Supplementary Information

Unique Hybrid Ni₂P/MoO₂@MoS₂ Nanomaterials as Bifunctional Non-noble-metal Electro-Catalysts for Water Splitting

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Figure s1. Optical photograph of Ti foil (left), NiMoO₄/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 chronopoteniometric 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 cm² of standard flat surface. The specific capacitance for 1 cm² of a flat surface is in the range of 20-60 μ F cm⁻². 40 μ F cm⁻² is generally to be used for calculations of TOF as a moderate value. The calculation process is according to reference 1.^{1, 2}

Calculated electro-chemical active surface area:

 A_{ECSA} = Specific capacitance/ 40 μ F cm⁻² per cm²_{ECSA} = 1.16*10³ cm²

Turnover Frequency Calculations.

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

TOF= (number of total hydrogen turnovers/cm² of geometric area)/(number of active sites/cm² of geometric area)

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

Number of $H_2=[j (mA/cm2)]*[(1 C s^{-1})/(1000 mA)]*[(1 mol of e^{-})/(96485.3 C)] * [(1 mol of H_2)/(2 mol of e^{-})]* [(6.022*10^{22} H_2 moleculars)/(1 mol H_2)] = 3.12*10^{15} (s^{-1} cm^{-2}) per (mA cm^{-2})$

Calculated active sites per real surface area of active materials:

Ni₂P (PDF card No. #03-0953) unit cell: Z= 3, Volume= 100.2 Å³; Contains 6 Ni and 3 P atoms

MoS₂ unit cell (PDF card No. #37-1429): Z= 2, Volume= 106.4 Å³; Contains 2 Mo and 4 S atoms

Active sites Ni₂P = [(9 atoms per unit cell)/ (100.2 Å³ per unit cell)] = $2.006*10^{15}$ * atoms cm⁻²_{real}

Active sites $MoS_2 = [(6 \text{ atoms per unit cell})/(106.4 \text{ Å}^3 \text{ per unit cell})] = 1.471 \times 10^{15} \times 10^{15} \text{ atoms cm}^{-2} \text{ real}$

TOF Calculations of Ni₂P-MoS₂ hybrid:

Since the surface sites of Ni_2P and MoS_2 are different, the TOF for Ni_2P -MoS₂ are roughly calculated based on the average value of surface sites of Ni_2P and MoS_2 . Therefore, the plot of current density can be converted into a TOF plot according to:

 $TOF_{NiMoO-SP} = [3.12*10^{15} (s^{-1} cm^{-2}) per (mA cm^{-2})] / [active surface sites*A_{ECSA}]*[j]$



Figure s8. TOF curves of NiMoO-SP.

Faradaic efficiency

The Faraday efficiency of hydrogen evolution reaction (FE_{HER}) was obtained according to the equation:

 $FE_{HER} = n_{H2} * 2*F/Q*100\%$

where n_{H2} 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 μ mol.

 $FE_{HER} = (257.29 \times 10^{-6} \text{ mol} \times 2 \times 96485 \text{ C} \cdot \text{mol}^{-1})/50C \times 100\% = 99.3\%$

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). H_2 was detected using a long (24 m length) column 4848 with a carrier with N_2 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

$$FE_{OER} = j_{ring} / (C_e * j_{disk})$$

where j_{disk} is the current density on the disk electrode. j_{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.

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- 2. J. Kibsgaard and T. F. Jaramillo, *Angewandte Chemie International Edition*, 2014, **53**, 14433-14437.
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