Electronic Supplementary Information

Facile synthesis of low crystalline MoS_2 nanosheet-coated CNTs for enhanced hydrogen evolution reaction

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Experimental details

Synthesis of MoS_2/CNTs: In a typical synthesis of MoS_2/CNTs composite, acid-treated CNTs (4mg) were dispersed in *N, N*-dimethylformamide (DMF, 15mL) by ultrasonication for 30min, and then 15mg ammonium thiomolybdate ($(NH_4)_2MoS_4$, 15 mg, Sigama-Aldrich) was added and ultrasonically dispersed for another 30min in the DMF solution. Then the mixture was transferred into an autoclave, and maintained at 210 ^{o}C for 18h, and was cooled to room temperature naturally. The black precipitate was collected by centrifugation and washed subsequently with DI-water and anhydrous ethanol several times, and finally dried at 60 ^{o}C for 24h. The preparation process of bare MoS_2 and the CNTs connected MoS_2 particles was similar to that described above, but without adding CNTs and replacing the DMF with water. The high-crystallinity MoS_2/CNTs was prepared by further treating the as-prepared MoS_2/CNTs materials at 800 ^{o}C in an atmosphere of H_2 balanced by N_2 for 2h with a heating rate of 1^{o}C min^{-1}.

Characterization: All transmission electron microscopy (TEM), high-resolution (HR)TEM images and element mapping were taken from JEOL JEM 2100F, while the field emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDX) spectra were taken on a JEOL JSM 6700F. XRD analysis of different samples was carried out on a X-ray diffractometer (Bruker AXS D8, Cu Kλ, λ = 1.5406 Å, 40 kV and 20 mA). Raman spectra were collected via a Renishaw Ramanscope in the backscattering configuration using 514 nm (2.41 eV) laser wavelengths over five random spots on the powers. X-ray photoelectron spectroscopy (XPS) spectrum was measured on a VG Escalab 250 spectrometer equipped with an Al anode (Al Kα = 1846.6 eV).

Electrochemical measurements: All electrochemical measurements were conducted on an Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands) in a three-electrode cell at room temperature. A Pt foil (4.0 cm^2) and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The working electrode was prepared on a glass carbon (GC) disk as the substrate. Typically, a mixture containing 2.0 mg catalyst, 2.5 mL ethanol and 0.5 mL Nafion solution (0.05 wt%, Gashub) was ultrasonicated for 15 min to obtain a well-dispersed ink. Then 40 μl of the catalyst ink (containing 26.6 μg of catalyst) was loaded onto a glassy carbon electrode of 5 mm in diameter (loading ~ 0.136 mg/cm^2). The presented current density refers to the geometric surface area of the glass carbon electrode. Linear sweep voltammetry with scan rate of 5 mV s^{-1} was conducted in 0.5 M H_2SO_4. The working electrodes were mounted on a rotating disc electrode with a rotating rate of 1000 rpm during the test. In all experiments, the electrolyte solutions were purged with N_2 for 15 min prior to the experiments in order to remove oxygen. During the measurements, the headspace of the electrochemical cell was continuously purged with N_2. AC impedance measurements were carried out in the same configuration at η= 0.15 V from 10^5-0.02 Hz with an AC voltage of 5 mV. All the potentials reported in our manuscript were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.241+0.059 pH) V.

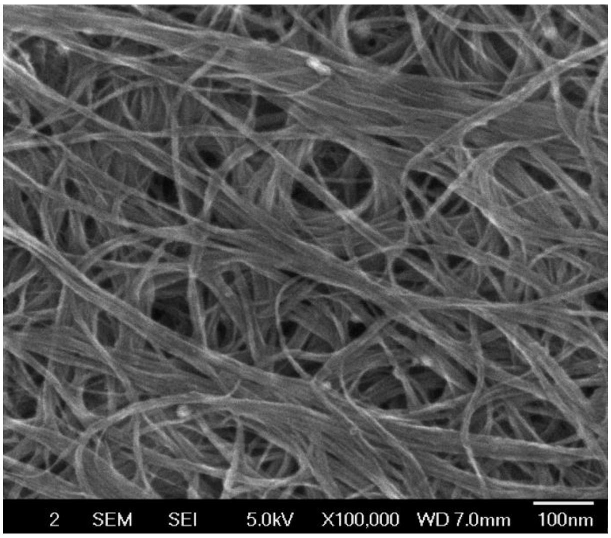


Fig. S1 SEM image of the acid-treated CNTs.

