S-rich single-layered MoS_2 nanoplates within in N doped carbon nanofibers: efficient electrocatalysts for hydrogen evolution reaction

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Experimental section

Preparation of PAN-$(NH_4)_2MoS_4$ precursor nanofibers

3.000 g polyacrylonitrile (PAN) powder was dissolved in 22 mL DMF under magnetic stirring at 65 ^{o}C to get a homogenous solution with a mass ration of 12 wt%. Then, 0.1000 g $(NH_4)_2MoS_4$ were added into the PAN/DMF solution and then transferred into a syringe with a stainless copper needle at the tip. The needle was connected to a high voltage power supply. The applied voltage was 12 kV, the needle to collector distance was 12 cm and the flow rate of the solution was 0.6 mL/h. Then the homogeneous PANMo nanofibers were successfully prepared. All experiments were performed at room temperature.

Synthesis of S-rich single-layered MoS_2 nanoplates embedded in N doped carbon nanofibers

In a typical procedure, the as-prepared electrospun PANMo nanofibrous mats were placed into a home-built chemical vapor deposition (CVD) system for the following heat treatment. The PANAMo nanofibrous mats was firstly heated to 280 ^{o}C in air at a rate of 2 ^{o}C/min and maintained for 6 h for stabilization, then the as-prepared products were heated up to 400 ^{o}C at a rate of 2 ^{o}C/min under S vapor using Ar gas as the carrier (150 sccm) for S treatment. After the S vapor treatment, the as-prepared products were heated up to 1000 ^{o}C at a rate of 2 ^{o}C/min and maintained for 8 h for the graphitization. Then the products were cooled to room temperature under Ar atmosphere.

Synthesis of S-NCNFs and MoS_2 nanoplates embedded in N doped carbon nanofibers

The procedure is similar to the preparation of NCNFs S-rich MoS_2-NCNFs hybrid nanomaterials without the S vapor treatment at 400 ^{o}C for 2 h.

Electrochemical measurements

Electrochemical performance of the samples were performed on a glassy carbon electrode in 0.5 M H_2SO_4 solution using a typical three-electrode system in which a S-rich MoS2-NCNFs fibrous mats modified glassy carbon electrode (GCE, 3 mm in diameter), graphite electrode and saturated Ag/AgCl electrode served as the working, counter and reference electrodes, respectively. 4 mg of catalyst and 80 μl of 5 wt% Nafion solution were dispersed in 1 ml of 4:1 v/v water/ethanol by at least 30 min sonication to form a homogeneous ink. Then 15 μL of the catalyst ink was loaded onto a GCE. The HER activity was evaluated by linear sweep voltammetry conducted with Autolab potentiostat/galvanostat (Model PGSTAT302N) workstation with scan rate of 2 mVs^{-1}. The polarization curves were obtained after iR-compensation. In all measurements, we used Ag/AgCl electrode as the reference and the potential values are corrected to reverse hydrogen electrode (RHE). In 0.5 M H_2SO_4, E(RHE) = E (Ag/AgCl)+0.204 V. Prior to any electrochemical measurement, the electrolyte solution was purified with N2 for 1h to remove completely the oxygen, and stable polarization performance were recorded after 10 cycles.

Material Characterizations

Transmission electron microscopy (TEM) images were taken by a JSM-2100 transmission electron microscopy (JEOL, Japan) at an acceleration voltage of 200 kV. The high-angle annular dark field scanning TEM (HAADF-STEM) image, STEM mapping and line-scan energy dispersive X-ray spectroscopy (EDX) were recorded by a STEM (Tecnai G2 F30S-Twin, Philips-FEI) at an acceleration voltage of 300 kV. The number of layers and lateral dimensional of MoS_2 nanoplates (200 counts) were measured with Image-Pro Plus 6.2 software. Field emission scanning electron microscopy (FE-SEM) images were characterized by a JSM-6700F FE-SEM (JEOL, Japan) at an acceleration voltage of 3 kV. X-ray photoelectron spectra of the products were recorded using an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) K_α source (1486.6 eV). The aluminum K_α source was operated at 15 kV and 10 mA. X-ray diffraction (XRD) patterns were analyzed by a Bruker AXS D8 DISCOVER X-ray diffractometer with Cu K_α radiation (λ=1.5406 A$^\circ$) at a scanning rate of 0.02 2θ s^{-1} in the 2θ range of 10-80^{o}. Raman spectra of all the samples were recorded by a RenishawinVia Raman microscope (LabRAM HR800) using a 532 nm laser excitation source. The excitation light intensity in front of the objective was 10 mW with a spectral collection time of 1s. The integration time for our measurements was set to 10 s.

