Electronic Supplementary Information

Three-Dimensional Carbon Foam/N-doped Graphene@MoS_2 Hybrid Nanostructures as Effective Electrocatalysts for Hydrogen Evolution Reaction

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Experiment

Preparation of carbon foam/N-doped graphene (CF-NG) composites

First, graphene oxide (GO) was synthesized by a modified Hummers method. In a typical synthesis process for CF-NG composites, a certain amount of GO was dispersed in 100 ml of distilled (DI) water. After one hour of sonication, a piece of melamine foam (MF) block was fully immersed into the homogeneous GO solution for a few seconds. Then, the MF block was removed from the dispersion and dried naturally at room temperature. During this process, the GO sheets were deposited on the MF framework. For both carbonization of the MF and reduction of GO, the brown coloured composite foam was heated at 700 ˚C for 2 h under Ar atmosphere**,** and finally**,** the black CF-NG monolith was obtained. With different concentrations of GO solution, such as 1, 3**,** and 6 mg ml^{-1}, CF/NG composites with different graphene loading densities were obtained. The corresponding composites are designated as CF-NG-1, CF-NG-3, and CF-NG-6, respectively.

Preparation of CF-NG@MoS_2 composites

To grow MoS_2 catalysts on the CF-NG surfaces, ammonium thiomolybdate (50 wt % of CF-NG composites) dispersed in *N*,*N*-dimethylformamide (DMF) was added to the CF-NG monolith using a pipette and dried in a vacuum oven at 70 ˚C for 2 h. The MoS_2 layers were formed after subsequent thermal treatment at 150 ˚C in Ar/H_2 (95 : 5 v/v %) atmosphere for 30 min. After cooling to room temperature, the obtained CF-NG@MoS_2 block was washed with DI water and ethanol.

Material characterization

The morphologies and shapes of all samples were observed by field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800). Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 instrument. X-ray photoelectron spectroscopy (XPS, SIGMA PROBE, ThermoFisher Scientific, UK, Al Kα (1486.6 eV)) was conducted to obtain the chemical information of samples. XPS curve fitting was conducted by the XPSPEAK41 software with Shirley background. X-ray diffraction (XRD) measurements were performed using a Rigaku system (D/MAX 2500) with Cu Kα (λ = 0.15418 nm) radiation (40 kV, 200 mA). For thermogravimetric analysis (TGA), a TGA/DSC 1 (Mettler Toledo) system was used (heating rate: 10 ^{o}C min^{-1} to 700 ^{o}C in air). Element Analyzer (TRSMCHNSC-6280TRSM) was used to confirm the element contents in samples.

Electrochemical measurements

The prepared samples (5 mg) were mixed with Nafion (Nafion® perfluorinated resin solution, 5 wt% in a mixture of lower aliphatic alcohols and water, contains 45% water, Aldrich, 15 wt%) as a binder and 2-propanol. The Pt/C result was measured using commercial 20 wt% (Pt loading mass, Johnson Matthey). 7 μL of the solution was deposited on a rotating ring disk electrode (disk area: 0.2475 cm2, PINE). The catalyst loading was 80 μg. Electrochemical measurements were conducted using an Autolab potentiostat (PGSTAT) in a standard three-electrode cell with a glassy carbon counter electrode and a saturated calomel electrode as the reference electrode. All the potentials were measured with respect to the reversible hydrogen electrode (RHE) with a H_2 oxidation/evolution potential. The HER was measured in 0.5 M H_2SO_4 electrolyte at 298 K. Electrochemical double layer capacitance was measured at

various scan rates (2, 5, 8, 10, and 15 mV s^{-1}). EIS was measured under 0.5 M H_2SO_4 electrolyte at -0.15 V (vs. RHE) with the frequency range of 10000 Hz to 50 mHz, 10 mV amplitude.

