Supporting Information

Molybdenum Sulfide/N-Doped CNT Forest Hybrid Catalysts for High Performance Hydrogen Evolution Reaction

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1. Experimental section.

Vertical N-Doped CNT forest Synthesis: Firstly, iron thin film was deposited on a Si/SiO_2 wafer via e-beam evaporation. Then, the wafer (1 cm × 1 cm) was heated to 750 °C along with hydrogen and ammonia gas mixture (H_2: 80 ccm, NH_3: 20 ccm) using plasma-enhanced chemical vapor deposition (PECVD). At this temperature the Fe thin film became agglomerated within 2 min. Afterwards, the chamber pressure and DC voltage were increased to 5 Torr and 440 V, respectively, which resulted in the production of plasma inside the chamber between the electrodes. Meanwhile, acetylene gas was injected into the chamber and dissociated into carbon atoms on the Fe particle surfaces, which promoted the growth of carbon in the form of N-doped CNT forest. For the control experiment, pristine CNT forest was also grown by PECVD. Except for absent of ammonia gas feeding, all other growth parameters were same with NCNT forest case.

Preparation for NCNT forest electrode robustly contacting with glassy carbon current collector: As grown NCNT forest was floated in HF solution diluted by DI water to detach undrenched NCNT forest from Si substrate in a way of wet-etching. After that the forest electrode was carefully transferred onto the rotating disc electrode or glassy carbon electrode of rod shape. For enhancing the contact between NCNT forest and glassy carbon, as-transferred sample was put on oven at 80 °C for 30min. CNT forest electrode was also followed the same transfer process route.

MoS_x decorated NCNT forest electrode: Ammonium thiomolybdate ($(NH_4)_2MoS_4$) was purchased from Sigma Aldrich. The NCNT forest contacted to glassy carbon sample was immersed in 2 ml HCl solution with PH=5 for 30 min and then 3 ml 0.01 M $(NH_4)_2MoS_4$ precursor was injected into the vial containing HCl and NCNT forest sample. The vial was then immediately put into silicon oil base calibrated at 90 °C and kept in there for several hours. For the control experiment, CNT forest electrode sample also underwent exact same wet chemical process.

Thermal annealing process for MoS_x/NCNT forest hybrid catalyst: MoS_x functionalized NCNT forest was annealed at 600 °C for 30 min in a high vacuum tube under the flow of H_2 and Ar gas (H_2 : Ar = 40 ccm: 60 ccm).

Preparation of control experiment of Pt/C and MoS_x sample: As a comparison, 4 mg of Pt/C 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 5 μl of the catalyst ink (containing 20 μg of catalyst) was loaded onto a glassy carbon electrode of 50 mm in diameter (loading ~ 0.102 mg/cm^2). In addition to that, Amorphous MoS_x catalysts were prepared by acidification of tetrathiomolybdate solution with aqueous HCl solution of pH = 2[1]. The solution was then boiled for 30 minutes and cooled to room temperature to give a dark paste. The paste was oven dried for 12 h at 80 °C to give a black vitreous solid that was ground into MoS_x powder with a mortar[1]. Again, 4 mg of MoS_x 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 5 μl of the catalyst ink (containing 20 μg of catalyst) was loaded onto a glassy carbon electrode of 50 mm in diameter (loading ~ 0.102 mg/cm^2) for HER test.

Characterization: The morphologies of all NCNT, CNT forest, before and after MoS_x modification, were characterized with the aid of field-emission scanning electronmicroscopy (Hitachi S-4800 SEM, Japan) and FE-TEM (Tecnai G2 F30). The Energy dispersive X-ray spectrometry (EDX) line scanning profile of elemental distribution of MoS_x/NCNT forest hybrids were performed with a Cs-corrected JEM-ARM200F STEM. XPS (Thermo VG Scientifi c, Sigma Probe) were performed to characterize the chemical structures of NCNTs and their hybrids. A Rigaku D/MAX-2500 diffractometer with Cu KR irradiation (λ = 1.5418 Å) was used for the XRD measurements. A topography image and the current response at a bias of applied voltage were investigated by using C-AFM (SPA 400, Seiko) with a Pt-coated AFM tip (EFM tips, Nanosensors). Raman spectroscopy analysis is performed using a Horiba Jobin Yvon France Aramis system with a Ar ion CW Laser (514.5nm).