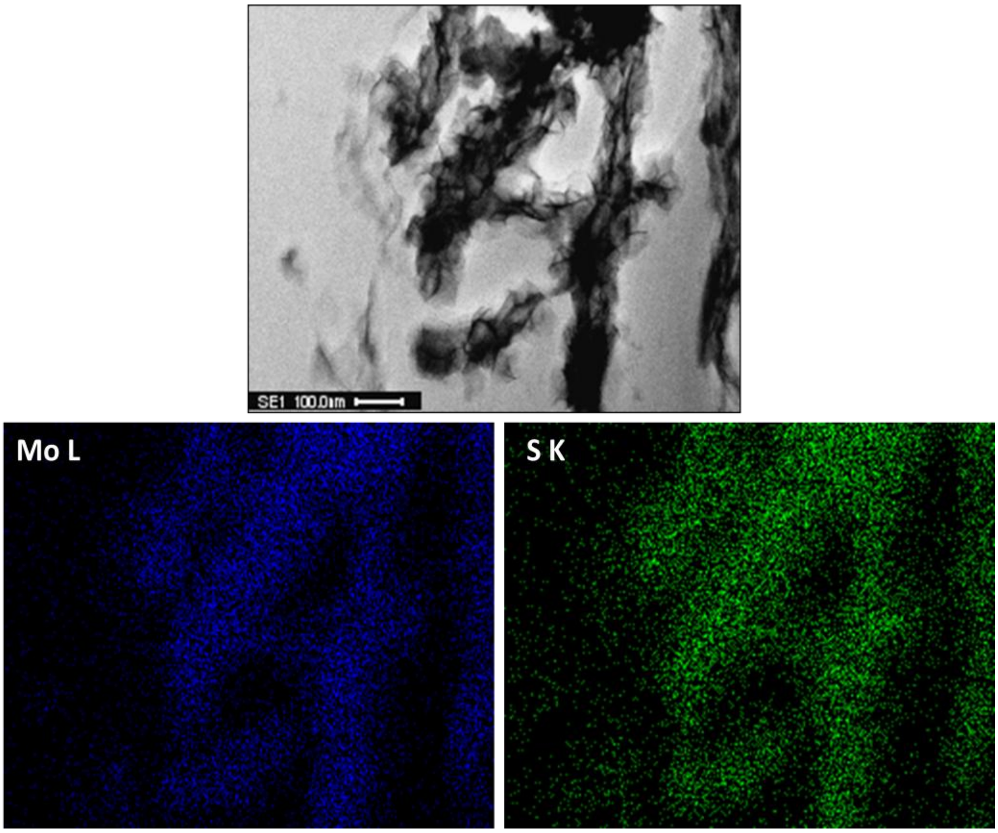


Fig. S2 TEM image of the selected area of the MoS2/CNTs composite for element mapping, showing the uniform distribution of Mo (blue), S (green) on the CNTs.

