Supplementary Information (SI) for Nanoscale Advances.

Electrocatalytic activity of MoP/CNTs Nanohybrid for Water Splitting: A step towards improved HER kinetics

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Supplementary File

Working Electrode Details

The (X-ray Diffraction) XRD pattern of the fresh electrode, as shown in **Figure S1**, indicates that the deposited material is highly crystalline, resembling MoP/CNTs with a hexagonal molybdenum phosphide structure. A prominent peak appears at approximately 45° corresponding to the (100) crystal planes, with a slight peak shift observed, likely due to homogeneous or heterogeneous strain. **Figure S2** presents the XRD pattern of the used electrode, which exhibits no significant changes compared to the fresh electrode. This suggests that the crystal structure of the deposited material remains intact after testing. The dominant peak for the used electrode is also observed around 45° with the (100) crystal plane.

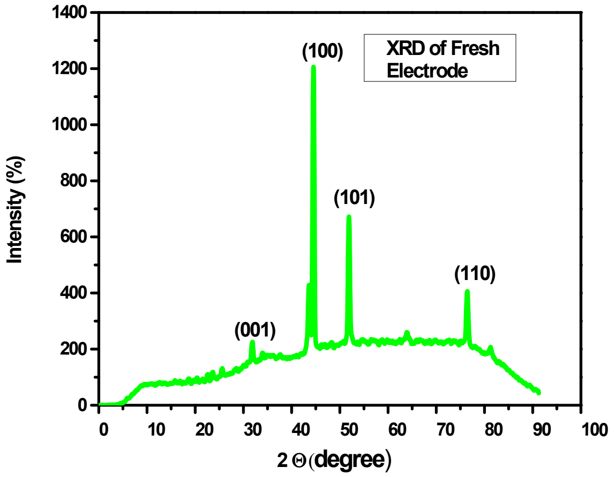

Figure S1: XRD graph for fresh Electrode

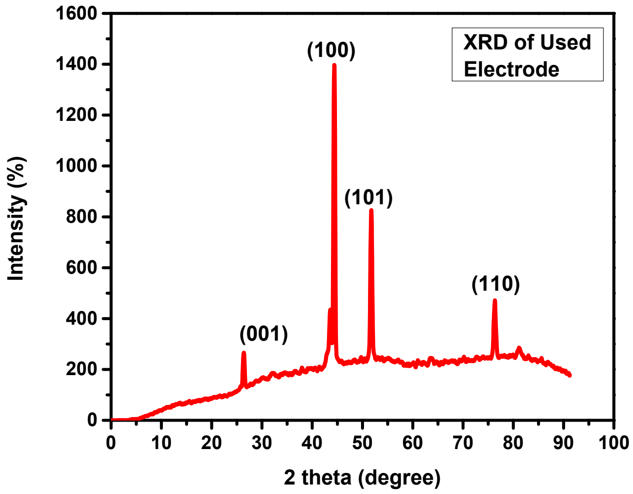

Figure S2 : XRD of used electrode

The Scanning Electron Microscopy (SEM) images of the fresh electrode, presented in Figure 3, demonstrate that the synthesized electrocatalyst is uniformly and completely deposited on the Ni foam electrode. Both vertical and horizontal views confirm the consistent coating of the material across the Ni foam surface. **Figure S3** showcases images at different magnifications, clearly illustrating the deposition of MoP/CNT nanoparticles onto the Ni foam, indicating successful and uniform distribution of the electrocatalyst.In **Figure S4** depicts that the there is still materail present on the surafce of Ni foam but there is some loses also happen in by using different tsetinghteachniques. A comparison of the SEM results before and after the cycling process indicates some degradation and loss of catalyst material from the electrode surface.