Electrochemical measurements: All the electrochemical tests were performed in a three-electrode system at an electrochemical station (Bio-Logic SP-200). Linear sweep voltammetry with scan rate of 5 mV s^{-1} was conducted in 250 mL of 0.5 M H_2SO_4 using Ag/AgCl (in 3 M KCl solution) electrode as the reference electrode, a graphite rod (Alfa Aesar, 99.9995%) as the counter electrode, and the glassy carbon electrode mounting NCNT forest as working electrode. Potentials were referenced to reversible hydrogen electrode (RHE) by adding a value of 0.2. AC impedance measurements were carried out in the same configuration when the working electrode was biased at a constant –0.2 V vs. RHE from 5 MHz to 10 mHz with an AC voltage of 5 mV. The electrochemical stability of the hybrid catalyst was evaluated by cycling the working electrode continuously 1000 times. The potential window was between -0.2 and 0.2V vs RHE with a scan rate of 50 mV/s. To estimate the double-layer capacitance, cyclic voltammograms taken with various scan rates (20, 40, 80, 160, 200 mV/s, etc.) were used under the potential window of 0–0.3 V vs. RHE.

2. SEM and Photo image of Vertical NCNT forest transferred onto glassy carbon electrode substrates (rod and rotating disc electrode).

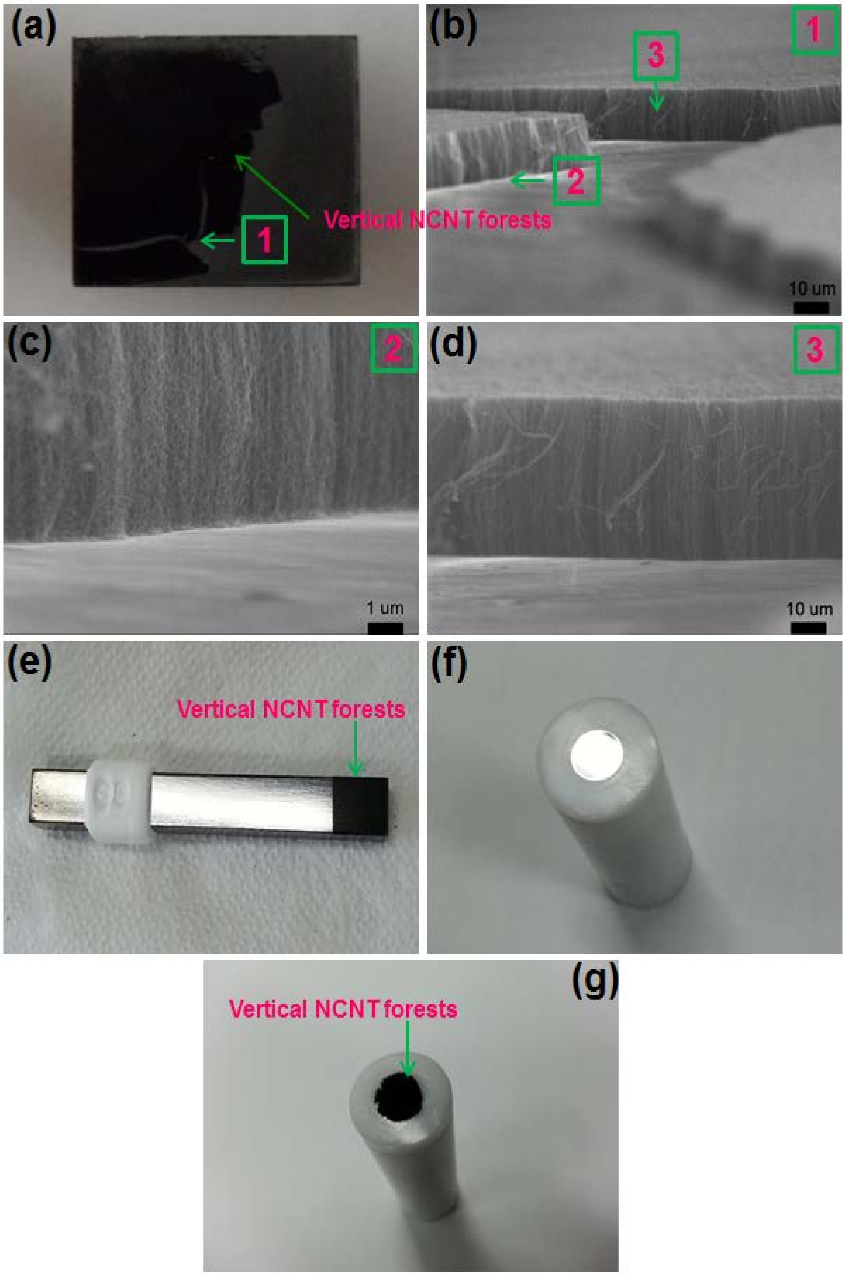

Figure S1. (a) Photo image of vertical NCNT forest transferred onto mirror-polished glassy carbon conductive support. (b) Magnified FE-SEM image of region 1. (c) Magnified FE-SEM image of region 2. (d) Magnified FE-SEM image of region 3. (e) Photo image of NCNT forest transferred onto glassy carbon rod. (f) Photo image of bare rotating disc electrode. (g) Photo image of rotating disc electrode after NCNTs loading.

