Supplementary Information

Calculation of Active Site Density:

The method used by *Benck et al.* was adopted to calculate active site density of the samples [1]. The calculated specific capacitance of MoS_2-commercial (0.99 mF/cm^2), MoS_2-synthesized (5.87 mF/cm^2) and MoS_2 grown over CNFs (15.66 mF/cm^2) was used for this calculation. Specific capacitance for a flat surface is generally in the range of 20–60 μF/cm^2. In these calculations, we adopted an average of this range, i.e., 40 μF/cm^2. Roughness factor was calculated using the equation given below:

$$\frac{\#\ surface\ sites\ (catalyst)}{cm^2\ geometric\ area} = \frac{\#\ surface\ sites\ (flat\ surface)}{cm^2\ geometric\ area} \times Roughness\ Factor \qquad (1)$$

Roughness factor of 24.8, 146.8 and 391.5 was calculated for MoS_2-commercial, MoS_2-synthesized, and MoS_2 grown over CNFs, respectively.

For the flat MoS_2, the number of surface sites per cm^2 geometric area of 1.164×10^{15} MoS_2/cm^2 was used [1]. Using the above equation, and value of the number of surface sites per cm^2 geometric area for flat MoS_2 (1.164×10^{15} MoS_2/cm^2) and roughness factor (calculated above), the value of the number of catalytic surface sites for MoS_2-commercial, MoS_2-synthesized and MoS_2 grown over CNFs was estimated to be 2.89×10^{16}, 1.71×10^{17}, and 4.56×10^{17} per cm^2, respectively.

Calculation of Turn over Frequency:

Turnover frequency per site was calculated using following equation [2]

$$TOF\ per\ site = \frac{\#\ total\ hydrogen\ turn\ overs\ per\ cm^2\ geometric\ area}{\#\ surface\ sites\ (catalyst)\ per\ cm^2\ geometric\ area}$$

The total # hydrogen turnover was calculated using the following formula [3]

$$\#_{H_2} = \left(j\frac{mA}{cm^2}\right)\left(\frac{1Cs^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right)\left(\frac{6.022 \times 10^{23}\ H_2\ molecules}{1\ mol\ H_2}\right)$$

$$= 3.12 \times 10^{15}\ \frac{H_2/s}{cm^2}\ per\ \frac{mA}{cm^2}$$

So the *TOF* per site for our samples at an overpotential of 200 mV is calculated using the expression given below:

At η = 200 mV, the TOF for

$$(a)\ For\ MoS_2 - comm,\ TOF = (3.12 \times 10^{15}\ \frac{\frac{H_2}{s}}{cm^2}\ per\ \frac{mA}{cm^2})(0.123\frac{mA}{cm^2})(\frac{1\ cm^2}{2.89 \times 10^{16}\ surface\ sites})$$

$$= 0.013\ \frac{H_2/s}{surface\ site}$$

$$(b)\ For\ MoS_2 - synt,\ TOF = (3.12 \times 10^{15}\ \frac{\frac{H_2}{s}}{cm^2}\ per\ \frac{mA}{cm^2})(1.34\frac{mA}{cm^2})(\frac{1\ cm^2}{1.71\times10^{17}\ surface\ sites})$$

$$= 0.025\ \frac{H_2/s}{surface\ site}$$

$$(c)\ For\ MoS_2 - CNFs,\ TOF = (3.12 \times 10^{15}\ \frac{\frac{H_2}{s}}{cm^2}\ per\ \frac{mA}{cm^2})(7.90\frac{mA}{cm^2})(\frac{1\ cm^2}{4.56\times10^{17}\ surface\ sites})$$