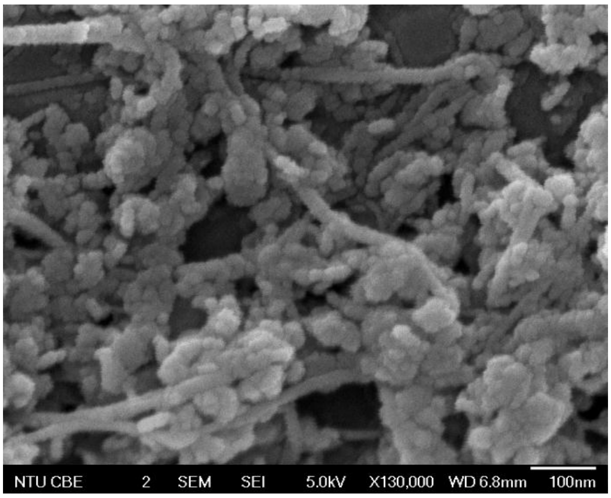


Fig. S3 SEM image of the MoS_2/CNTs hybrid by replacing the DMF with water as solvent.

Ohmic drop correction

In general, an electrochemical cell can be analyzed using an equivalent Randles circuit model, as shown in the Figure S1.

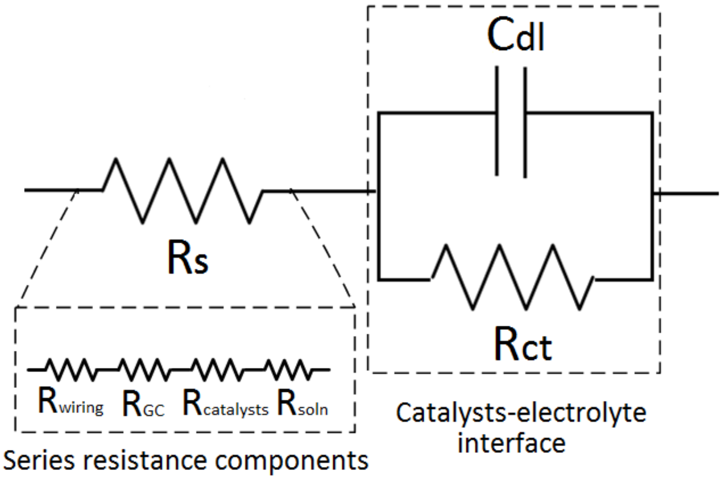


Fig. S4 Randles equivalent circuit model as applied for the electrochemical system of amorphous MoS_2/CNTs supported on glass carbon (GC) electrode. Rs represents the series resistance of the system. Cdl and Rct represent the double layer capacitance and charge transfer resistance of the catalyst-electrolyte interface. Rs can be obtained from the impedance at the high frequencies of AC impedance spectroscopy, as shown below.

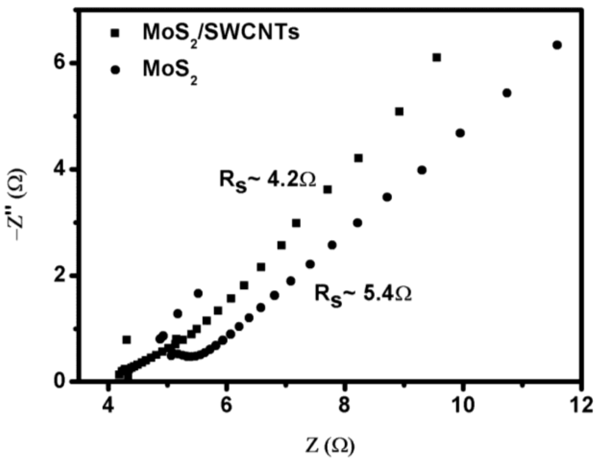


Fig. S5 AC impedance spectroscopy of MoS_2/CNTs and bare MoS_2 performed in the same configuration at η=0.15V from 10^6-0.02 Hz with an AC voltage of 5mV.

It shows close-up views in the high-medium frequency region. The intercept of the semicircle on the real axis is assigned to the ohmic series resistance (Rs). iR correction to data with the series resistance (Rs) is performed by ηcorr = η − jR.