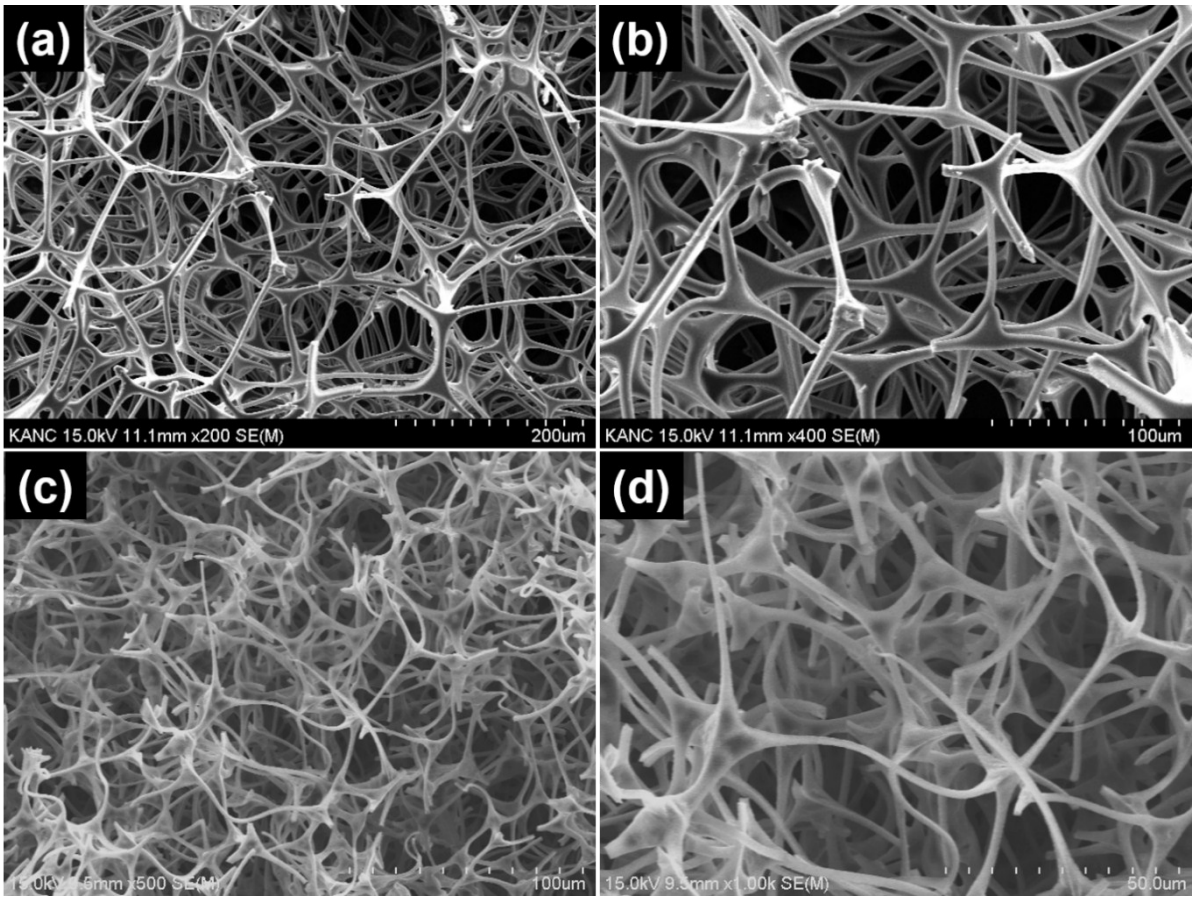

Fig. S1 SEM images of (a, b) bare MF and (c, d) CF monolith.