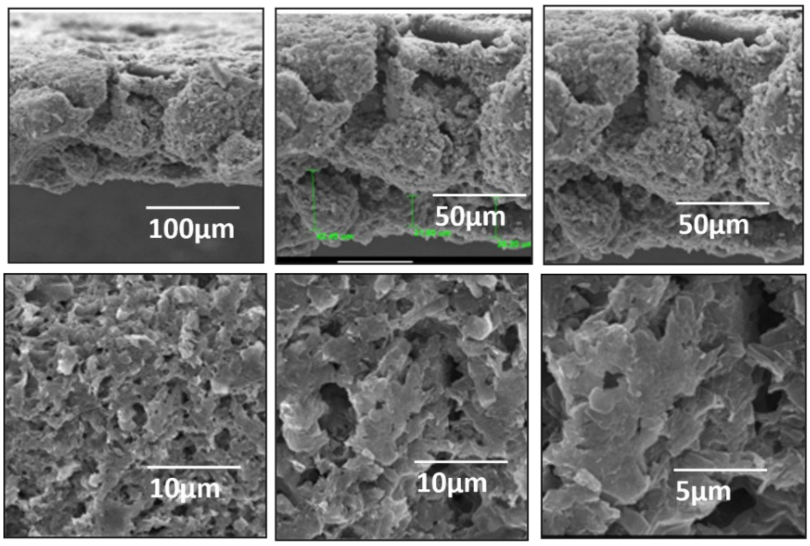

Figure S3 : SEM images for fresh electrode

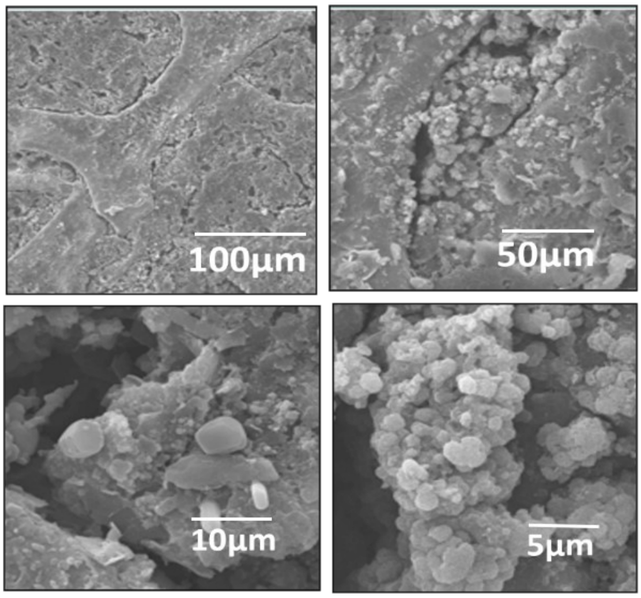

Figure S4 : SEM images for used Electrode

Comparison of HER & OER and CV curve of Maximum CNTs and Optimized CNTs concentration

The CV curves for MoP/CNT hybrids with higher CNT concentrations (140 mg to 260 mg) exhibit poor HER performance, characterized by low current densities and elevated overpotentials. Excessive CNT content leads to the agglomeration of CNTs, which physically blocks the active MoP sites. This reduces the ECSA, as evidenced by the lower current densities in the CV curves as shown in **Fig S5**. The lack of well-defined HER peaks further confirms the limited availability of active sites for proton adsorption and reduction. While CNTs enhance electrical conductivity, an excessive amount disrupts the optimal electronic interaction between MoP and CNTs. This results in inefficient charge transfer, as indicated by the higher overpotentials required to drive the HER. The Tafel analysis would likely show higher Tafel slopes for these samples, reflecting slower reaction kinetics. High CNT concentrations create dense, intertwined networks that hinder the diffusion of protons (H^+) to the active sites and the release of hydrogen gas (H_2). This mass transport limitation is reflected in the suppressed current densities at higher overpotentials. The synergistic interaction between MoP and CNTs, which is critical for enhancing HER performance, is compromised at higher CNT concentrations. The excessive CNT content overshadows the catalytic contribution of MoP, leading to sub-optimal HER activity. The CV data clearly demonstrates that higher CNT concentrations (140 mg to 260 mg) are detrimental to HER performance due to reduced ECSA, inefficient charge transfer, mass transport limitations, and loss of synergistic effects. This underscores the importance of optimizing the CNT concentration to achieve a balance between conductivity, active site exposure, and structural porosity for efficient HER catalysis. The LSV curves for MoP/CNT hybrids with higher CNT concentrations (140 mg, 180 mg, 220 mg, and 260 mg) reveal significantly higher overpotentials (e.g., up to 258 mV) compared to the optimized MoP/CNT (20 mg) sample, which exhibits a much lower overpotential of 81 mV. This trend indicates that increasing the CNT concentration beyond an optimal level (e.g., 20 mg) deteriorates HER performance Excessive CNTs physically obscure the active MoP sites, reducing their availability for proton adsorption and hydrogen evolution

