Electronic Supplementary Information

MoS_2 nanosheet/Mo_2C-embedded N-doped carbon nanotubes: Synthesis and electrocatalytic hydrogen evolution performance

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Experimental sections

Fabrication of MoO_3/PANI hybrids

0.15 g of α–MoO_3 nanorods was dispersed in 100 mL of 1 mol L^{-1} HCl solution by sonication treatment and then the mixture was cooled down to 0 °C under stirring. 0.2 mL of aniline was dissolved in 100 mL of 1 mol L^{-1} HCl solution, and then transferred to the solution of ammonium persulfate (0.25 g) dissolved in 100 mL of 1 mol L^{-1} HCl solution in the beaker. The mixture solution above was cooled down to 0 °C, then transferred to the suspension and kept at the temperature for 4 h under stirring. The precipitate was washed by distilled water and ethanol, and then dried at 40 °C for 24 h.

Fabrication of MoO_2/Mo_2C-NCNTs

After the MoO_3/PANI hybrids were thermally treated at 700°C for 2 h at Ar gas flow, the MoO_2/Mo_2C-NCNTs were obtained.

Fabrication of MoS_2/Mo_2C-NCNTs

50 mg of the as-obtained MoO_2/Mo_2C-NCNTs was dispersed in 30 mL of 0.15 mol L^{-1} thiourea solution. The mixture was sonicated for 10 min and stirred for 30 min at room temperature, and then was transferred to a 50 mL Teflon-lined stainless steel autoclave and treated in an oven at 200 °C for 48 h. The resulting precipitate was collected and washed by deionized water and ethanol, and then dried at 40 °C for 24 h.

Fabrication of MoS_2 nanoflowers

50 mg of α–MoO_3 nanorods was dispersed in 30 mL of 0.15 mol L^{-1} thiourea solution. The mixture was sonicated for 10 min and stirred for 30 min at room temperature, and then was transferred to a 50 mL Teflon-lined stainless steel autoclave and treated in an oven at 200 °C for 48 h. The resulting precipitate was collected and washed by deionized water and ethanol, and then dried at 40 °C for 24 h.

Structural Characterization

The morphology and size of the synthesized 3D architectures were characterized by

scanning electron microscope [HSD/SU70] and an FEI Tecnai-F20 transmission electron microscope equipped with a Gatan imaging filter (GIF). The crystal structure of the sample was determined by X-ray diffraction (XRD) [D/max 2550 V, Cu Ka radiation]. XPS measurements were carried out using a spectrometer with Al Kα radiation (K-Alpha, Thermo Fisher Scientific Co.). The binding energy was calibrated with the C 1s position of contaminant carbon in the vacuum chamber of the XPS instrument (284.8 eV).

Electrochemical measurements

Electrochemical measurements were performed in a three-electrode system at an electrochemical station (CHI660D). The three-electrode configuration using an Ag/AgCl (KCl saturated) electrode as the reference electrode, a graphite rod as the counter electrode, and the carbon paper coated with catalyst was used as the working electrod. The working electrode was fabricated as follow: the catalyst was dispersed in N-methyl-2-pyrrolidone (NMP) solvent containing 7.5 wt% polyvinylidene fluoride (PVDF) under sonication, in which the weight ratio of the catalyst to PVDF is 8:1. Then the slurry was coated onto a piece of carbon paper (length×diameter×thickness = 6 cm×1 cm×0.03 cm). The loading density of the catalyst was ~ 2 mg cm^{-2}. Linear sweep voltammetry with scan rate of 5 mV s^{-1} was conducted in 0.5 M H_2SO_4 (deaerated by N_2). For a Tafel plot, the linear portion is fit to the Tafel equation. All data have been corrected for a small ohmic drop based on impedance spectroscopy. In 0.5 M H_2SO_4, $E_{(RHE)} = E_{(SCE)} + 0.21$ V. All the potentials reported in our manuscript were calibrated to a reversible hydrogen electrode (RHE).

