Supplementary Information

Unique Hybrid Ni$_2$P/MoO$_2$@MoS$_2$ Nanomaterials as Bifunctional Non-noble-metal Electro-Catalysts for Water Splitting

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Figure S1. Optical photograph of Ti foil (left), NiMoO$_4$/Ti (middle) and NiMoO-SP/Ti (right).
Figure s2. Physical characterization of NiMoO-S/Ti. Low (a) and high magnification (b) SEM images; Low (c) and high (d) magnification TEM images.
Figure s3. Physical characterization of NiMoO-P/Ti. Low (a) and high magnification (b) SEM images; Low (c) and high (d) magnification TEM images.

Figure s4. XRD patterns of Ti foil, NiMoO-S/Ti (a) and NiMoO-P/Ti (b).
Figure s5. Line-scan EDX spectra of NiMoO-SP (a), HAADF (b), BF_DF(c) and EDS mapping of NiMoO-SP (d-i).

Figure s6. Polarization of NiMoO-SP/Ti served as both cathode and anode electrocatalysts (NiMoO-SP/Ti catalyst couple) in a two electrode configuration at a scan rate of 5 mV·s⁻¹ in 1.0 M KOH (inset shows corresponding chronopotentiometric curve of the NiMoO-SP/Ti catalyst couple at a current density of 10 mA·cm⁻² for 10 h).
Figure s7. Scan rate dependence of the current densities of NiMoO-S, NiMoO-P and NiMoO-SP at 0.2 V vs RHE.

Turnover frequency calculations

The specific capacitance can be transformed into an electrochemically active surface area (ECSA) based on the specific capacitance value of 1 cm$^2$ of standard flat surface. The specific capacitance for 1 cm$^2$ of a flat surface is in the range of 20-60 μF cm$^{-2}$. 40 μF cm$^{-2}$ is generally to be used for calculations of TOF as a moderate value. The calculation process is according to reference 1,2

**Calculated electro-chemical active surface area:**

$A_{ECSA} = \text{Specific capacitance}/\text{40 μF cm}^{-2}\text{ per cm}^2_{\text{ECSA}} = 1.16 \times 10^3 \text{ cm}^2$

**Turnover Frequency Calculations.**

To calculate the per-site turnover frequency (TOF), the following formula is used:

$\text{TOF} = \frac{\text{(number of total hydrogen turnovers/cm}^2\text{ of geometric area)}}{\text{(number of active sites/cm}^2\text{ of geometric area)}}$

The total number of hydrogen turnovers was calculated from the current density as follows:

$\text{Number of H}_2 = \left[ j (\text{mA/cm}^2) \right]*[(1 \text{ C s}^{-1})/(1000 \text{ mA})]*[(1 \text{ mol of e}^-)/(96485.3 \text{ C})] * [(1 \text{ mol of H}_2)/(2 \text{ mol of e}^-)]* [(6.022 \times 10^{23} \text{ H}_2 \text{ moleculars})/(1 \text{ mol H}_2)] = 3.12 \times 10^{15} \text{ (s}^{-1}\text{ cm}^{-2}) \text{ per (mA cm}^{-2})$

**Calculated active sites per real surface area of active materials:**

Ni$_2$P (PDF card No. #03-0953) unit cell: $Z=3$, Volume= 100.2 Å$^3$; Contains 6 Ni and 3 P atoms

MoS$_2$ unit cell (PDF card No. #37-1429): $Z=2$, Volume= 106.4 Å$^3$; Contains 2 Mo and 4 S atoms

Active sites Ni$_2$P = [(9 atoms per unit cell)/(100.2 Å$^3$ per unit cell)] = 2.006$\times$10$^{15}$ * atoms cm$^{-2}_{\text{real}}$

Active sites MoS$_2$ = [(6 atoms per unit cell)/(106.4 Å$^3$ per unit cell)] = 1.471$\times$10$^{15}$ * atoms cm$^{-2}_{\text{real}}$

**TOF Calculations of Ni$_2$P-MoS$_2$ hybrid:**
Since the surface sites of Ni$_2$P and MoS$_2$ are different, the TOF for Ni$_2$P-MoS$_2$ are roughly calculated based on the average value of surface sites of Ni$_2$P and MoS$_2$. Therefore, the plot of current density can be converted into a TOF plot according to:

$$\text{TOF}_{\text{NiMoO-SP}} = \frac{[3.12 \times 10^{15} \text{ (s}^{-1} \text{ cm}^{-2}) \text{ per (mA cm}^{-2})]/ [\text{active surface sites} \times \text{ECSA}]}{[j]}$$

**Figure s8.** TOF curves of NiMoO-SP.

**Faradaic efficiency**

The Faraday efficiency of hydrogen evolution reaction (FE$_{\text{HER}}$) was obtained according to the equation:

$$\text{FE}_{\text{HER}} = \frac{n_{\text{H}_2} \times 2 \times F}{Q \times 100\%}$$

where $n_{\text{H}_2}$ was the amount of H$_2$ produced from HER, F was Faradaic constant and Q was the total charge input on the working electrode.

**Figure s9.** Chronoamperometric curves obtained at the -0.1 V vs RHE for quantification of hydrogen.

When 50 C of charge passed through the working electrode, the amount of obtained H$_2$ was detected by GC, which was 257.29 μmol.

$$\text{FE}_{\text{HER}} = \frac{(257.29 \times 10^{-6} \text{ mol} \times 2 \times 96485 \text{ C} \cdot \text{mol}^{-1})}{50 \text{ C} \times 100\%} = 99.3\%$$
Gas chromatography data were obtained using an Agilent (7820 A) gas chromatography system equipped with a HP-plot molecular sieve (5 Å) column and a thermal conductivity detector (TCD). H₂ was detected using a long (24 m length) column 4848 with a carrier with N₂ carrier gas.

**Figure s10.** Chronoamperometric curves obtained at the rotating Pt ring GC disc electrode for quantification of oxygen.

The Faraday efficiency of oxygen evolution reaction was 99.6% which was obtained according to the previous literature:\(^3\)

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\text{FE}_{\text{OER}} = j_{\text{ring}} / (C_e \cdot j_{\text{disk}})
\]

where \(j_{\text{disk}}\) is the current density on the disk electrode. \(j_{\text{ring}}\) is the collection current density on the Pt ring electrode at a constant potential of 0.4 V vs RHE. \(C_e\) is the oxygen collection co-efficiency (~0.28) for this type of electrode configuration.
**Figure s11.** SEM image of NiMoO-SP after 40 h electrolysis for OER in 1 M KOH solution.

**Figure s12.** EDS spectra of NiMoO-SP after 40 h electrolysis for OER in 1 M KOH solution.
Figure s13. XRD patterns of Ti and NiMoO-SP before and after 40 h electrolysis for OER in 1 M KOH solution.