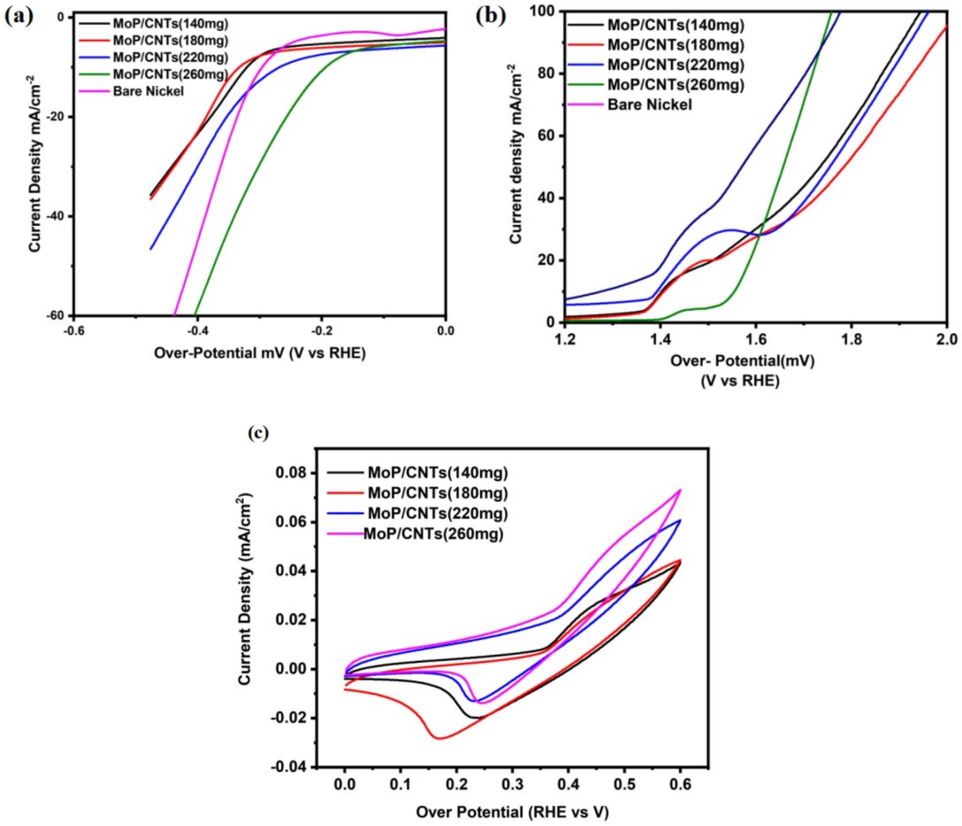

Figure S5 : (a) LSV curves for the hydrogen evolution reaction (HER) and (b) oxygen evolution reaction (OER), (c) cyclic voltammetry (CV) curves of pristine MoP and MoP–CNT hybrid catalysts with CNT loadings ranging from 140 to 260 mg

Kinetics for HER

1. Number of active sites

$$R_{ct} = \frac{RTN_A}{n\,FA\,X\,N}$$

Rct=C*h*arge transfer resistance (o*h*m)

R=Ideal gas constant (8.314 J⁄mol.K)

T=Temperature (298.15 K)

n=no. of electrons transferred in HER (2)

F=Faraday's constant (98485 C/mol)

A=Area of electrode (1cm^2)

N=no. of active sites (cm^{-2})

N$_A$=Avogadro′s number (6.022×10^{23})

Electrocatalyst	Rs(ohm)	Rct (ohm)	ECSA (cm^2)	J$_o$(mA)
MoP	4.2	3.78	2500	6.79
MoP/CNTs (10 mg)	0.035	3.58	2875	7.17
MoP/CNTs (15 mg)	0.0172	2.35	5541.667	10.92
MoP/CNTs (20 mg)	0.015	2.11	6958.33	12.16

For MoP/CNTs (20mg)