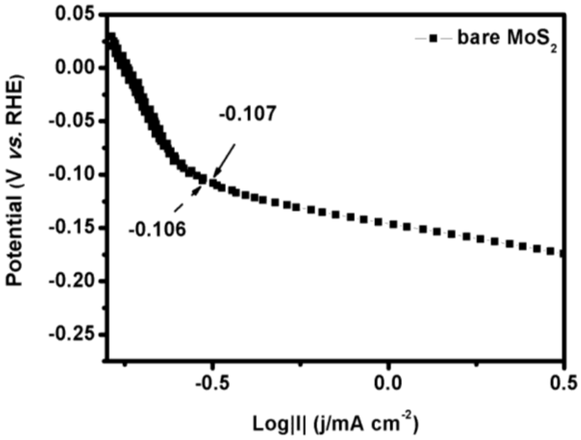


Fig. S6 The Tafel plot of bare MoS_2 in the region of low current densities.

The onset potential for HER was read from the semi-log (Tafel) plot. For example, the semi-log plot of bare MoS_2 in the region of low current densities as displayed in Fig.S6 shows a linear relationship below -0.107 V but starts to deviate above -0.106 V. Therefore, -0.107 was chosen as the onset potential for bare MoS_2. The same method was applied to determine the onset for other samples.

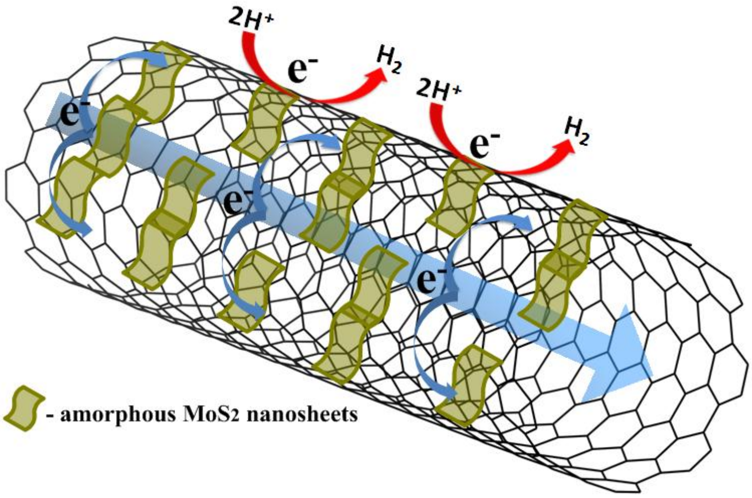


Fig. S7 Schematic illustration of the eletrocatalytic mechanism of HER on MoS_2/CNTs.

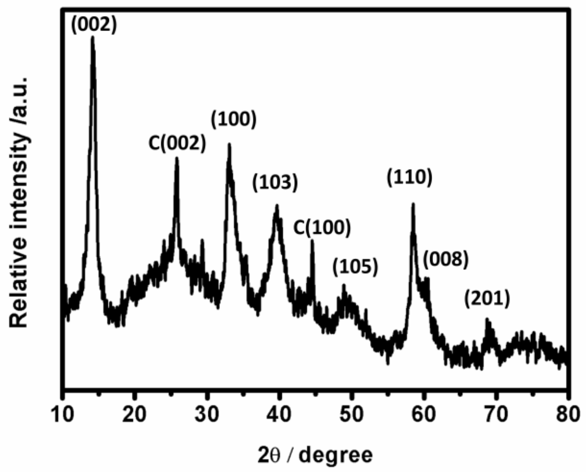


Fig. S8 XRD pattern of the MoS_2/CNTs composite after annealed at 800°C for 2h.

It shows sharp peaks with very high intensity in comparison with the as-prepared MoS_2/CNTs, and especially the strong (002) peak at 2θ=14.4 signifies a well-stacked layered structure, which demonstrates the high crystallinity of MoS_2 in the hybrid after annealing.