3. Conduction AFM measurement.

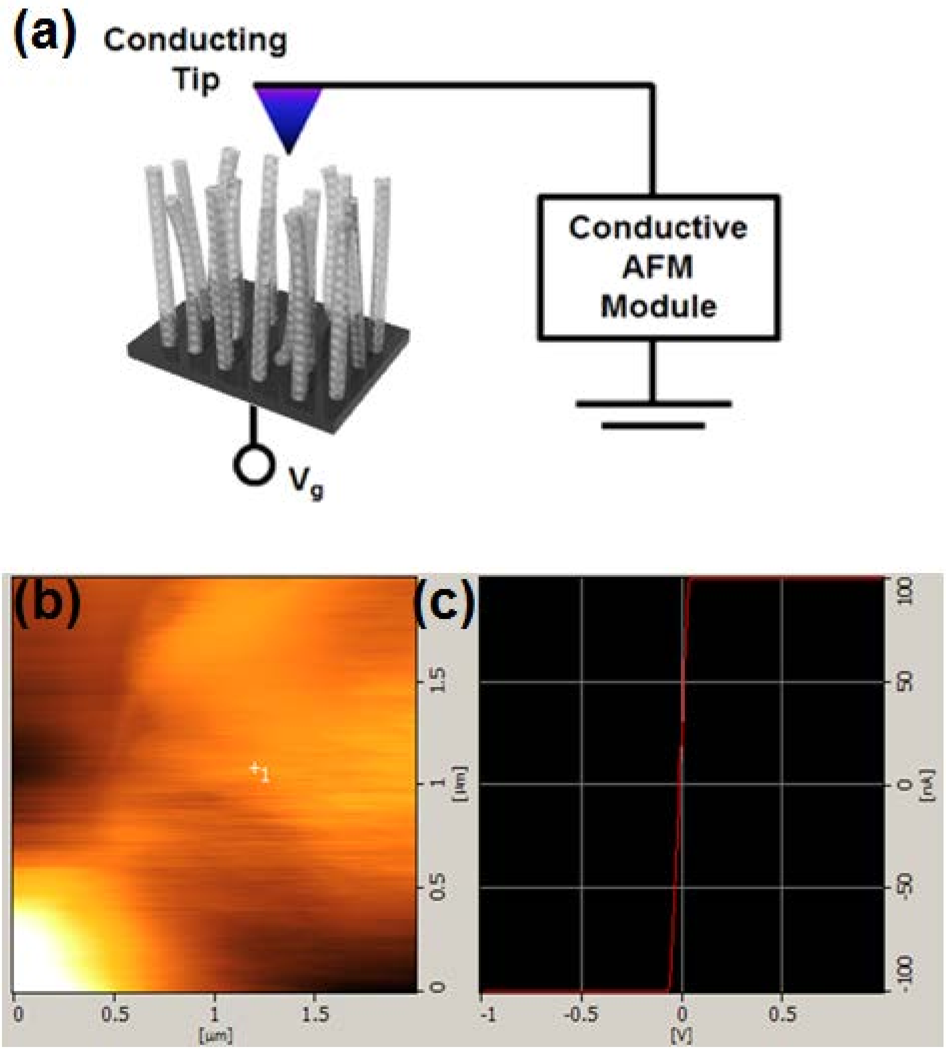

Figure S2. (a) Schematic representation of the conductive AFM (C-AFM) setup. (b) Topography image. (c) Generated current between vertical NCNT forest and glassy carbon electrode at 1V, 2µm scan.

4. Line scans of MoS_x observed in TEM images of MoS_x/NCNT hybrid before and after annealing at 600 °C.