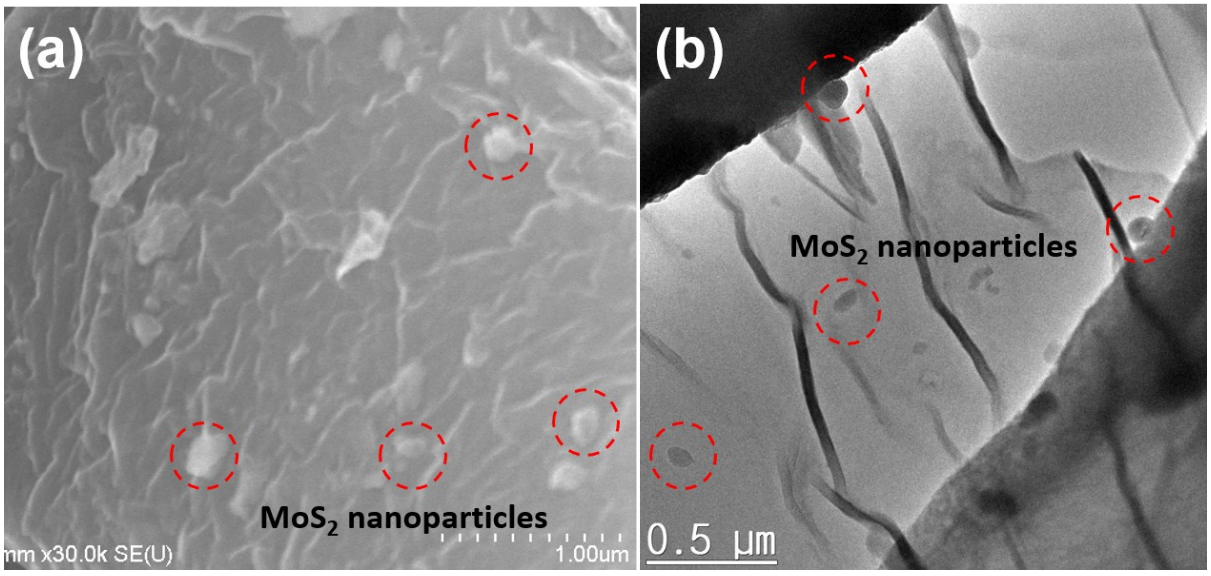

Fig. S2 High magnification of SEM and TEM images of CF-NG@MoS_2 composite (red circles: MoS_2 nanoparticles).

