$_2$	139	78	J. Mater. Chem. A 9, 922-927 (2021)
H–MoS$_2$NS/MWCNT	284	97	Int. J. Hydrogen Energy 45, 16489-16499 (2020)
MoS$_2$@FePS$_3$	168	127	Appl. Surf. Sci. 525, 146623 (2020)
Ag/MoS$_2$	440	131	Mater. Lett. 382, 137866 (2024)
Cu-Pd-MoS$_2$	93	77	Appl. Surf. Sci. 529, 147117 (2020)
Ni-SAs/MoS$_2$	161	81	Adv. Funct. Mater. 28, 1807086 (20 18)
TCO/MoS$_2$	269	82	ACS Sustainable Chem. Eng. 11, 14528-14537 (2023)

Table S1. A comparison of the HER performances of recently reported electrocatalysts in acid electrolytes.

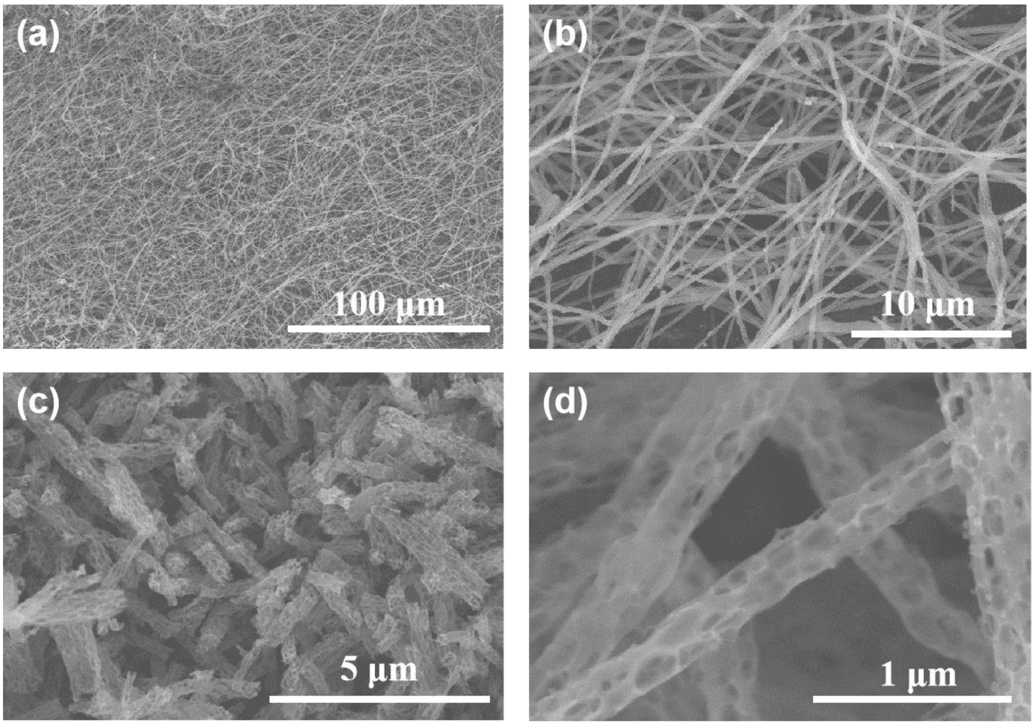

Fig. S1. (a-d) SEM images of pCNF films at different magnifications.