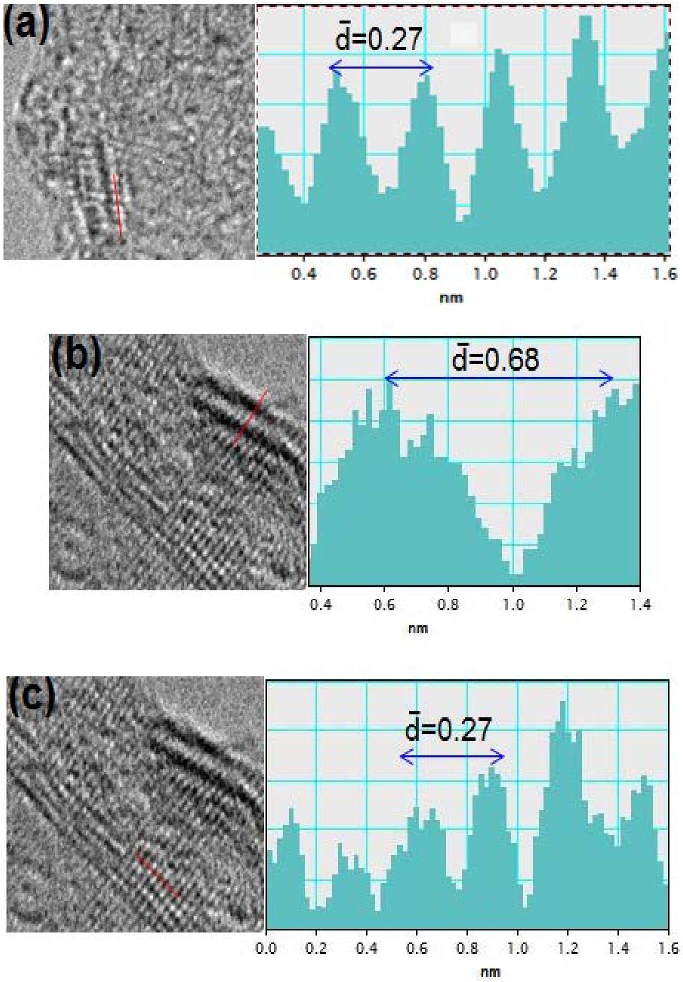

Figure S3. (a) A line scan of designated spot showing fringe lattice spacing of average distance of around 0.27 nm in MoS_x tiny crystal region. (b) A line scan of interlayer spacing showing distance of 0.68 nm in MoS_2 layers after heat treatment. (c) A line scan of fringe lattice spacing showing average distance of around 0.27 nm in MoS_2 layers after heat treatment.