$$= 0.054\ \frac{H_2/s}{surface\ site}$$

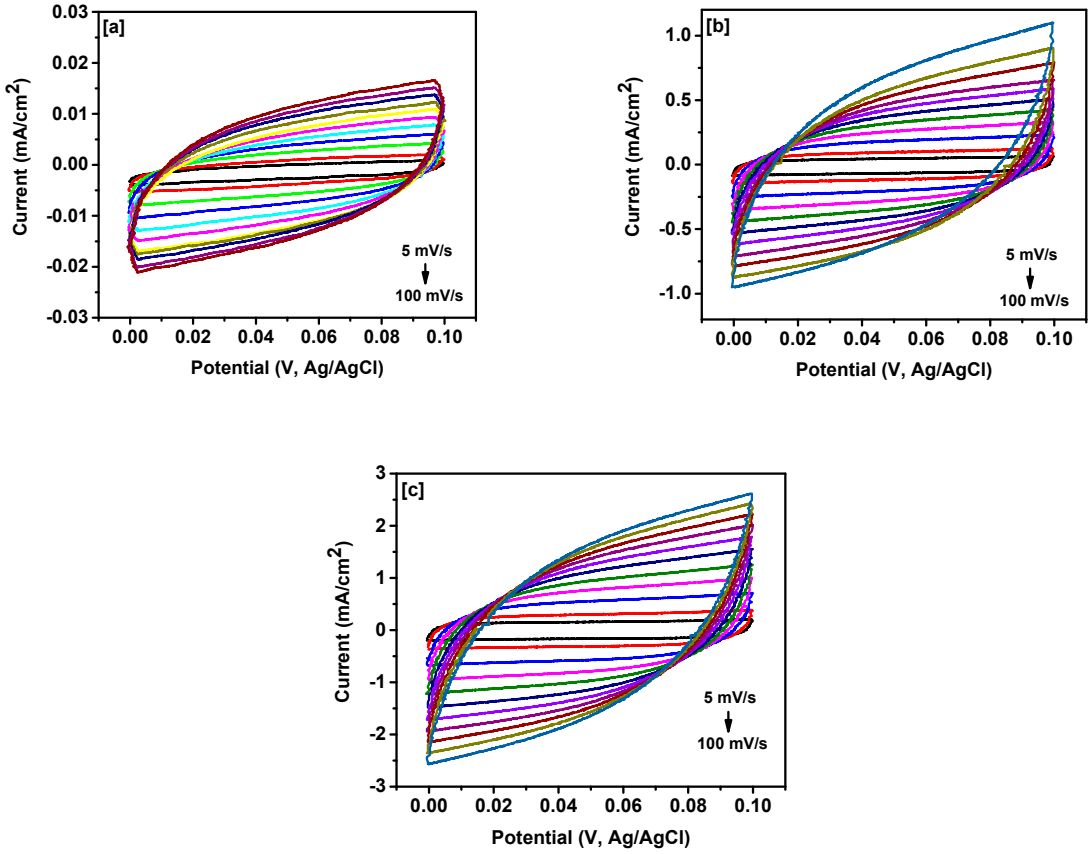

Figure S1. (**a**) CV curves of (**a**) MoS_2-commercial; (**b**) MoS_2-synthesized, and (**c**) MoS_2 grown over CNFs at various scan rates.

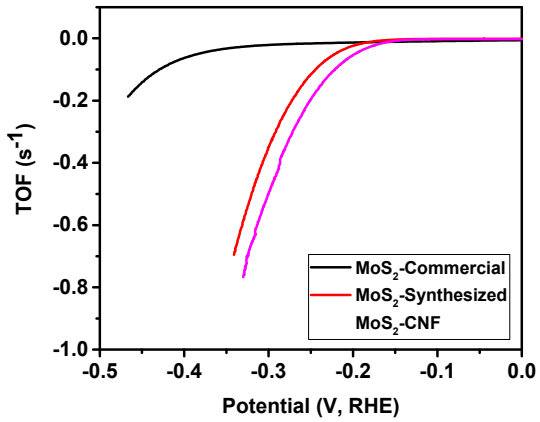

Figure S2. Calculated turnover frequency for MoS_2-commercial, MoS_2-synthesized and MoS_2 grown over CNFs.