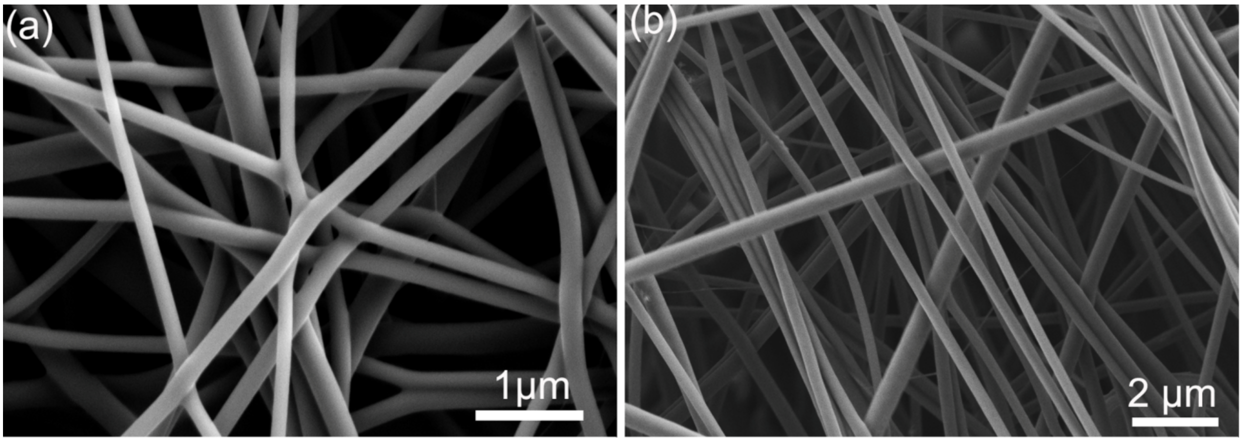

Fig. S1 FE-SEM image of the pure CNFs and MoS_2-CNFs.

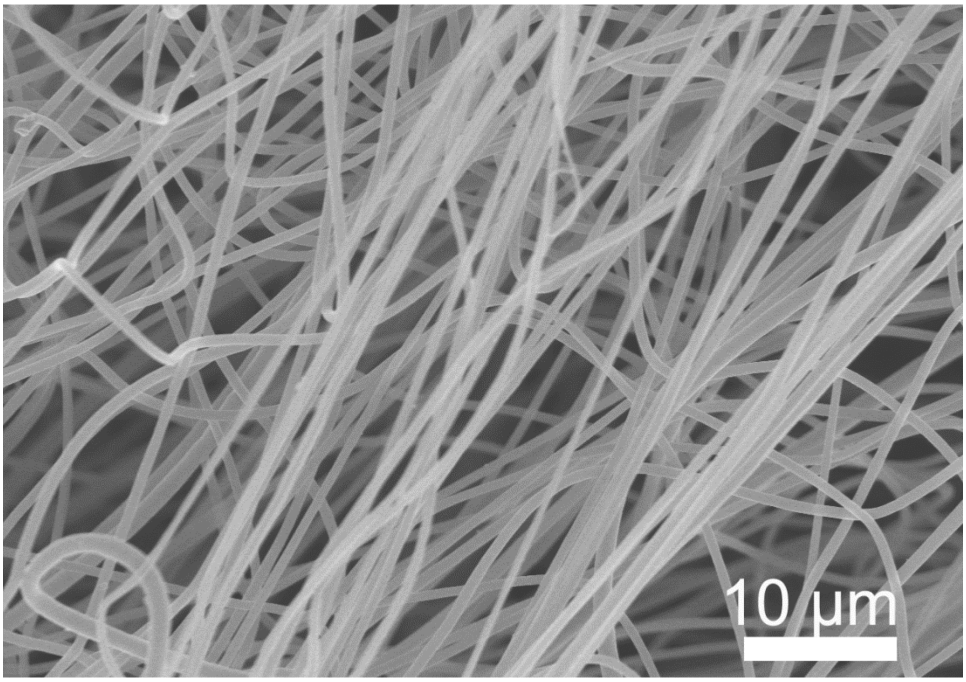

Fig. S2 FE-SEM image of the PAN-$(NH_4)_2MoS_4$ precursor (PANMo) nanofibers.