5. X-ray diffraction spectra and Raman spectra of MoS_x/NCNT hybrid before and after thermal annealing at 600 °C.

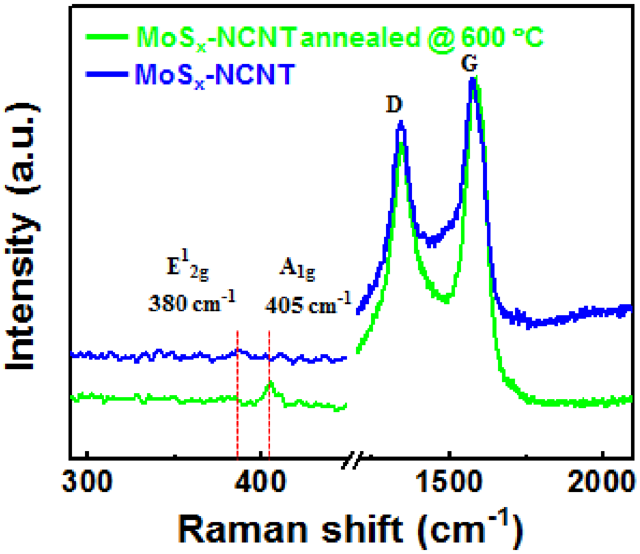

Figure S4. Raman spectra comparison of MoS$_x$/NCNT and MoS$_x$/NCNT annealed at 600°C under a hydrogen and argon atmosphere for 30 min.

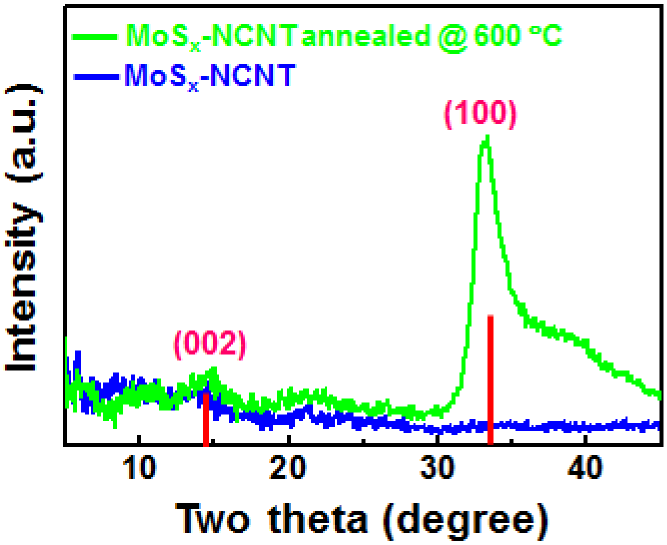

Figure S5. XRD of MoS$_x$/NCNT and MoS$_x$/NCNT annealed at 600°C under a hydrogen and argon atmosphere for 30 min.

6. Exchange current densities of various samples.

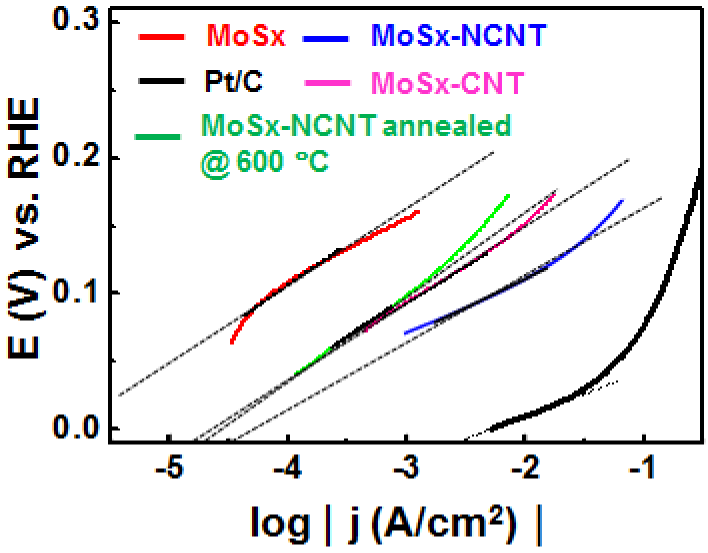

Figure S6. Exchange current densities of various samples by using extrapolation method.