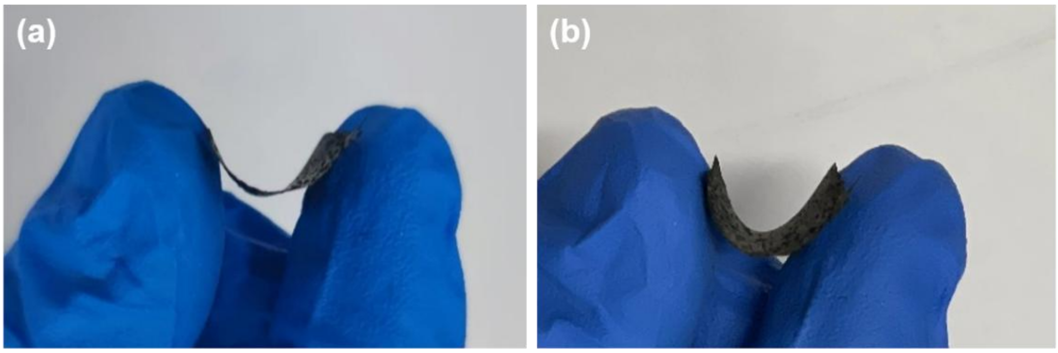

Fig. S2. Flexible characterization of (a) MoS_2@pCNF films and (b) C@MoS_2@pCNF films.

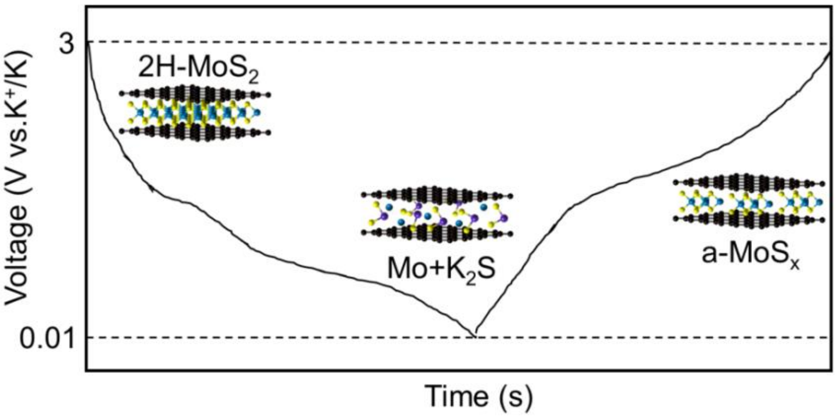

Fig. S3. Charge-discharge curves of potassium electrochemical intercalation and a simplified model of the MoS_2 crystal structure.

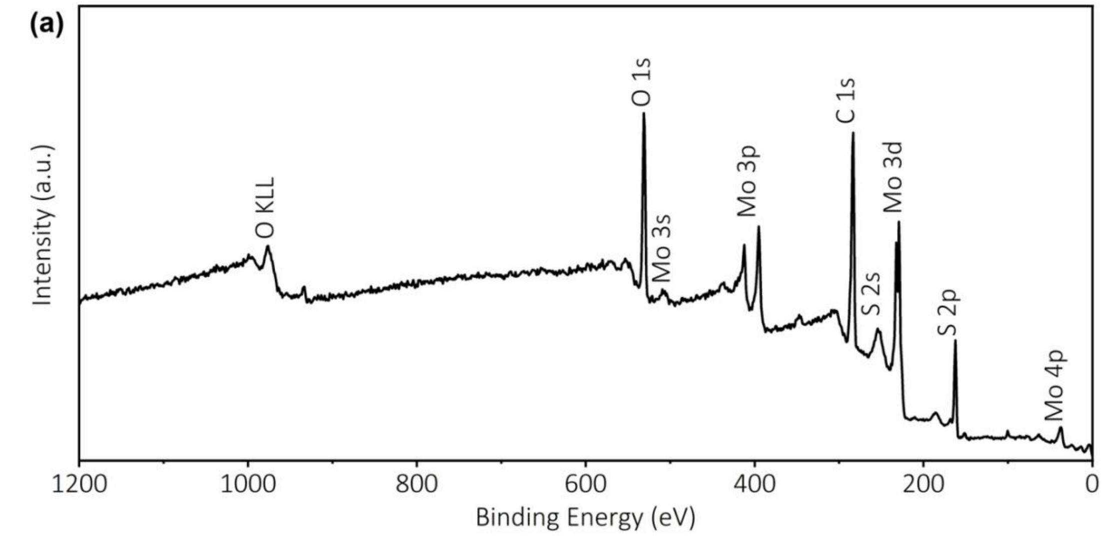

Fig. S4. XPS full spectrum of C@MoS_2@pCNF thin films.