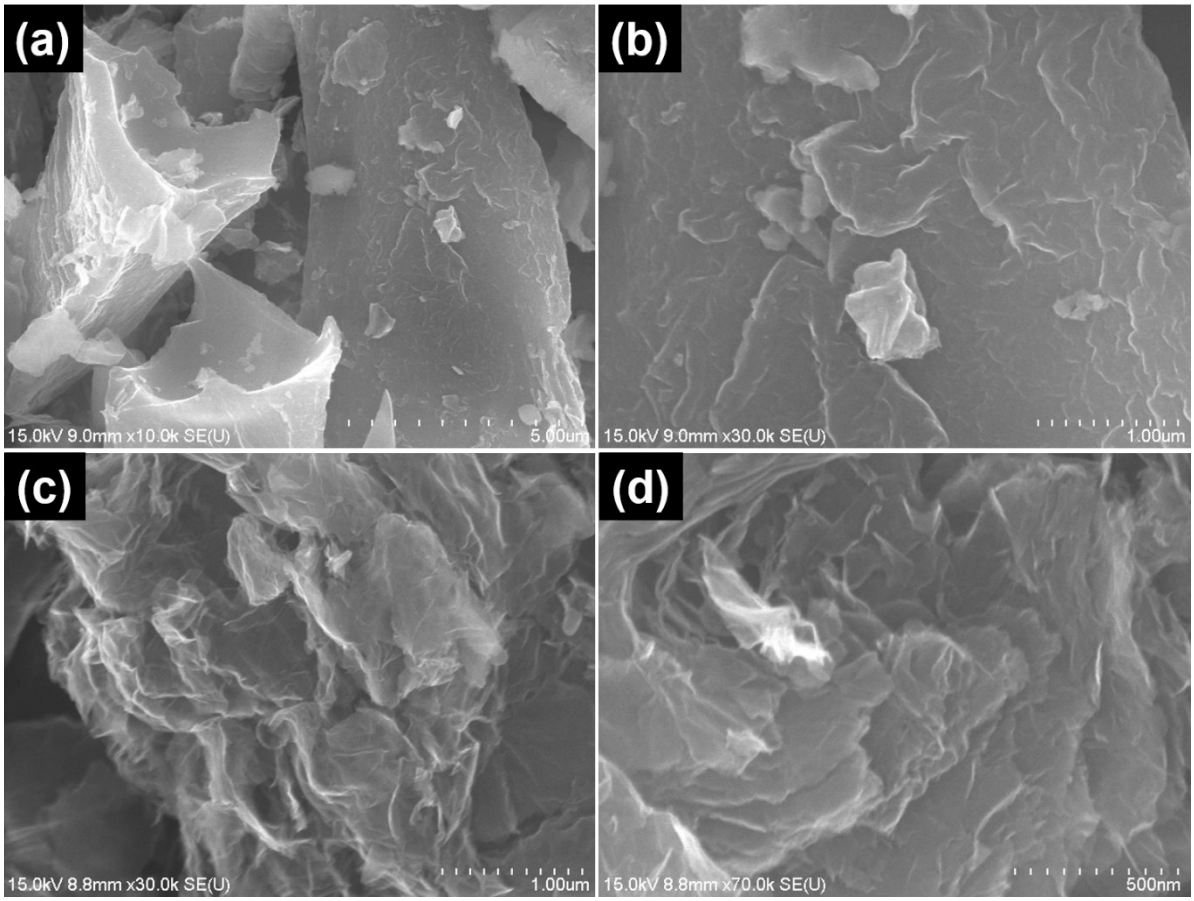

Fig. S3 SEM images of (a, b) CF@MoS_2 and (c, d) G@MoS_2 composites.

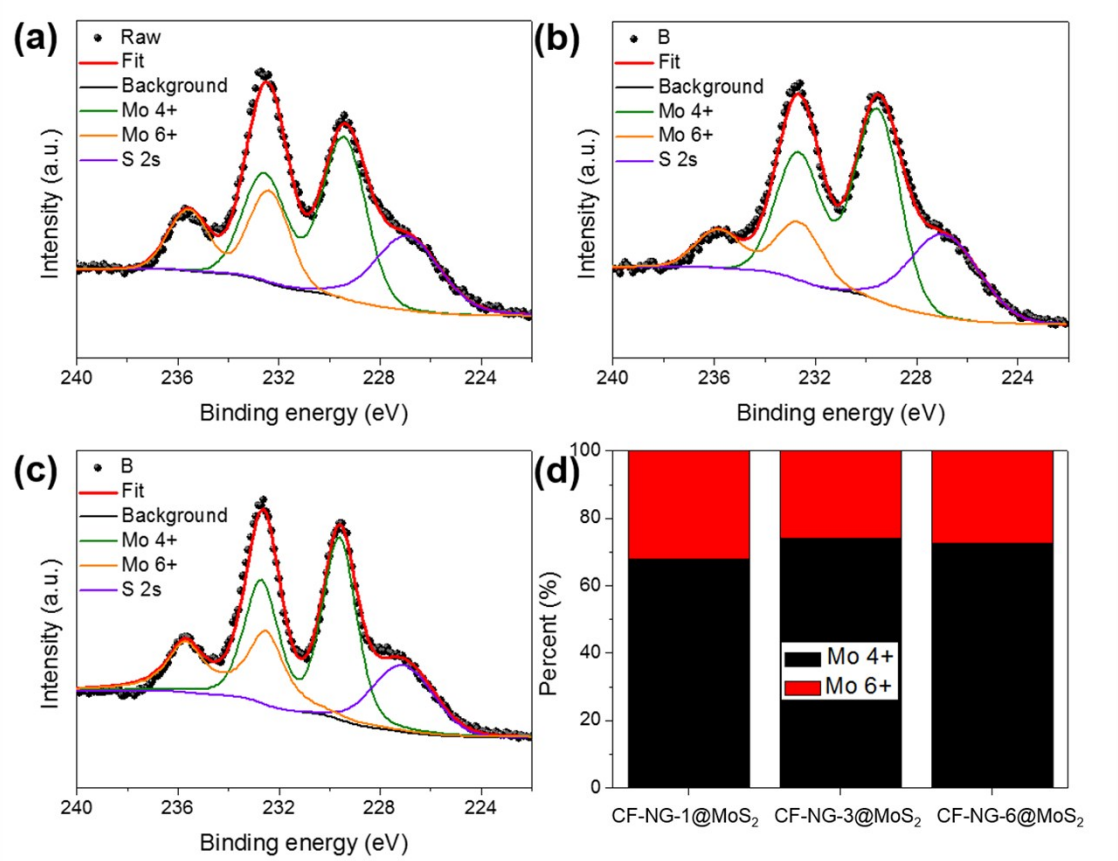

Fig. S4. Mo 3d XPS analysis of samples (a) CF-NG-1@MoS_2, (b) CF-NG-3@MoS_2, (c) CF-NG-6@MoS_2 and summary of fitting results.