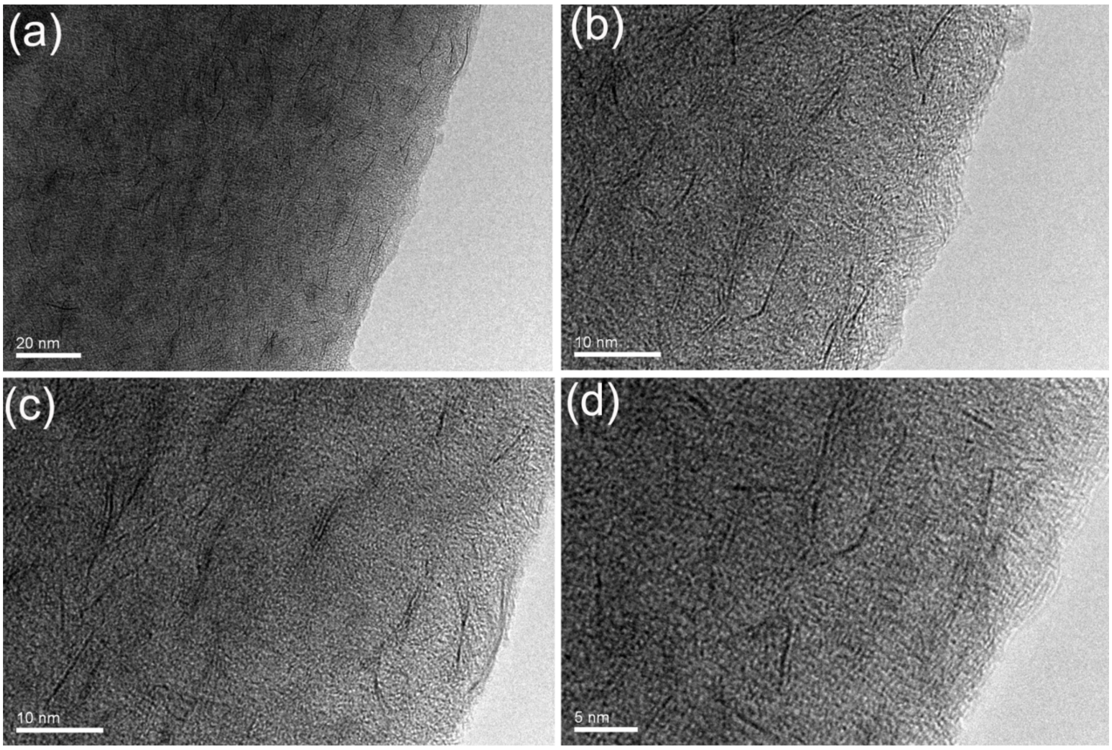

Fig. S3 TEM images of different S-rich MoS_2-NCNFs.

We investigated different S-rich MoS_2-NCNFs randomly, and the MoS_2 nanoplates were randomly distributed in NCNFs without any stacking layers. Most of the MoS_2 nanoplates exhibit one line and that means the nanoplates are single-layered.

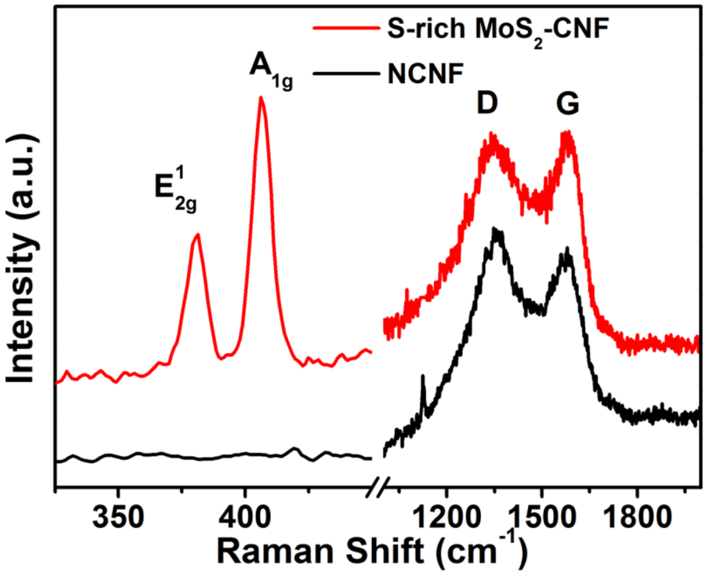

Fig. S4 Raman spectra of the pure NCNFs and S-rich MoS_2-NCNFs hybrid.

Fig. 2b displays the Raman spectra of NCNFs and S-rich MoS_2-NCNFs. The Raman spectrum of NCNFs exhibits a D peak at around 1360 cm^{-1} and a G peak 1576 cm^{-1}, which are consistent with previous reports.[4] For the S-rich MoS_2-NCNFs hybrid, two characteristic peaks of MoS_2 appear at 379 and 405 cm^{-1}, which belong to the E^1_{2g} and A_{1g} modes, respectively.[4,9]