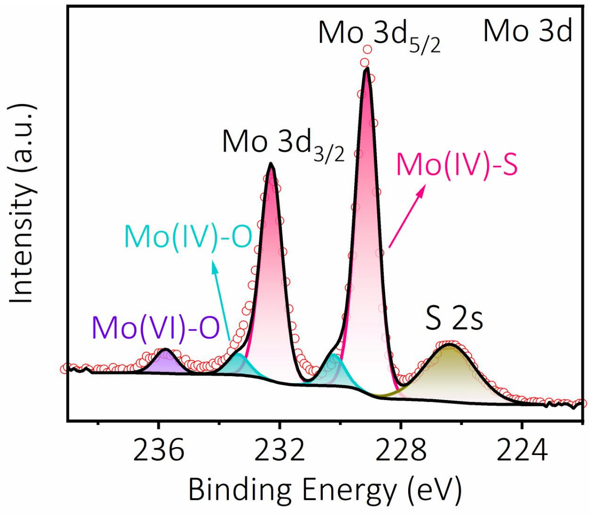

Fig. S5. XPS spectra of Mo 3d for C@MoS$_2$@pCNF.

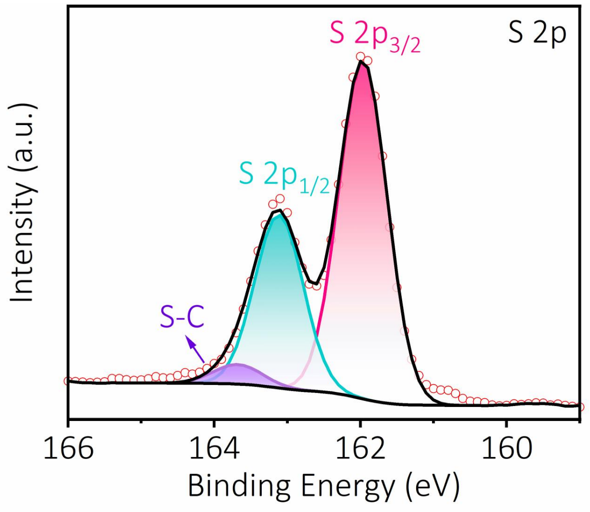

Fig. S6. XPS spectra of S 2p for C@MoS$_2$@pCNF.

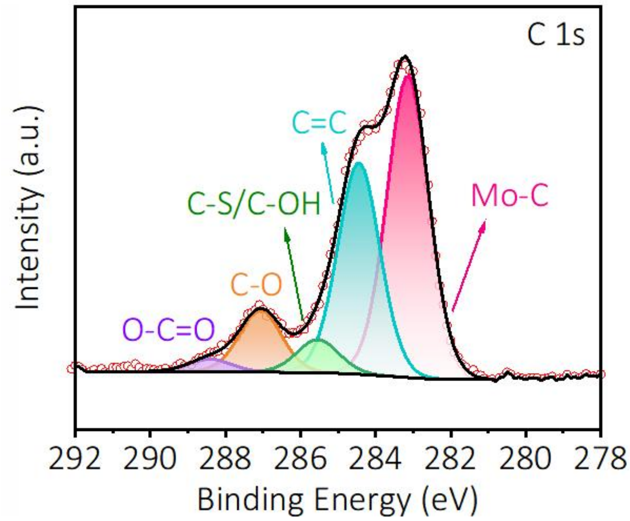

Fig. S7. XPS spectra of C 1s for C@MoS$_2$@pCNF.