Rct = 2.11 o*h*m

$$R_{ct} = \frac{RTN_A}{n\,FA\,\times\,N}$$

$$N = \frac{Rct \times n \times F \times A}{R \times T \times N_A}$$

$$N = \frac{RTN_A}{nFA \times Rct}$$

$$N = \frac{8.314 \times 298.15 \times 6.02 \times 10\text{^}23}{2 \times 96485 \times 1 \times 2.11}$$

$$N = 3.65 \text{ x } 10^{21} \text{ cm}^{-2}$$

2. Reaction rate constant (k)

$$k = \frac{TOF}{N \times [H^+]}$$

$$k = \frac{1.87 \times 10^{-7}}{3.65\, x\, 10^{21} \times [1 \times 10^{-14}]}$$

$$k = 4.96 \times 10^{-15} \text{ mol / m}^3\text{.s}$$

3. Rate of HER

$$\textbf{Rate of HER} = \frac{TOF \times N \times [H^+]}{n \times M}$$

$$= \frac{1.82 \times 10^{-7} \times 3.65 \times 10^{21} \times 1 \times 10^{-14}}{2 \times 0.042}$$

$$\text{Rate} = 79.3 \frac{mol\, H_2}{g\ of\ catalyst\ .s}$$

For MoP/CNTs (15mg)

1. Number of active sites

Rct = 2.35 o*h*m

$$R_{ct} = \frac{RTN_A}{nFA \times N}$$

$$N = \frac{Rct \times n \times F \times A}{R \times T \times N_A}$$

$$N = \frac{RTN_A}{nFA \times Rct}$$

$$N = \frac{8.314 \times 298.15 \times 6.02 \times 10\text{^}23}{2 \times 96485 \times 1 \times 2.35}$$

$$N = 3.2 \text{ x } 10^{21} cm^{-2}$$

2. Reaction rate constant (k)

$$k = \frac{TOF}{N \times [H^+]}$$

$$k = \frac{1.87 \times 10^{-7}}{3.2\, x\, 10^{21} \times [1 \times 10^{-14}]}$$

$$k = 5.84 \times 10^{-15} \text{ mol} / m^3.s$$

3. Rate of HER

$$\textbf{Rate of HER} = \frac{TOF \times N \times [H^+]}{n \times M}$$

$$= \frac{1.87 \times 10^{-7} \times 3.2 \times 10^{21} \times 1 \times 10^{-14}}{2 \times 0.042}$$

$$\text{Rate} = 71.2 \frac{mol\, H_2}{g\ of\ catalyst\ .s}$$

For MoP/CNTs (10mg)

1. **Number of active sites**

Rct = 3.58 o*h*m

$$R_{ct} = \frac{RTN_A}{nFA \times N}$$

$$N = \frac{Rct \times n \times F \times A}{R \times T \times N_A}$$

$$N = \frac{RTN_A}{nFA \times Rct}$$

$$N = \frac{8.314 \times 298.15 \times 6.02 \times 10\text{^}23}{2 \times 96485 \times 1 \times 3.58}$$

$N = 2.16 \text{ x } 10^{21}\ \mathrm{cm}^{-2}$

2.Reaction rate constant (k)

$$k = \frac{TOF}{N \times [H^+]}$$

$$k = \frac{1.87 \times 10^{-7}}{2.16\, x\, 10^{21} \times [1 \times 10^{-14}]}$$

$k = 9.81 \text{ x } 10^{-15}\ \mathrm{mol / m^3.s}$

3.Rate of HER

$$\textbf{Rate of HER} = \frac{TOF \times N \times [H^+]}{n \times M}$$

$$= \frac{2.12 \times 10^{-7} \times 2.16 \times 10^{21} \times 1.0 \times 10^{-14}}{2 \times 0.042}$$

$$\text{Rate} = 53\ \frac{mol\, H_2}{g\ of\ catalyst\ .s}$$

For Pure MoP

1. **Number of active sites**

Rct = 3.78 o*h*m

$$R_{ct} = \frac{RTN_A}{nFA \times N}$$

$$N = \frac{Rct \times n \times F \times A}{R \times T \times N_A}$$

$$N = \frac{RTN_A}{nFA \times Rct}$$

$$N = \frac{8.314 \times 298.15 \times 6.02 \times 10\text{^}23}{2 \times 96485 \times 1 \times 3.78}$$