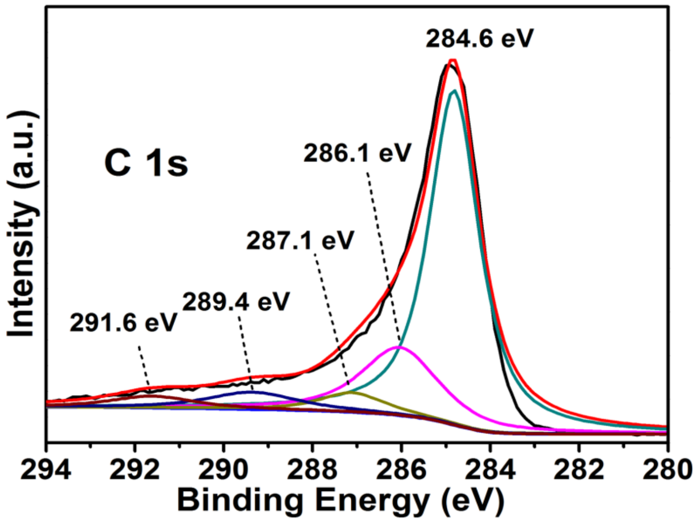

Fig. S5 High-resolution XPS C 1s spectra of S-rich MoS_2-NCNFs.

Fig. S5 exhibit five characteristic peaks located at 284.6, 286.1, 287.1, 289.4 and 291.6 eV, attributing to graphitized carbon, carbon in C=O groups, carbon in carbonyl or quinine groups, carbon in ester groups, and carbon in adsorbed CO_2, respectively. Compared with the graphitized carbon peak of pristine CNFs (285.0 eV), the binding energy of graphitized carbon (284.6 eV) is downshifted by ~ 0.4 eV, demonstrating a significant amount of charge transfer from graphitic carbon to the MoS_2 nanoplates, which could improve both the current density and catalytic activity of the MoS_2-NCNFs nanomaterials.

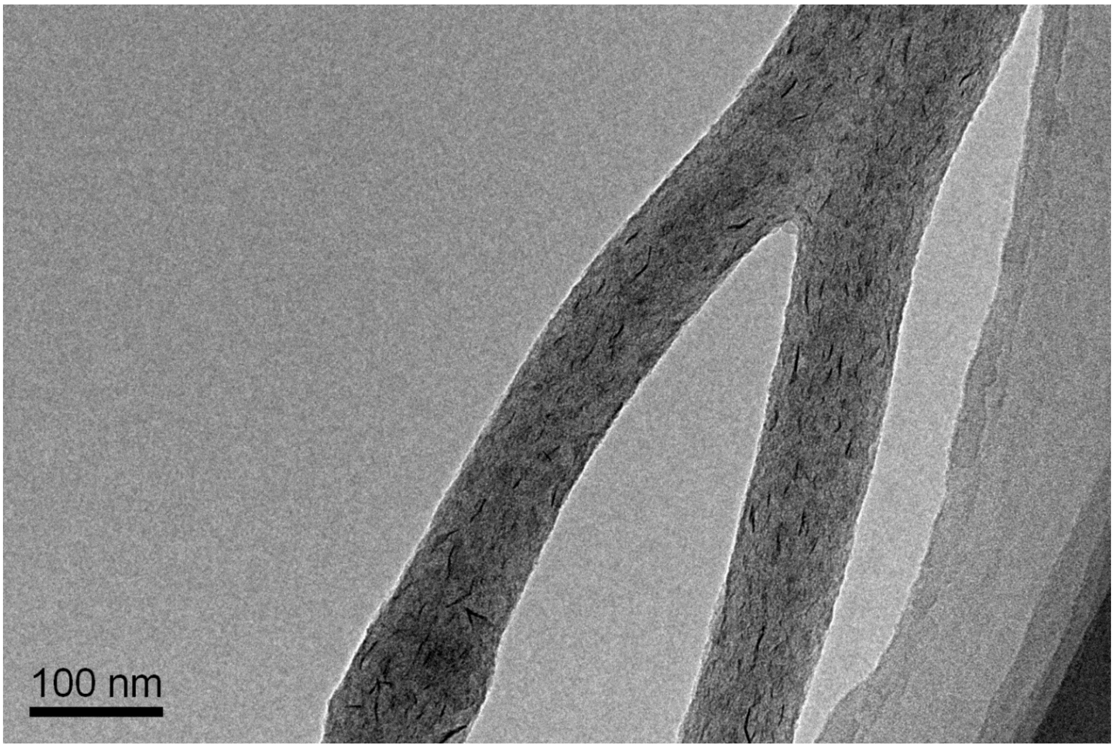

Fig. S6 TEM image of the MoS_2-NCNFs prepared at 1000 °C without any treatment by S vapor.

References

1. W. J. Zhou, D. M. Hou, Y. H. Sang, S. H. Yao, J. Zhou, G. Q. Li, L. G. Li, H. Liu and S. W. Chen, *J. Mater. Chem. A,* 2014, **2**, 11358-11364.
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