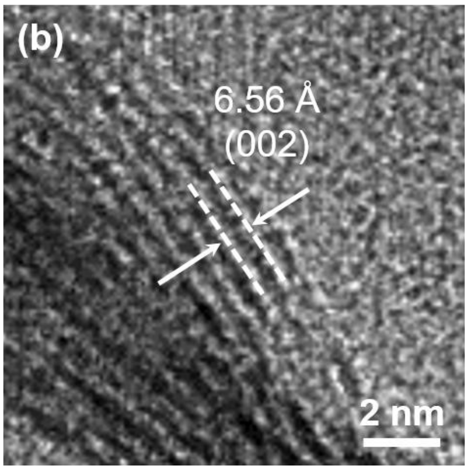

Fig. S8. HRTEM images of MoS$_2$ nanosheet edges.

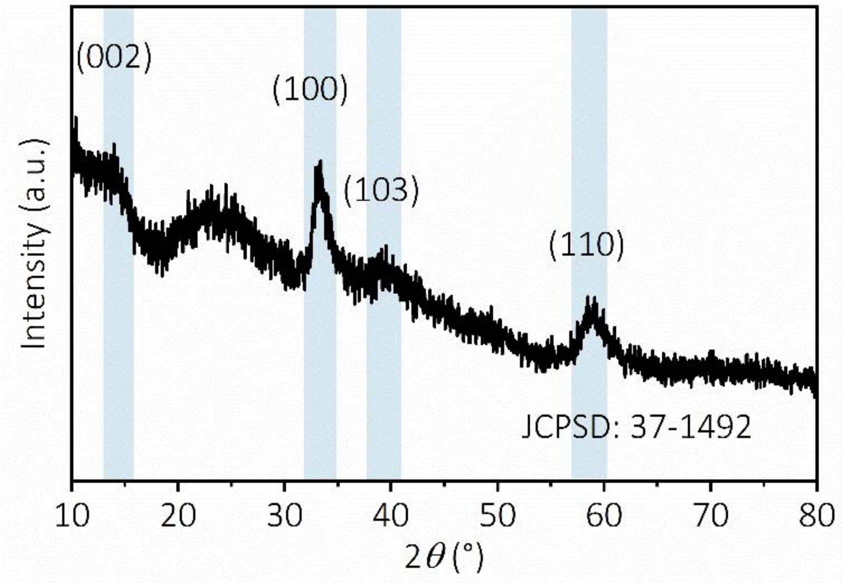

Fig. S9. XRD of C@MoS$_2$@pCNF films.