$N = 2.04 \text{ x } 10^{21} cm^{-2}$

2.Reaction rate constant (k)

$$k = \frac{TOF}{N \times [H^+]}$$

$$k = \frac{2.14 \times 10^{-7}}{2.04 \, x \, 10^{21} \times [1 \times 10^{-14}]}$$

$k = 1.046 \text{ x } 10^{-14} \text{ mol / } m^3.s$

3.Rate of HER

$$\textbf{Rate of HER} = \frac{TOF \times N \times [H^+]}{n \times M}$$

$$= \frac{2.17 \times 10^{-7} \times 2.04 \times 10^{21} \times 1 \times 10^{-14}}{2 \times 0.042}$$

$$\text{Rate} = 50.9 \frac{mol\, H_2}{g\ of\ catalyst\ .s}$$

Catalyst Mass Loading:

The catalyst mass loading on the working electrode was carefully controlled during electrode preparation. A known amount of catalyst ink was drop-cast onto the electrode surface and dried under ambient conditions to ensure uniform coverage.

The mass loading was calculated using the following relation:

$$\text{Catalyst loading (mg cm}^{-2}\text{)} = \frac{mcat}{A\ electrode}$$

where m_{cat} is the total mass of catalyst deposited on the electrode (mg), and $A_{electrode}$ is the geometric surface area of the working electrode (cm^2). For the present study, 42 **mg** of catalyst was deposited on a working electrode with an effective geometric area of 1 **cm^2**, resulting in a catalyst mass loading of:

$$\text{Catalyst loading} = 0.42\ \text{mg cm}^{-2}$$

This mass loading was kept constant for all electrochemical measurements to ensure reliable comparison of catalytic activity.

Mass Normalized Activity

Figure S6 compares the mass activity (A g^{-1}) of pristine MoP and MoP/CNT hybrid catalysts with varying CNT contents (10, 15, and 20 mg) as a function of applied potential vs. RHE. The mass activity was calculated by normalizing the measured current density to the catalyst loading, thereby providing an intrinsic assessment of catalytic efficiency independent of mass effects [1].

Pristine MoP exhibits relatively low mass activity over the entire potential window, reaching only 40 A g^{-1} at 0.10 V and 57 A g^{-1} at 0.15 (V vs. RHE), which can be attributed to its limited electronic conductivity and partial utilization of active sites. Upon integration with CNTs, a pronounced enhancement in mass activity is observed, highlighting the critical role of the conductive carbon scaffold.

Specifically, the MoP/CNTs (10 mg) hybrid delivers a mass activity of 65 A g^{-1} at 0.10 V, increasing to 95 A g^{-1} at 0.15 V, representing nearly a twofold improvement compared to bare MoP. A further increase in CNT content to 15 mg leads to a substantial rise in mass activity, reaching 100 A g^{-1} at 0.10 V and 140 A g^{-1} at 0.15 V. Notably, the MoP/CNTs (20 mg) catalyst exhibits the highest mass activity across the entire potential range, achieving 170 A g^{-1} at 0.10 V and exceeding 230 A g^{-1} at 0.15 V, corresponding to an approximately fourfold enhancement relative to pristine MoP.

The systematic increase in mass activity with increasing CNT loading suggests progressively improved charge-transfer kinetics, enhanced dispersion of MoP active sites, and more effective utilization of catalyst mass. Moreover, the monotonic increase in mass activity with applied potential reflects accelerated reaction kinetics and reduced transport limitations. Collectively, these results demonstrate that optimizing the MoP–CNT interfacial architecture is decisive for maximizing intrinsic, mass-normalized electrocatalytic performance