Materials	log (|j (Acm^{-2})|) at η=0 V	Exchange current densities
MoS$_x$/NCNT forest	-4.48	33.11
MoS$_x$	-5.82	1.59
MoS$_x$/CNT forest	-4.85	14.13
Thermal annealed MoS$_x$/NCNT forest	-4.78	16.59

Table S1. Calculation of the exchange current densities of various samples.

7. Calculation of Active Site Density and Per-Site Turn Over Frequency (TOF).

To calculate the active surface site density and per-site turn over frequency (TOF) for the amorphous molybdenum sulfide/NCNT forest hybrid catalyst, we adopt the approach that used in Jaramillo *et al*[2]. So the number of electrochemically accessible surface sites on the molybdenum sulfide catalyst was calculated by the following formula:

$$\frac{\#\ of\ surface\ sites\ (catalyst)}{cm^2\ geometric\ area}=\frac{\#\ of\ surface\ sites\ (flat\ standard\ )}{cm^2\ geometric\ area}\times Roughness\ Factor$$

To obtain the value of roughness factor, we first carried out cyclic voltammograms to estimate the double-layer capacitance of MoS_x/NCNT forest (Figure S5). By comparing it with the double-layer capacitance of flat MoS_2 standard (~60 μF/cm^2) provided in Jaramillo *et al*,[2, 3] the relative roughness factor was determined to be 85. As a result, the number of surface active sites of MoS_x/NCNT forest hybrid corresponds to 9.8×10^{16} according to above formula.

To further access the per-site TOF, we used following formula:

$$\text{TOF per site}=\frac{\#\ Total\ Hydrogen\ Turn\,Over/cm^2\ \ geometric\ area}{\#\ Surface\ Sites\ \ (Catalyst)/cm^2\ \ geometric\ area}$$

However, total number of hydrogen turn over events per geometric area happened at 1mA/cm^2 close to[4]

$$3.12\times10^{15}\,\frac{H_2/s}{cm^2}$$

So the TOF per site at η = 200 mV vs. RHE (current density of 110.01 mA/cm^2) and pH = 0 is determined as follows.

$$\left(3.12\times10^{15}\,\frac{H_2/s}{cm^2}\right)(110.01)\left(\frac{1\ cm^2}{9.8\times10^{16}\ surface\ sites}\right)=3.5\ \frac{H_2/s}{surface\ site}$$