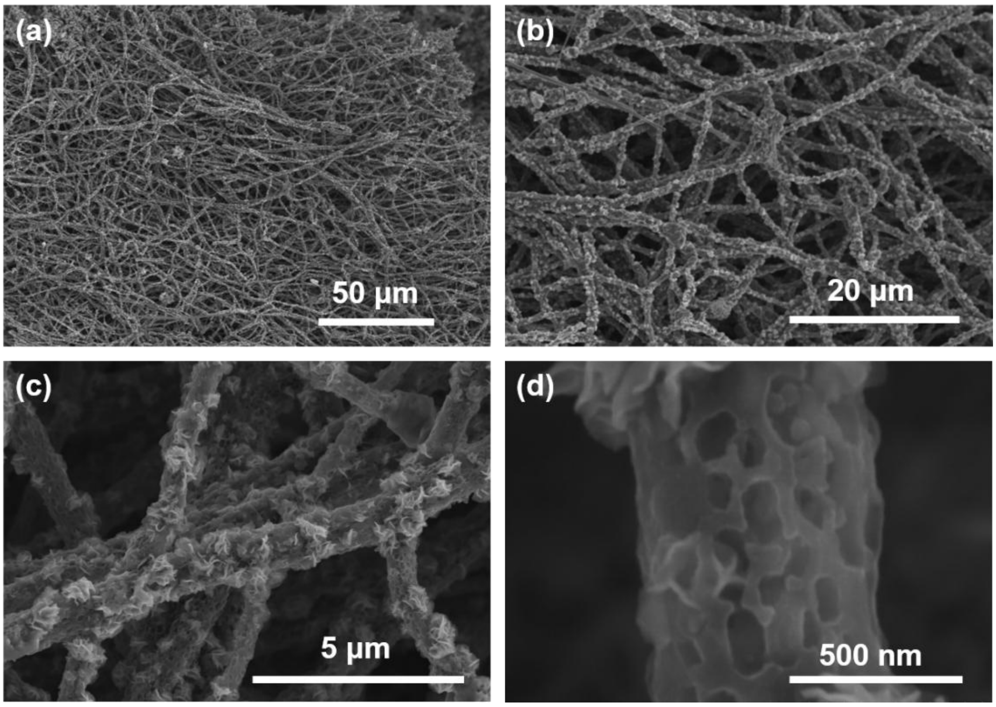

Fig. S10. (a-d) SEM images of C@MoS$_x$@pCNF films at different magnifications

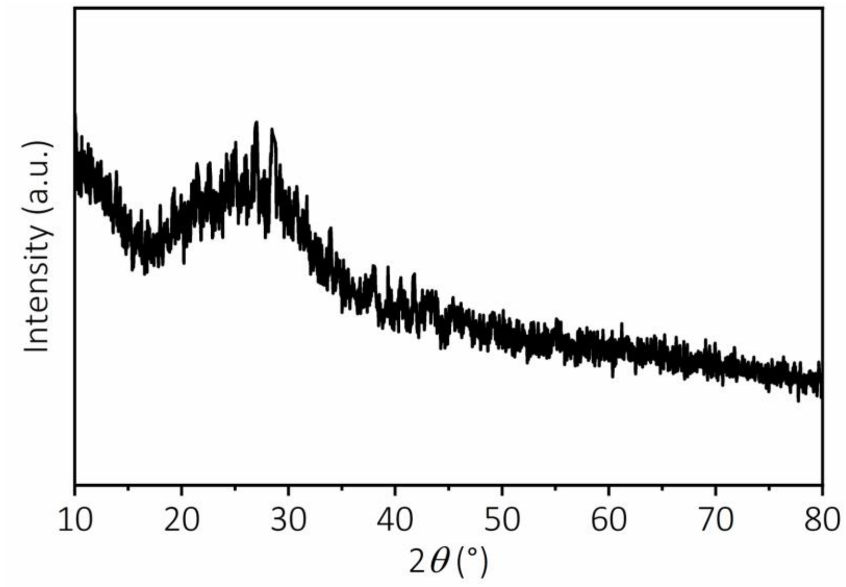

Fig. S11. XRD of C@MoS$_x$@pCNF films.