Table S1. Comparisons of HER performances among different MoS_2 and Mo_2C-based catalysts

Catalyst type	Loading density [mg cm^{-2}]	Tafel slope [mV dec^{-1}]	Exchange current j_0 [μA cm^{-2}]	j [mA cm^{-2}]at η=150 mV	j [mA cm^{-2}] at η=200 mV	j [mA cm^{-2}]at η=300 mV	Refs
Double-gyroid MoS_2	0.06×10^{-3}	50	—	1	4	—	3 b)
Oxygen-Incorporated MoS_2	0.285	55	12.6	4	19	127	3 g)
Rich-defect MoS_2	0.285	50	9	0	13	70	3 f)
MoS_x/3D Graphene	5	43	—	13	42	140	6 a)
Mo_2C/CNT	2.0	55.2	14	9.8	—	—	12
Mo_2C/XC	2.0	59.4	8.1	3.2	~7	—	12
Mo_2C/NWs	0.357	55.8	—	~1.5	10.2	~65	13
Mo_2C/NSs	0.357	64.5	—	~1	5.3	~30	13
Mo_2C	0.8	54	3.8	2	14	—	7 a)
MoS_2/Mo_2C-NCNTs	2.0	69	21	5.7	15.4	280	This work
Bulk MoS_2	2.0	120	—	1.4	3	21	This work
MoS_2 nanoflowers	3.0	113	—	10.7	16.9	123	This work

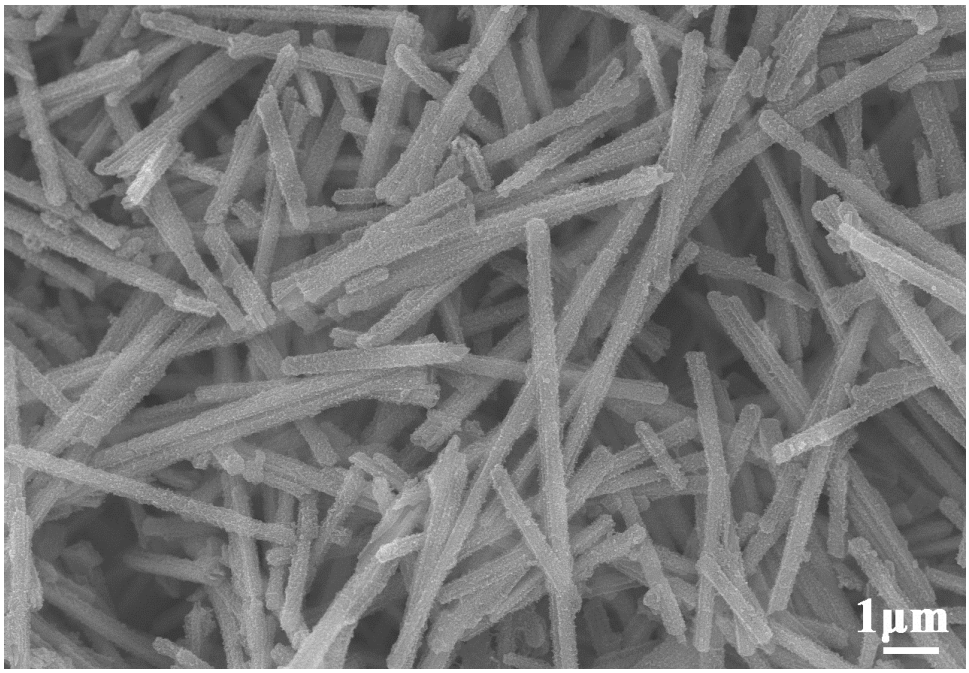

Figure S1. SEM images of MoO_3/PANI composite.

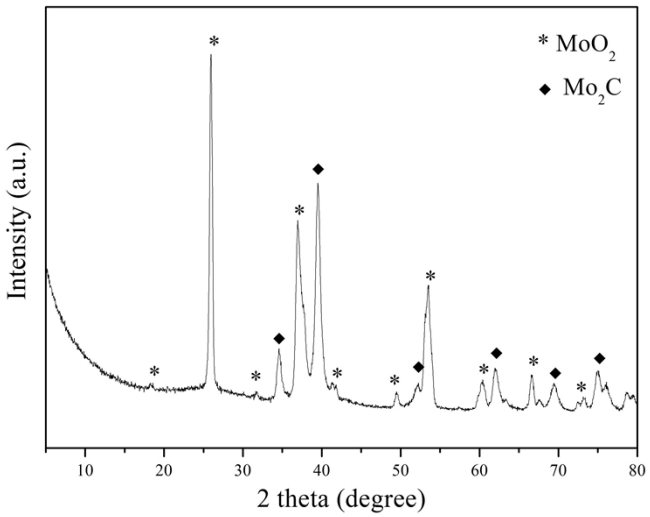

Figure S2. XRD pattern of MoO_2/Mo_2C-NCNTs.