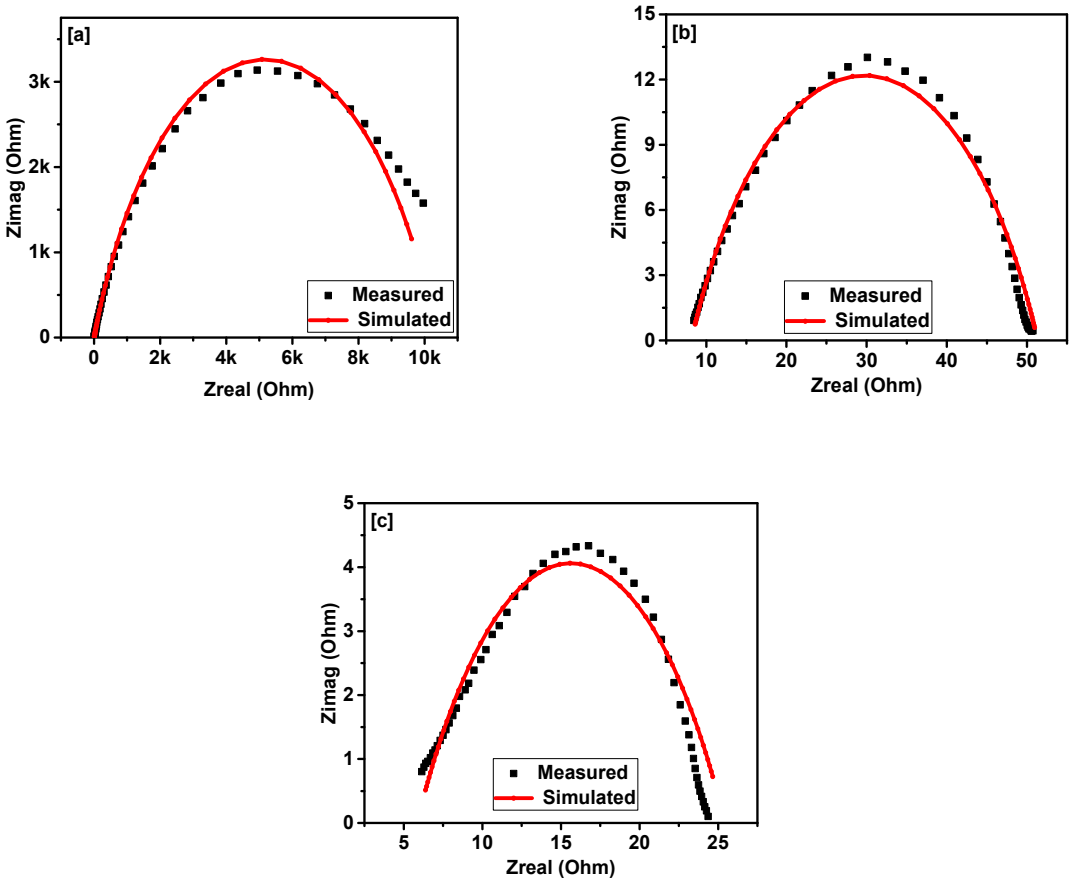

Figure S3. (**a**) Measured and simulated [using R(RQ) equivalent circuit] Nyquist plots for (**a**) MoS_2-commercial; (**b**) MoS_2-synthesized, and (**c**) MoS_2 grown over CNFs at 0.45 V vs. Ag/AgCl.

Table S1. Some important parameters for HER catalysts.

Catalyst	Electrolyte	Onset Potential (V)	Tafel Slope	References
MoS_2 nanosheets	0.5 M H_2SO_4	0.27	115	[2]
MoS_2 dots on Au	0.1 M KOH	0.16	82	[3]
MoS_2 embedded in ordered mesoporous carbon	0.5 M H2SO4	0.12	60–65	[4]
MoS_2/CNT	0.5 M H_2SO_4	~0.12	44.5	[5]
MoO_2 nanobelts@nitrogen self-doped MoS_2 nanosheets	0.5 M H_2SO_4	0.156	47.5	[6]
1T-MoS_2 nanosheets	0.5 M H_2SO_4	~0.100	40	[7]
2H-MoS_2 nanosheets	0.5 M H_2SO_4	~0.200	75–85	[7]
MoS_2/rGO	0.5 M H_2SO_4	0.130	42	[8]
MoS_2 nanoparticles	0.5 M H_2SO_4	-	62	[9]
MoS_2 sponges	0.5 M H_2SO_4	-	185	[10]
MoS_2-carbon cloth	0.5 M H_2SO_4	-	50	[11]
MoS_2-Toray carbon paper	0.5 M H_2SO_4	-	120	[12]
MoS_2NF/rGO paper	0.5 M H_2SO_4	0.19	95	[13]
MoS_2/rGO	0.5 M H_2SO_4	0.100	41	[14]
MoS_2 quantum dot decorated rGO	0.5 M H_2SO_4	-	63	[15]
MoS_2 quantum dots	0.5 M H_2SO_4	0.160	59	[16]
MoS_2 nanosheets on S-doped carbon	0.5 M H_2SO_4	0.06	72	[17]
MoS_2 nanoparticles/CNT-graphene hybrid	0.5 M H_2SO_4	0.140	100	[18]
MoS_2-CNF	**0.5 M H_2SO_4**	**0.145**	**59**	**This work**

Table S2. Electrical properties of various MoS_2 samples.

Sample	Rs (Ohm)	Rct (Ohm)	Q (Faraday)/n
MoS_2-Comm.	12.19	1.03×10^4	3.14×10^{-5}/0.719
MoS_2-Synth.	8.15	4.32×10^1	8.06×10^{-4}/0.655
MoS_2-CNFs	5.85	1.96×10^1	5.16×10^{-3}/0.800

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