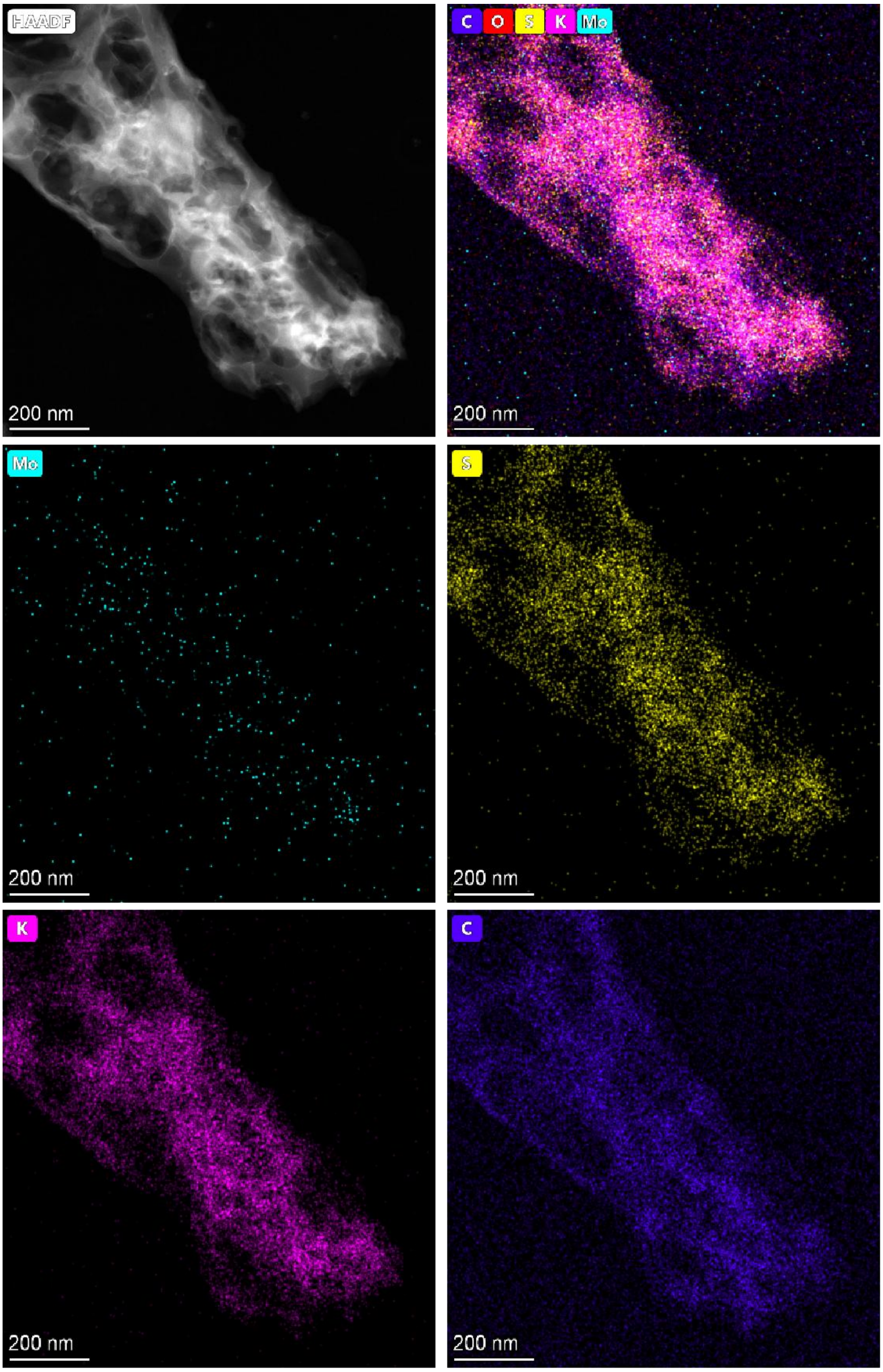

Fig. S12. HAADF image and corresponding mapping images for Mo, S, K and C elements of C@MoS$_x$@pCNF films.