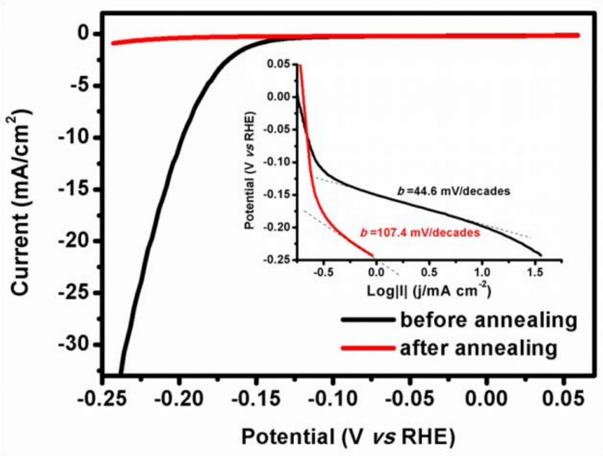


Fig. S9 The polarization curves and the Tafel slope (inset) of as-prepared MoS_2/CNTs and MoS_2/CNTs annealed at 800°C.

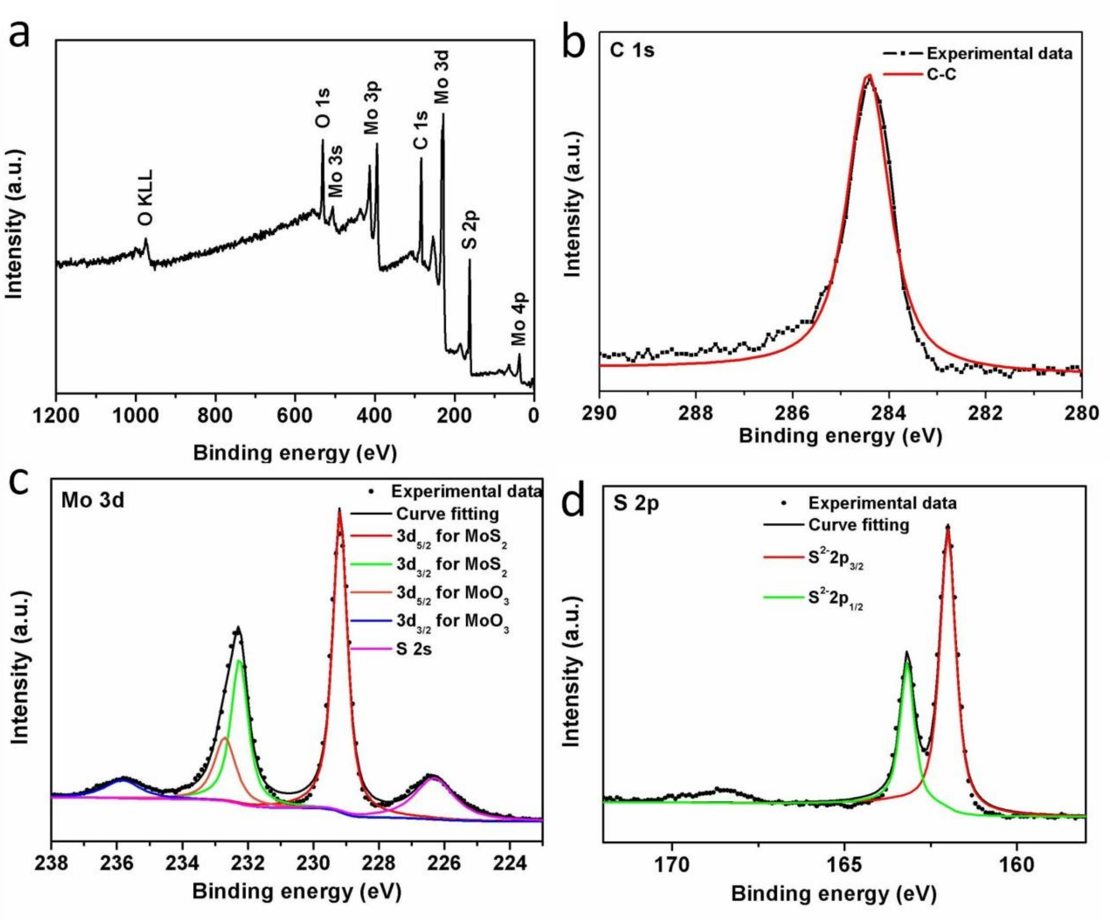


Fig. S10 (a) XPS survey spectra and (b-d) high-resolution XPS spectra of MoS_2/CNTs composites.