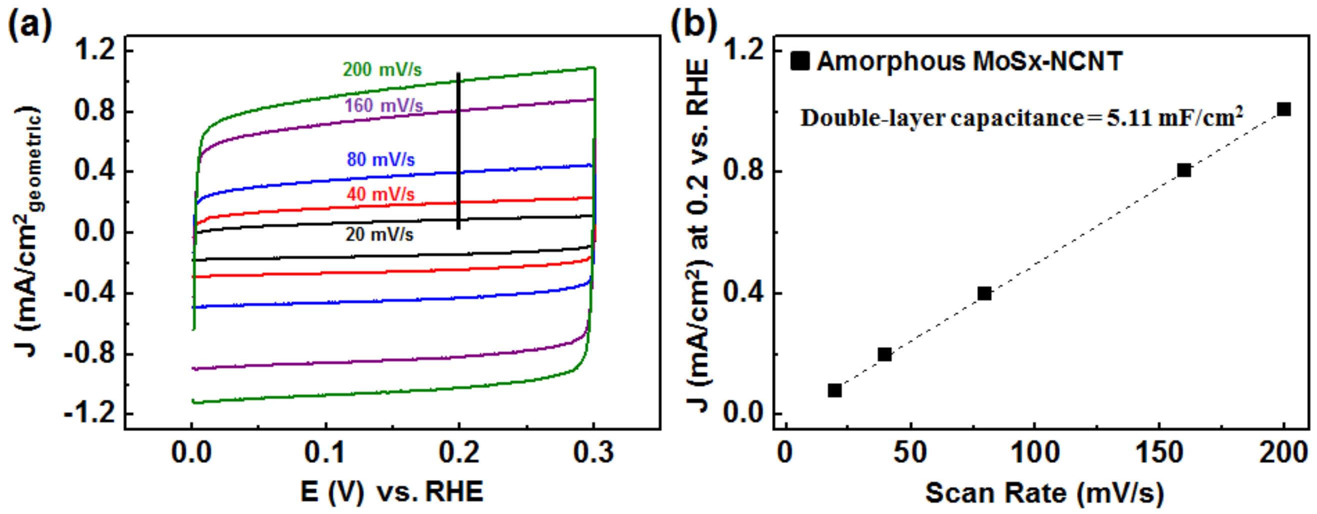

Figure S7. Cyclic voltammograms (a) were measured in a potential range, in which no faradic processes were observed to obtain the capacitive current from double layer charging. The capacitive current measured at 0.20 V vs RHE was plotted as a function of scan rate (b) for the wet-chemical-synthesized

Journal	Materials	Active site density [10^{17}/cm^2]	TOF [s^{-1}]	Tafel slope [mV decade^{-1}]	Tafel region [mV]	Overpotential η [mV] *vs* RHE	j [mA cm^{-2}]	j_0 [μA cm^{-2}]
My results	**MoS_x/NCNT**	**0.98**	**3.5**[a]	**40**	**80-120**	**200**	**111.01**[b]	**33.11**[c]
ACS catalyst 2013 T. Jamarillo et al	**Amorphous MoS_3**	**1**	**0.03~3**	**53~65**	**-**	**272**	**~10**	**-**
Chem. Sci., 2011 X. L. Hu et al	**Amorphous molybdenum sulfide films**	**-**	**0.8**	**40**	**170-200**	**200**	**14**	**13**
Energy Environ. Sci., 2012 X. L. Hu et al	**MoS_3 and MoS_2 particles**	**-**	**-**	**54**	**120-170**	**200**	**2.3**	**-**
Chem. Commun., 2013 X. L. Hu et al	**amorphous molybdenum sulphide particles**	**-**	**-**	**47**	**-**	**230**	**10**	**-**
ACS Catal. 2013 X. L. Hu et al	**Amorphous MoS_3 Film**	**-**	**-**	**-**	**-**	**170**	**20**	**-**

[a] TOFs were measured at η = 200 mV;
[b] Cathodic current densities (j) were recorded at η = 200 mV;
[c] Exchange current densities (j_0) were obtained from Tafel curves by using extrapolation methods.

Table S2. HER parameters of MoS_x/NCNT forest hybrid samples and other literature values.

8. Comparison of polarization curves of MoS_x/NCNT forest hybrid before and after thermal annealing at 600 °C.

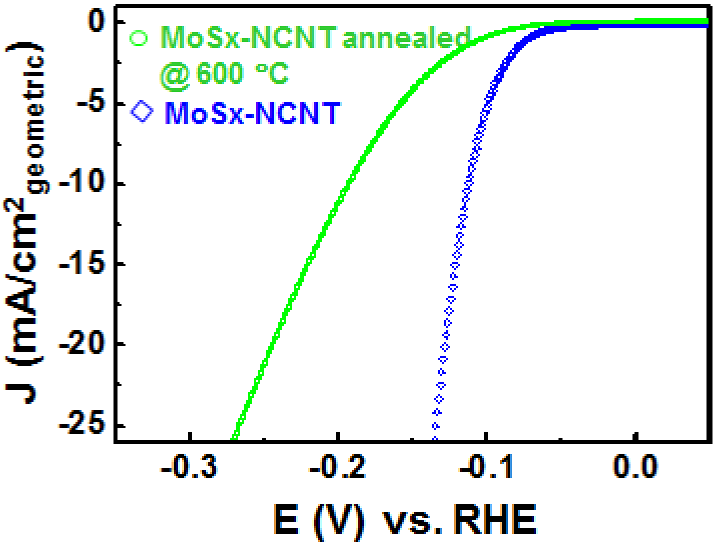

Figure S8. The polarization curves of as-prepared MoS_x/NCNTs and MoS_x/NCNTs annealed at 600 °C.

References

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(4) Chen, Z. B.; Cummins, D.; Reinecke, B. N.; Clark, E.; Sunkara, M. K.; Jaramillo, T. F. Nano lett. 2011, 11 (10), 4168-4175.