$$M_{\text{normalized}} = \frac{I\,(mA/cm-2)}{mcatalyst}$$

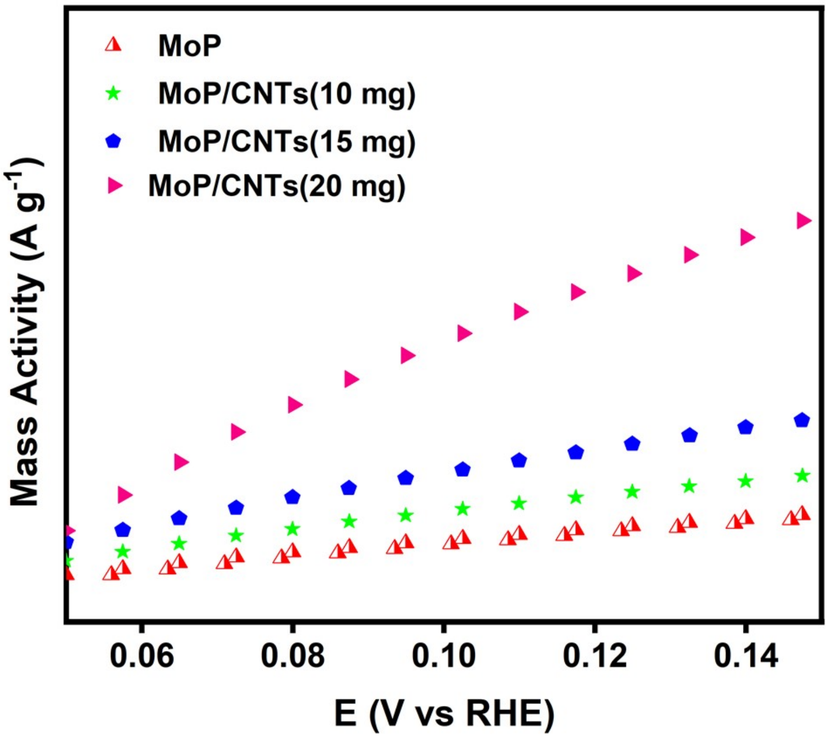

Figure S6 : CV curve after mass normalization

ECSA-Normalized Electrocatalytic Activity

The electrochemical active surface area (ECSA) was estimated from double-layer capacitance (Cdl) measurements obtained via cyclic voltammetry in a non-faradaic potential window (0.05– 0.15 V vs. RHE). CVs were recorded at scan rates ranging from 10 to 100 mV s^{-1}. The capacitive current was extracted at 0.10 V vs. RHE, where no faradaic contribution was observed. The slope of the linear fit between capacitive current and scan rate yielded the double-layer capacitance (Cdl) from **Figure S7.**

$$\textbf{ECSA}= \frac{Cdl}{Cs}$$

where I is the current and ECSA represents the electrochemically active surface area of the catalyst.

Cs = 0.00004 F cm^{-2}

Table 1: ECSA calculation

Sample	Cdl (F cm^{-2})	ECSA = Cdl / Cs (cm^2)
MoP	0.10	2500
MoP/CNTs (10 mg)	0.115	2875
MoP/CNTs (15 mg)	0.2217	5541.7
MoP/CNTs (20 mg)	0.2783	6958.3

The resulting ECSA-normalized activity is expressed in units of **mA cm^{-2} (ECSA)**.

$$j_{ECSA}= \frac{I\ (mA/cm-2)}{ECSA}$$

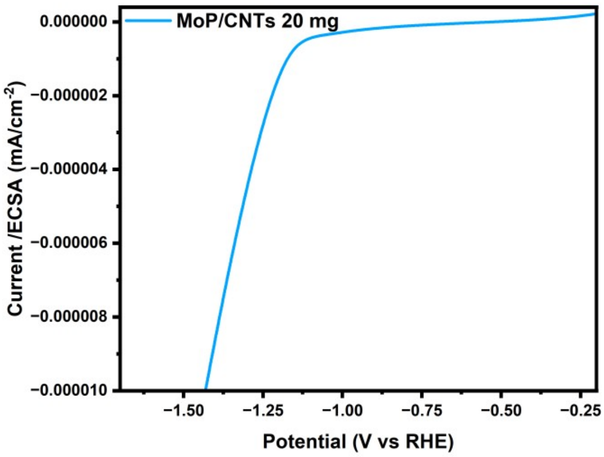

Figure S7: LSV curve after ECSA normalization

References

1. Sub-1.1 nm ultrathin porous CoP nanosheets with dominant reactive {200} facets: a high mass activity and efficient electrocatalyst for the hydrogen evolution reaction.