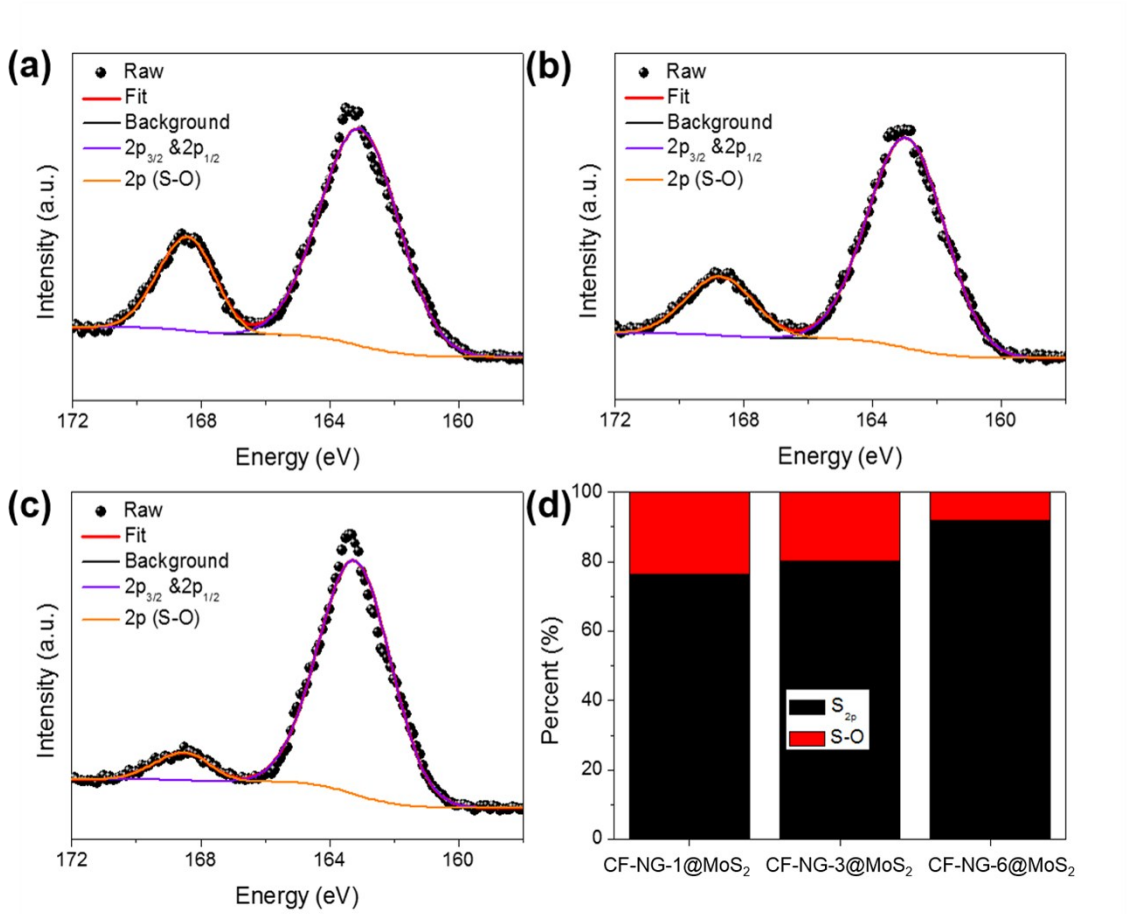

Fig. S5. S 2p XPS analysis of samples (a) CF-NG-1@MoS_2, (b) CF-NG-3@MoS_2, (c) CF-NG-6@MoS_2 and summary of fitting results.