A highly crystalline product was obtained when the as-prepared MoS_2/CNTs were heated at 800 °C for 2h. From the XPS spectra in Fig. S10, the +4 oxidation state of Mo is clearly dominant for the samples after annealing at 800°C, whereas the S2p region exhibits a single doublet with the 2p3/2 peak at 162.0 eV consistent with a -2 oxidation state for the sulphur and no shoulder at higher energy position (bridging S_2^{2-}) is observed.

Calculation of active sites

The absolute components of voltammetric charges (cathodic and anodic) can be obtained from the CV of Figure S11. Assuming a one electron redox process, the total charge was divided by two. The value was further divided by the Faraday constant to get the number of active sites of the film.

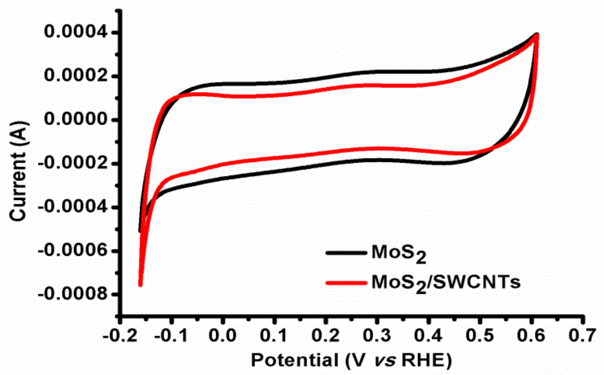


Fig. S11 Cyclic voltammograms of the MoS_2/CNTs and MoS_2 catalysts recorded in 0.5M H_2SO_4; scan rate: 50 mVs^{-1}.

Assessment of turnover frequency (TOF)

When the number of active sites is obtained, the per-site turnover frequencies (in s^{-1}) were calculated with the following equation:

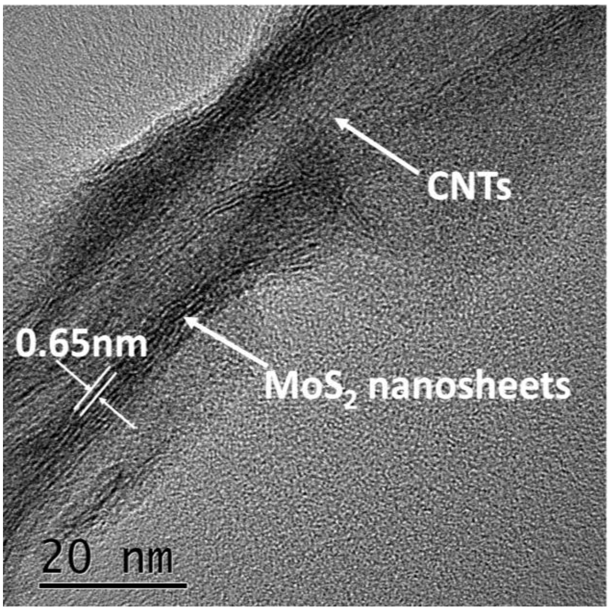
$$\mathrm{TOF} = \frac{I}{\mathrm{F}n}\frac{1}{2}$$

I —Current (in A) during the linear sweep measurement.

F —Faraday constant (in C mol^{-1}).

n —Number of active sites (in mol).

The factor 1/2 in the equation represents that two electrons are required to form one hydrogen molecule from two protons ($2H^{+} + 2e^{-1} = H_2$).



Enlarged Fig. 3 inset. HRTEM image of MoS_2 on the CNTs.