Electronic Supplementary Information

Self-Supported NiMoP₂ nanowires on carbon cloth as an efficient and durable electrocatalyst for overall water splitting

Xu-Dong Wang, Hong-Yan Chen, Yang-Fan Xu, Jin-Feng Liao, Bai-Xue Chen, Hua-Shang Rao, Dai-Bin Kuang* and Cheng-Yong Su

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, Lehn Institute of Functional Materials, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, P. R. China. * Corresponding author. E-mail address: kuangdb@mail.sysu.edu.cn.



Fig. S1 SEM images for MoO_3 (a), MoP (b), NiO (d) and Ni_5P_4 (e); XRD patterns for MoP (c) and Ni_5P_4 (f).



Fig. S2 The XRD patterns of NiMoO₄ NW/CC and NiMoP₂ NW/CC.



Fig. S3 The XPS patterns for NiMoP₂ NW/CC.



Fig. S4 Cyclic voltammograms in the region of 0.13-0.4 V vs. RHE at various scan

rates and the corresponding linear fitting of the capacitive currents *vs.* scan rates to estimate the Cdl: (a) Ni_5P_4 (b) MoP and (c) $NiMoP_2$; (d) The capacitive currents were measured at 0.265 V *vs.* RHE plotted as a function of scan rate.

The specific capacitance can be converted into an electrochemically active surface area (ECSA) using the specific capacitance value for a flat standard with 1 cm² of real surface area. The specific capacitance for a flat surface is generally found to be in the range of 20-60 μ F cm⁻².¹⁻⁴ In the following calculations of TOF, we assume 40 μ F cm⁻² as a moderate value.

Calculated electrochemical active surface area:

$$A_{ECSA} = \frac{\text{specific capacitance}}{40 \ \mu F \ cm^{-2} \ per \ cm^{2}_{ECSA}}$$

Turnover Frequency Calculations.

To calculate the per site turnover frequency (TOF), we used the following formula:²

$$TOF = \frac{number of total hydrogen turnovers/cm2 of geometric area}{number of active sites/cm2 of geometric area}$$

The total number of hydrogen turnovers was calculated from the current density according to:⁵

no. of
$$H_2 = \left(j\frac{mA}{cm^2}\right) \left(\frac{1C \text{ s}^{-1}}{1000mA}\right) \left(\frac{1\text{mol of } \text{e}^{-}}{96485.3 \text{ C}}\right) \left(\frac{1\text{ mol of } H_2}{2\text{mol of } \text{e}^{-}}\right) \left(\frac{6.022 \times 10^{22} \text{ H}_2\text{moleculars}}{1 \text{ mol } H_2}\right)$$

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

On the basis of the electrochemical active surface area together with the unit cell (volume of 28.71 Å³) of the MoP crystal structure in the case of Ni₅P₄ and NiMoP₂, a similar approach was used to estimate TOF for Ni₅P₄ and NiMoP₂. Active sites per real surface area:

Active sites
$$_{MOP} = \left(\frac{2 \text{ atom/unit cell}}{28.71 \text{ Å}^3 / \text{unit cell}}\right)^{\frac{2}{3}} = 1.693 \times 10^{15} \times \text{ atoms cm}_{real}^{-2}$$

Active sites $_{Ni_5P_4} = \left(\frac{36 \text{ atom/unit cell}}{438.51 \text{ Å}^3 / \text{unit cell}}\right)^{\frac{2}{3}} = 1.889 \times 10^{15} \times \text{ atoms cm}_{real}^{-2}$
Active sites $_{NiMOP_2} = \left(\frac{8 \text{ atom/unit cell}}{107.68 \text{ Å}^3 / \text{unit cell}}\right)^{\frac{2}{3}} = 1.177 \times 10^{15} \times \text{ atoms cm}_{real}^{-2}$
TOF = $\frac{(3.12 \times 10^{15} \frac{\text{H}_2/\text{s}}{\text{cm}^2} \text{ per } \frac{\text{mA}}{\text{cm}^2})}{\text{surface sites } \times A_{\text{ECSA}}} \times |\mathbf{j}|$

TOF of Ni₅P₄ is 1.44 s⁻¹ at the overpotential of 0.2 V vs. RHE, while the TOF of the

NiMoP₂ is 0.15 s⁻¹ which is close to that of the MoP (0.19 s⁻¹).



Fig. S5 SEM images (a-c) of NiMoP₂ after 24h stability measurement at -155 mV (RHE), none iR corrected.



Fig. S6 XRD patterns and XPS for NiMoP₂ before and after 24h stability

measurement at -155 mV (RHE), none iR corrected.



Fig. S7 (a) Polarization data for NiMoP₂ (iR corrected) in 1 M KOH electrolytes at 2 mV s⁻¹, along with plot of Pt/C for comparison; (b) Corresponding Tafel plots.



Fig. S8 SEM and TEM images for NiMoP₂ NW/CC after 24h OER stability measurement at 10 mA cm⁻², in 1 M KOH solution.