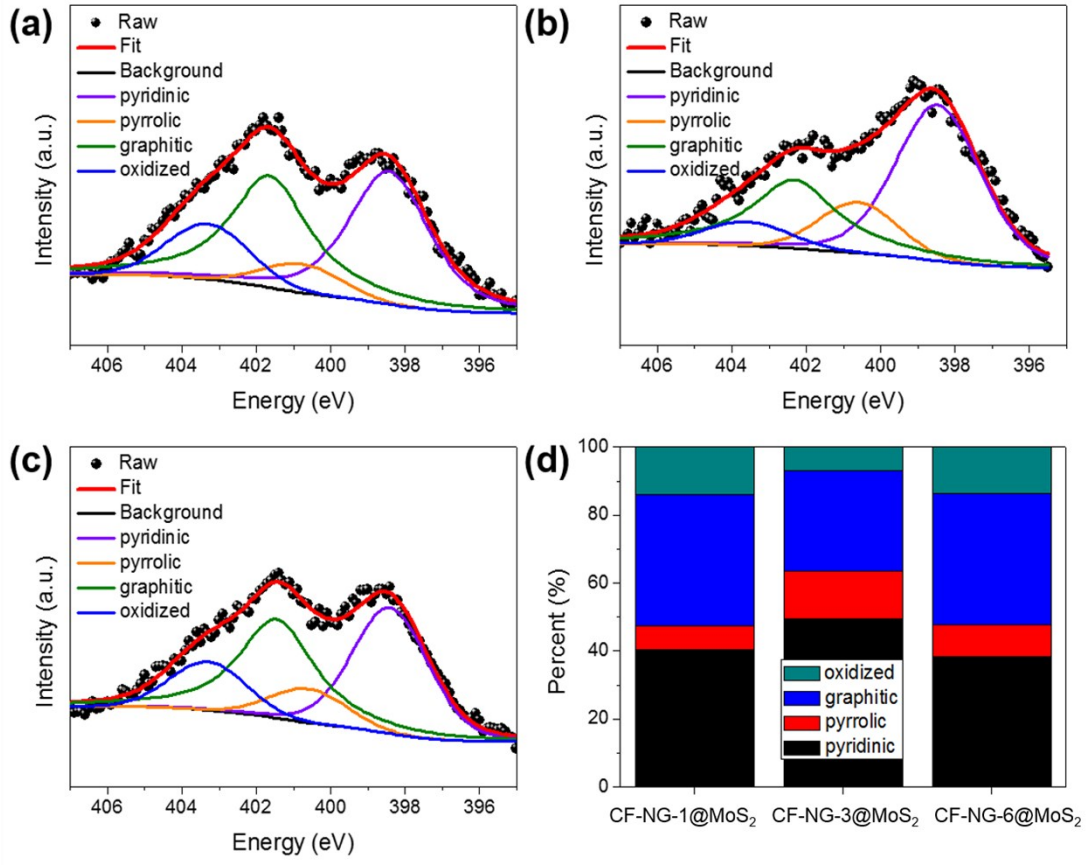

Fig. S6. N 1s XPS analysis of samples (a) CF-NG-1@MoS_2, (b) CF-NG-3@MoS_2, (c) CF-NG-6@MoS_2 and summary of fitting results.

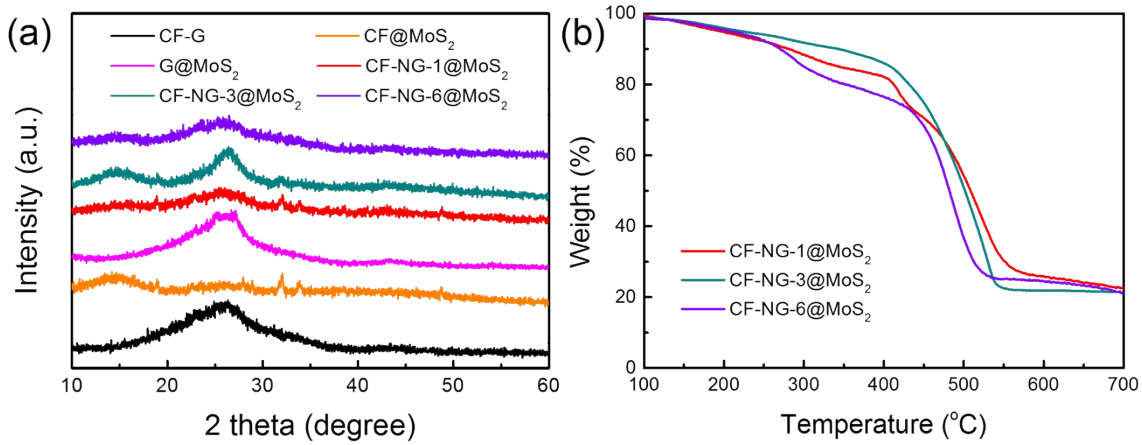

Fig. S7 (a) XRD patterns of all samples and (b) TGA curves of CF-NG@MoS_2 samples.