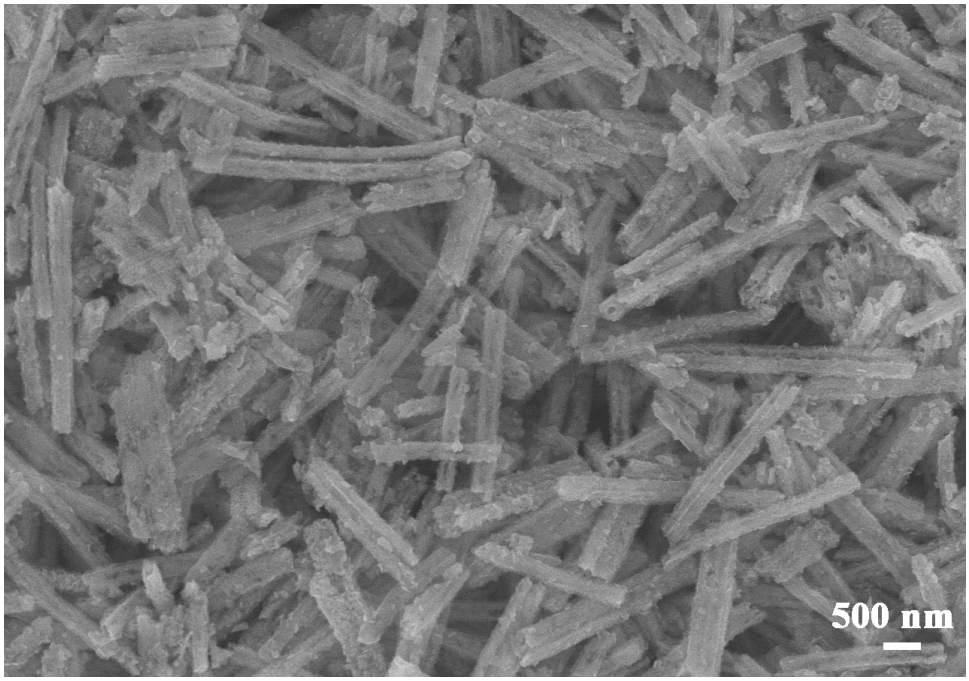

Figure S3. SEM image of MoO_2/Mo_2C-NCNTs.

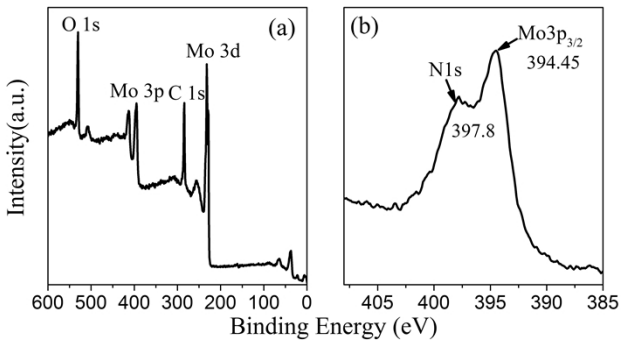

Figure S4. XPS spectra of MoO_2/Mo_2C-NCNTs. (a) The survey, and (b) N1s spectra.

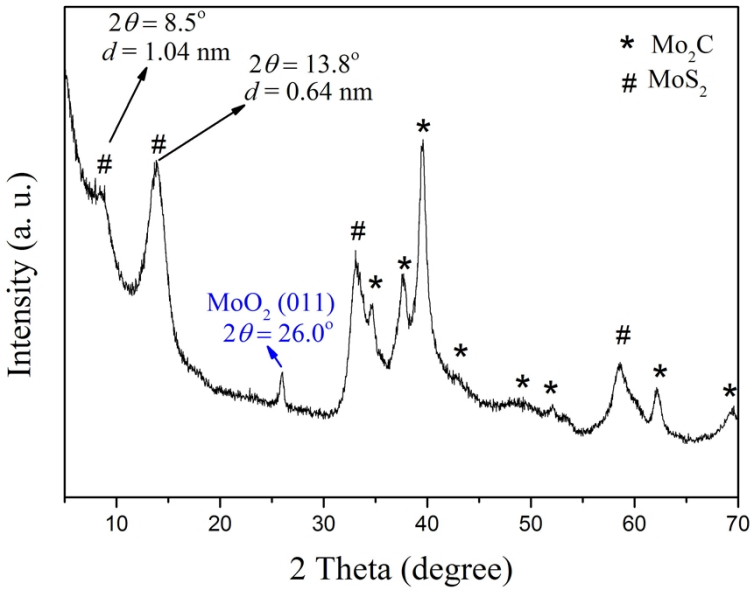

Figure S5. XRD pattern of MoS_2/Mo_2C-NCNTs.