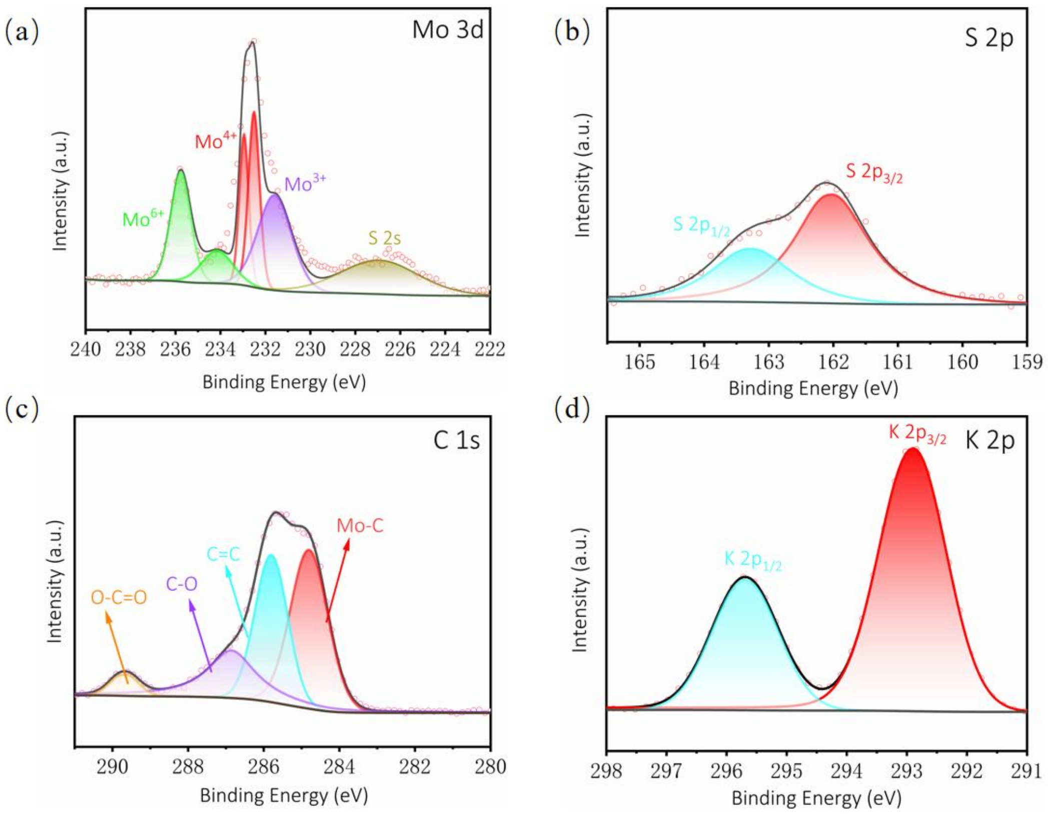

Fig. S13. XPS spectra of (a) Mo 3d, (b) S 2p, (c) C 1s and (d) K 2p for C@MoS_x@pCNF.

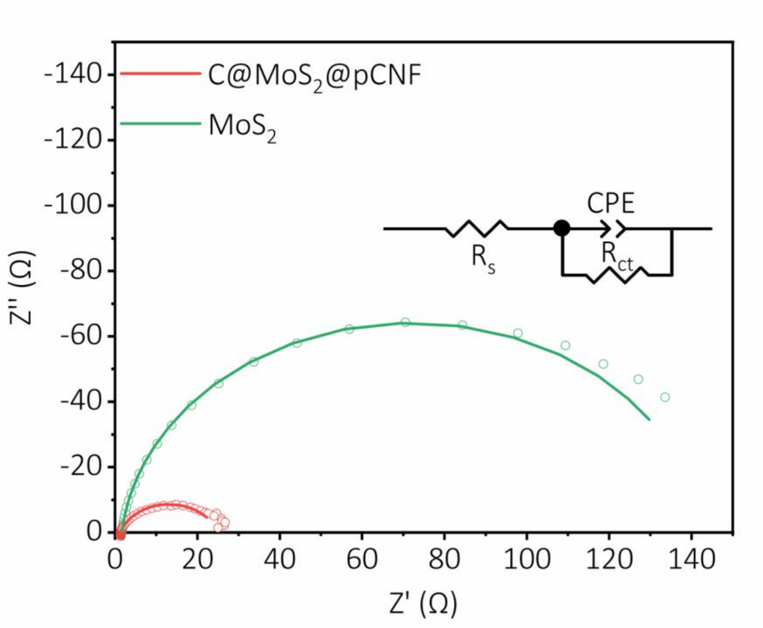

Fig. S14. Nyquist curves for C@MoS_2@pCNF and pure MoS_2.