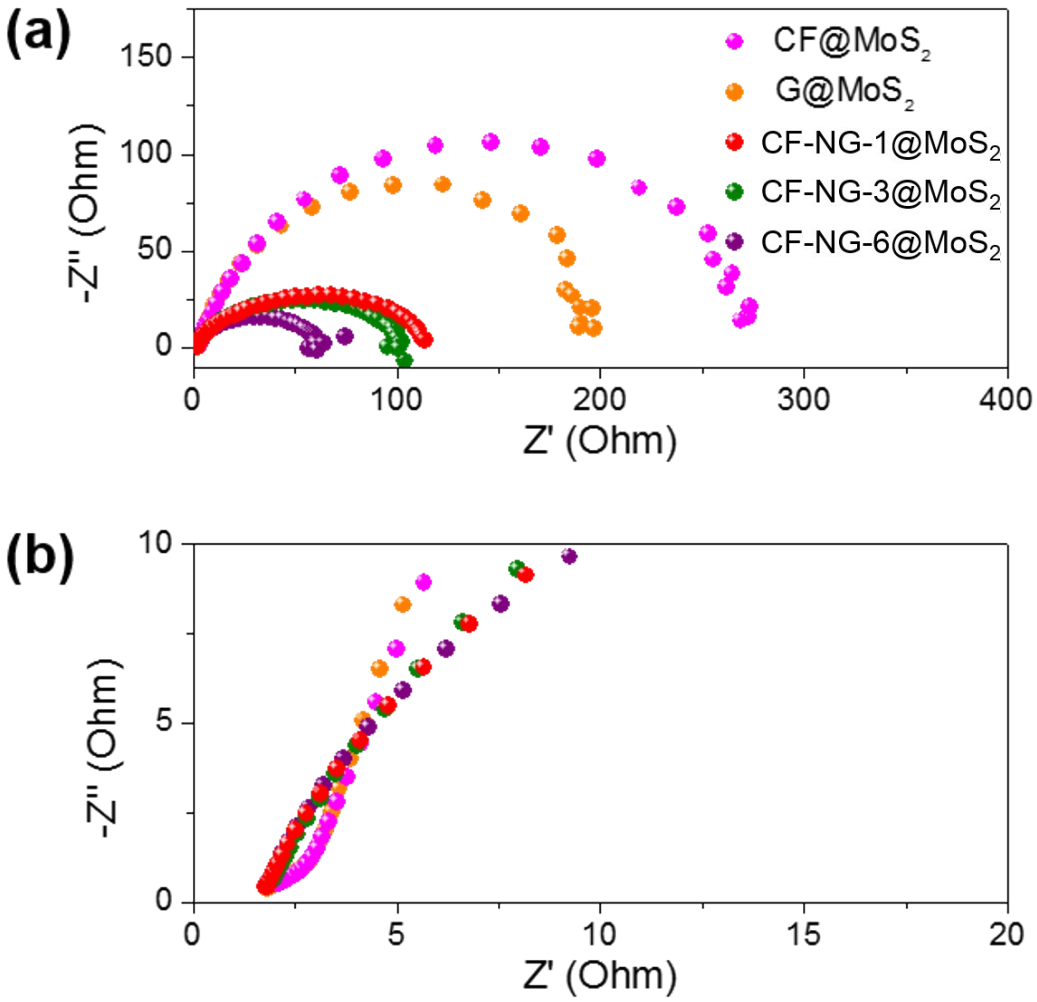

Fig. S8 (a) Nyquist plots of electrochemical impedance spectroscopy (EIS) results for MoS_2 based samples (b) enlarged image for comparing series resistance.