Fig. S9 XPS patterns for NiMoP₂ after 24h OER stability measurement at 10 mA cm⁻², in 1 M KOH solution.



Fig. S10 (a) Polarization data of water electrolysis for NiMoP₂ \parallel PE-NiMoP₂ (None iR corrected) in 1.0 M KOH electrolytes at 2 mVs⁻¹; (b) Chronopotentiometric curve of water electrolysis for NiMoP₂ \parallel PE-NiMoP₂ with a constant current density of 10 mA cm⁻² (None iR corrected).



Fig. S11 The amount of H_2 and O_2 from theoretically calculation and experimentally measurement as the function of time for the overall water splitting of NiMoP₂ || PE-NiMoP₂.

Table S1	Composition	of the NiMoP ₂	catalyst.

Catalyst	Ni (mg/L)	Mo (mg/L)	P (mg/L)
NiMoP ₂	0.196	0.286	0.193

The result reveals that the atomic ratio of Ni: Mo : P is 1.1 : 1 : 2.1, determined by ICP-AES spectroscopy.

Table S2 Composition of the PE-NiMoP₂ catalyst.

Catalyst	Ni (mg/L)	Mo (mg/L)	P (mg/L)
PE-NiMoP ₂	0.213	0.156	0.152

The result reveals that the atomic ratio of Ni: Mo : P is 2.2 : 1 : 3, determined by ICP-AES spectroscopy.

Table S3 Comparison of HER and OER performance for $NiMoP_2$ and $NiMoO_4$ nanowires on carbon cloth ($NiMoP_2 NW/CC$, $NiMoO_4 NW/CC$) with other reported electrocatalysts.

Catalyst	Water splitting test	Current density (j, mA cm ⁻²)	Overpotential at corresponding <i>j</i> (mV)	Electrolyte	Ref.
NiMoP ₂ NW/CC	HER	100	195	0.5 M H ₂ SO ₄	This work
	HER	100	199	1.0 M KOH	
	OER	100	330	1.0 M KOH	
NiMoO ₄ NW/CC	OER	100	400	1.0 M KOH	This work
	HER	100	Ca. 320	1.0 M KOH	Adv. Energy
	OER	100	Ca. 415	1.0 M KOH	1502585
Ni _s S ₂ /Ni foil	HER	100	Ca. 440	1.0 M KOH	J. Am. Chem.
NI ₃ S ₂ /NI foil	OER	20	Ca. 290	1.0 M KOH	14023 - 14026
MoP	HER	100	Ca. 180	0.5 M H ₂ SO ₄	Angew. Chem. Int. Ed. 2016,53, 14433-14437
MoP/CC	HER	100	195	0.5 M H ₂ SO ₄	RSC Adv., 2016, 68568- 68573
MoP	HER	100	Ca. 228	0.5 M H ₂ SO ₄	Adv. Funct. Mater. 2015, 25, 3899-3906
MoP/C	HER	100	Ca.200	0.5 M H ₂ SO ₄	AJAC, 2014, 5, 1200-1213
MoP-CA2	HER	100	Ca. 200	0.5 M H ₂ SO ₄	Adv. Mater. 2014, 26, 5702- 5707
MoP@PC	HER	50	Ca. 205	0.5 M H ₂ SO ₄	Angew. Chem. Int. Ed. 2016,55, 12854-12858
MoP/CF	HER	50	310	0.5 M H ₂ SO ₄	Appl. Catal. B- Environ., 2015, 164, 144-150
MoP	HER	50	Ca. 355	0.5 M H ₂ SO ₄	Adv. Mater, 2016, 28, 1427- 1432
MoP	HER	20	Ca.400	0.5 M H ₂ SO ₄	Appl. Catal. A- Gen., 2016, 524, 134-138

Ni ₁₂ P ₅ nanoparticle	HER	45	200	0.5 M H ₂ SO ₄	ACS Nano 2014, 8, 8121- 8129.
Ni ₃ C/C	OER	100	390	1.0 M KOH	Adv. Mater. 2016, 28, 3326- 3332.
Sub-1 nm NiMoO₄ nanowires	OER	100	Ca. 460	1.0 M KOH	Small, 2016, 12, 1006-1012

Reference:

- 1 D. C. Grahame, Chem. Rev., 1947, 41, 441-501.
- 2 R. Kötz and M. Carlen, *Electrochim. Acta*, 2000, 45, 2483-2498.
- 3 B. E. Conway and B. V. Tilak, *Electrochim. Acta*, 2002, **47**, 3571-3594.
- 4 J. D. Benck, Z. B. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, ACS Catal., 2012, 2, 1916-1923.
- 5 J. Kibsgaard and T. F. Jaramillo, Angew. Chem. Int. Ed., 2014, 53, 14433-14437.

Supplementary Movie 1

This movie shows the overall water splitting reaction was investigated in a twoelectrode configuration employing NiMoP₂ NW/CC and PE-NiMoP₂ NW/CC as cathode and anode in 1.0 M KOH, which driven by a dry battery with a nominal voltage of 1.5 V.