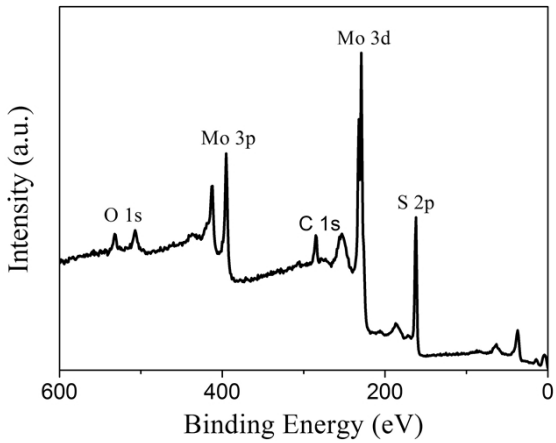

Figure S6. The survey XPS spectrum of MoS_2/Mo_2C-NCNTs

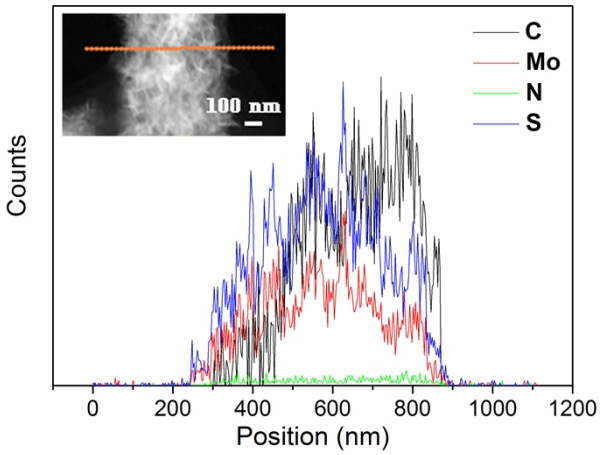

Figure S7. EELS spectrum for MoS_2/Mo_2C-NCNTs

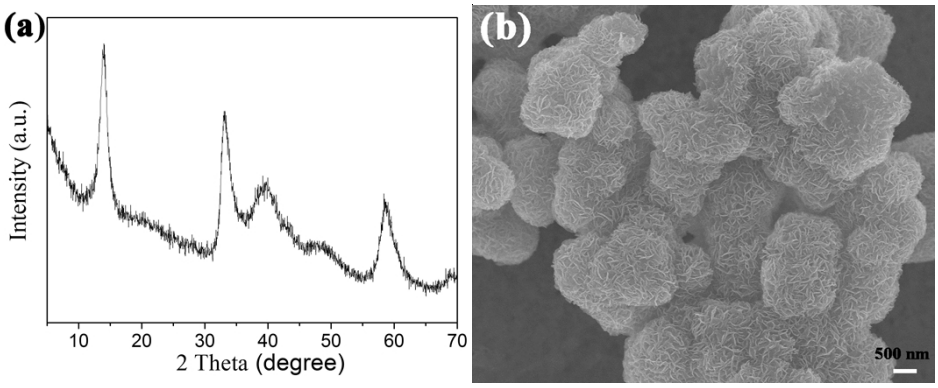

Figure S8. (a) XRD and (b) SEM image of MoS_2 nanoflowers.

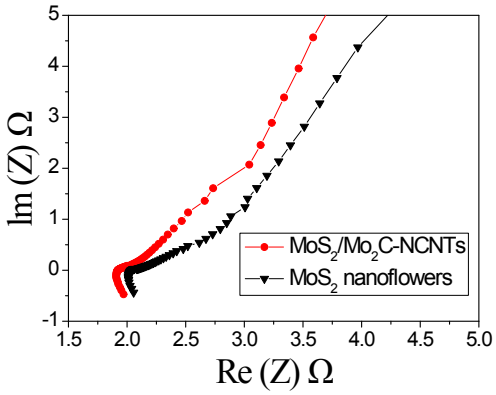

Figure S9. ESI spectra of MoS_2/Mo_2C-NCNTs and MoS_2 nanoflowers.