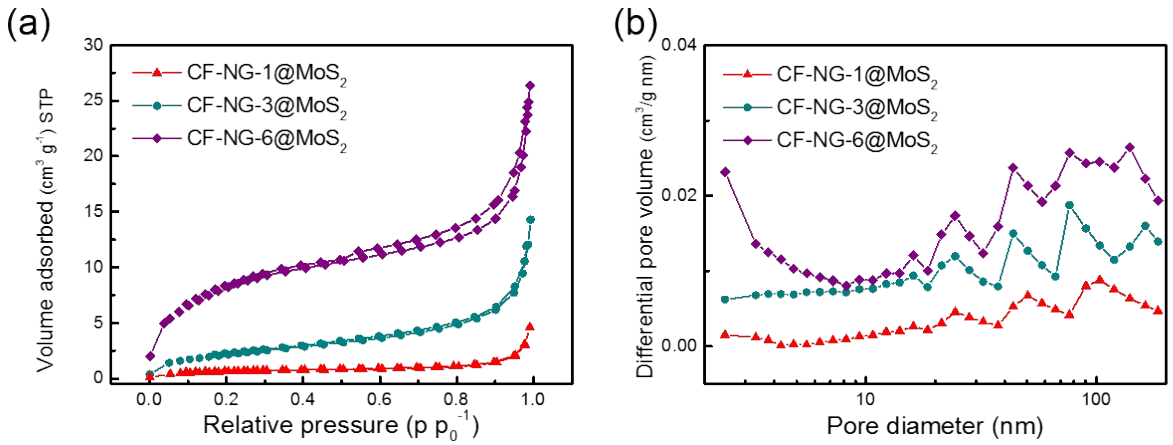

Fig. S9 (a) N_2 adsorption and desorption isotherm and (b) pore size distribution of the CF-NG@MoS_2 composites.

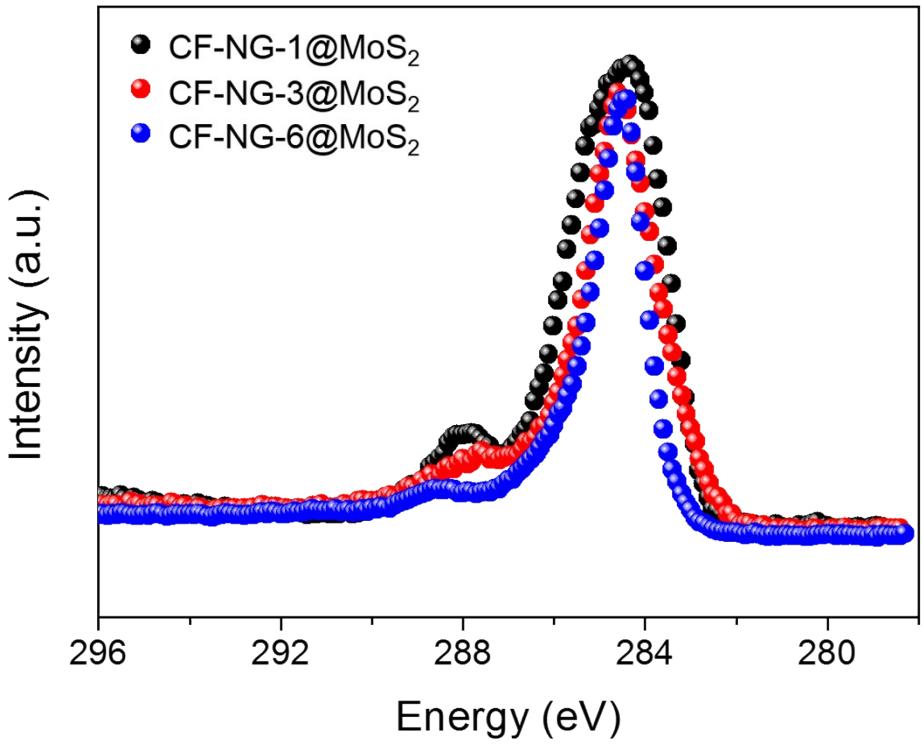

Fig. S10 C 1s regions of the CF-NG@MoS_2 composites XPS spectrum.

Table S1. Composition (wt %) of the CF-NG and CF-NG-6@MoS_2 resulted from Elemental Analyzer.

Sample	C	H	N	S
CF-NG	60.62	0.84	16.49	7.3
CF-NG-6@MoS_2	31.35	1.39	5.28	24.16

Table S2. Comparison of the HER performance of some reported MoS_2-based catalysts in the literature.

Catalysts	**Tafel slope (mV dec^{-1})**	**Current density (mA cm^{-2})** *η = overpotential	**References**
CF-NG@MoS_2	**53**	**10 (at η= 171 mV)**	**Our work**
MoS_2 QD/rGO	63	10 (at η= 64 mV)	[s1]
MoS_2/CNT/Graphene	100	10 (at η= 255 mV)	[s2]
MWCNT@Cu@MoS_2	62	85.5 (at η= 300 mV)	[s3]
MoS_2/Carbon aerogel	59	9.68 (at η= 200 mV)	[s4]
Graphene/MoS_2 flower	95	30 (at η= 300 mV)	[s5]

Reference

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