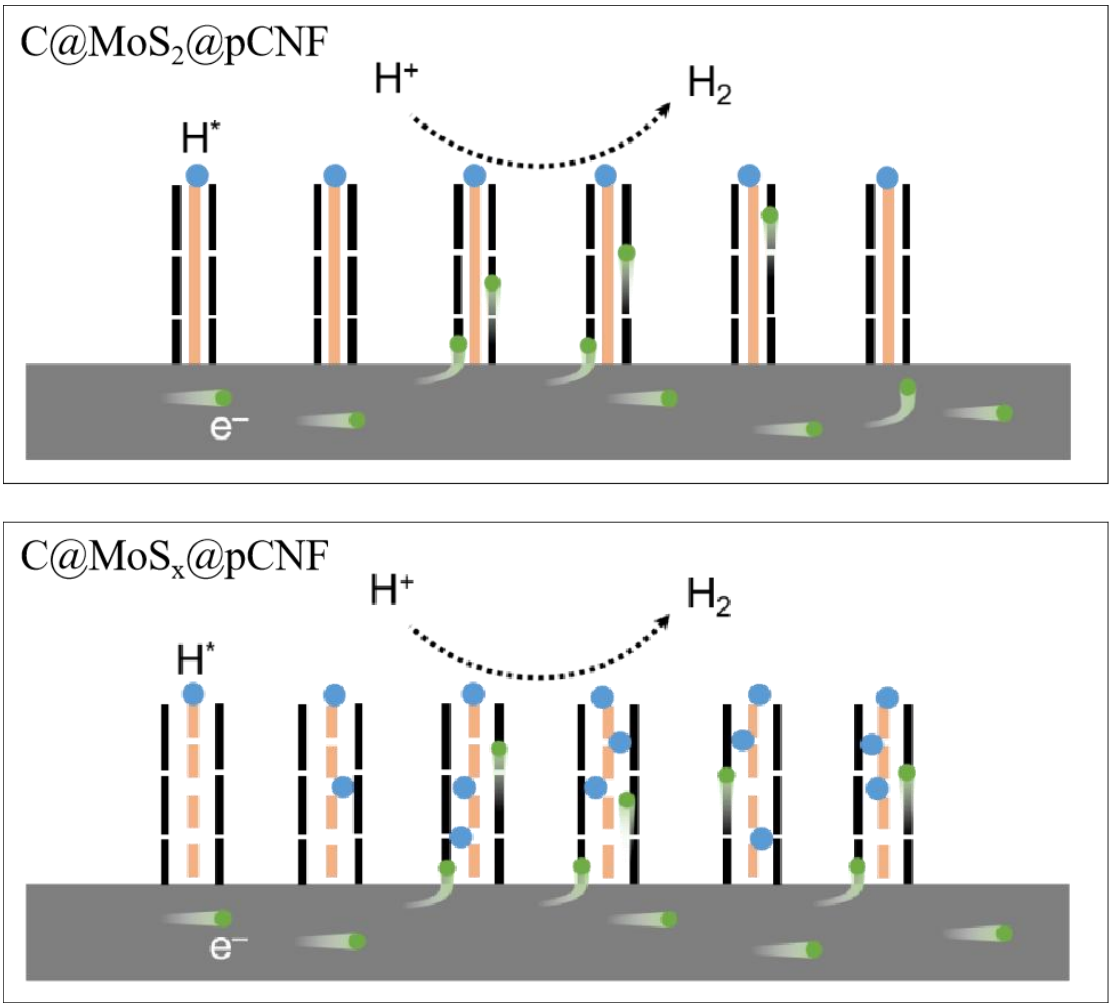

Fig. S15. A simplified model for the hydrogen evolution reaction (HER) mechanism of C@MoS$_2$@pCNF and C@MoS$_x$@pCNF.