Supporting Information

Heterogeneous Synergetic Effect of Metal-oxide Interfaces for Efficient Hydrogen Evolution in Alkaline Solutions

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Experimental Section

Structural Characterizations

Sample structures were investigated by powder X-ray diffraction (XRD) measurements, using an X-ray diffractometer (Bruker D8 advance), with Cu Ka

radiation (0.15418 nm) at 40 kV and 40 mA. Raman spectra were collected using a Raman system (Thermo Scientific DXR3) with 532 nm laser excitation. The chemical states were investigated by X-ray photoelectron spectroscopy (XPS, ESCA Lab 250Xi), using an Al K α anode (1486.6 eV). The morphologies and structures of the products were characterized using scanning electron microscopy (SEM, JEOL-7800), and transmission electron microscopy (TEM, JEOL JEM-2100). Elemental mapping imagery was collected using a TEM equipped with energy-dispersive X-ray spectroscopy. Hydrogen temperatureprogrammed reduction analysis (H₂-TPR) was performed using a ChemStar (Quantachrome Instruments, USA), with a quartz tube for heating samples.

Electrochemical Measurements

All electrochemical measurements were performed at 25 °C, using an Autolab workstation (PGSTAT 204) in a three-electrode setup, in a hydrogensaturated, 1M KOH solution. Catalysts grown on the NF, graphite rod, and Hg/HgO electrodes were used as the working, counter, and reference electrodes, respectively. All potentials were converted to the RHE potential, using the Nernst equation: E (RHE) = E (Hg/HgO) + 0.059*pH + 0.098. Polarization curves were obtained using linear sweep voltammetry (LSV), at a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was performed, at -200 mV vs RHE, in the frequency range of 10⁻¹ to 10⁵ Hz. The stability of the catalyst was evaluated using chronoamperometry, at -68 mV vs RHE, over a 14 h duration. Cyclic voltammograms (CV)—for calculating double-layer capacitance (C_{dl})—were collected in the potential range of 0.056–0.156 V vs RHE, using scan rates of 5, 20, 40, 60, and 80 mV s⁻¹. The specific capacitance for a flat surface is generally in the range of 20-60 μ F cm⁻², and so in this part, we assumed 60 μ F cm⁻² as the specific capacitance for a smooth surface. The ECSA was calculated by the below function: ECSA = C_{dl}/C_s. TOF was calculated by the following equation:

$$\Gamma OF = \frac{\#_{\text{total hydrogen turn overs / cm}^2 \text{ geometric area}}{\#_{\text{activesites / cm}^2 \text{ geometric area}}$$

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

$$\begin{aligned} \#_{H_2} &= (j\frac{mA}{cm^2}) (\frac{1\ C\ s^{-1}}{1000\ mA}) (\frac{1\ mol\ e^{-}}{96485.3C}) (\frac{1\ mol\ H_2}{2\ mol\ e^{-}}) (\frac{6.022 \times 10^{23}\ H_2\ molecules}{1\ mol\ H_2}) \\ &= 3.12 \times 10^{15} \frac{H_{2/s}}{cm^2} per\frac{mA}{cm^2} \end{aligned}$$

where # is the active sites per real surface area. In this paper, we assumed that the H₂ generated site was WO₂. The coverage of WO₂ was calculated according to the XPS results.

$$\#_{\text{active sites}} = \left(\frac{4 \text{ atoms/unitcell}}{133 \text{ Å}^3/\text{unit cell}}\right)^{2/3}$$

TOF is calculated by the following equation:

$$TOF = \frac{\#_{H_2}}{\#_{active sites}} \times \frac{|j|}{A_{ECSA}}$$



Figure S1. XRD patterns of $Ni_4W_6O_{21}(OH)_2$ and standard crystallographic spectrum of $Ni_4W_6O_{21}(OH)_2$ (JCPDS no. 47-0143). The red line represents the sample grown on the nickel foam, and the black line represents the sample obtained in the reaction solution.

As **Figure S1** shown, the sample on Ni foam and sample powder obtained in the reaction solution both are $Ni_4W_6O_{21}(OH)_2$. The XRD patterns of $Ni_4W_6O_{21}(OH)_2$ on Ni foam contains the Ni peaks, attributed to Ni foam.



Figure S2. SEM images of the R-X samples obtained H₂ annealing at various temperatures, X represents the annealing temperature. (a-b) $Ni_4W_6O_{21}(OH)_2$ – the precursor of R-Ni₁₇W₃/WO₂ samples. (c-d) R-500, $Ni_4W_6O_{21}(OH)_2$ annealed at 500 °C. (e-f) R-600, $Ni_4W_6O_{21}(OH)_2$ annealed at 600 °C. (g-h) R-700,

expressed as $R-Ni_{17}W_3/WO_2$ in this paper, the $Ni_4W_6O_{21}(OH)_2$ annealed at 700 °C. (i-j) R-800, $Ni_4W_6O_{21}(OH)_2$ annealed at 800 °C.



Figure S3. XRD patterns of WO₃•xH₂O and standard crystallographic spectrum of WO₃• $0.12H_2O$ (JCPDS no. 33-1387) and WO₃• $0.5H_2O$ (JCPDS no. 44-0363). The red line represents the sample grown on the nickel foam and the black line represents the sample powder obtained in the reaction solution.



Figure S4. SEM images of the P-X samples obtained by H₂ annealing at various temperatures, X represents the annealing temperature. (a-b) WO₃•xH₂O, containing WO₃• 0.12H₂O and WO₃• 0.5H₂O. (c-d) P-500, WO₃•xH₂O annealed at 500 °C. (e-f) P-600, WO₃•xH₂O annealed at 600 °C. (g-h) P-700, expressed

as P-Ni₁₇W₃/WO₂ in this paper, the WO₃•xH₂O annealed at 700 °C. (i-j) P-800, WO₃•xH₂O annealed at 800 °C.



Figure S5. XPS spectra of WO₃•xH₂O powder obtained in the reaction solution: (a) Ni 2p and (b) W 4f.

The surface composition and chemical states were studied by XPS and the results (**Figure S5**) indicates that even WO₃•xH₂O powder obtained in the solution contains Ni element which is Ni²⁺ state (~855-858 eV). It implies that WO₃•xH₂O was doped with Ni, and to further confirm it, XRD was thoroughly analyzed in **Figure 2a**. There are no other phases detected in the sample, but for WO₃• 0.12H₂O which is hexagonal phase, the peaks of (001) and (002) crystal facets shift to the high angle as shown in **Figure S3**. These results indicate that Ni is the substitution atoms of W in the structure of WO₃• 0.12H₂O, as when the Ni atom with small radius replace the W atom with large radius, the interplanar spacing (d) could decrease. Moreover, the Ni element is Ni²⁺ state. The phenomenon that only the *c* direction lattice parameter in hexagonal

phase has clear decrease has been reported in ZnO sample¹, which indicate that the substitution has a *c*-axis orientation. The Ni element in WO₃• xH_2O originate from the Ni substrate as no Ni(NO₃)₂ was added at first.



Figure S6. Polarization curves of the as prepared precursor $Ni_4W_6O_{21}(OH)_2$, and R-500, R-600, R-700 and R-800 (the precursors annealed at 500 °C, 600 °C, 700 °C and 800 °C, respectively). The Annealing condition: 5% H₂/Ar, 100sccm, 0.1 MPa. The annealing temperatures were hold for 1h, with the ramping rate of 10 °C min⁻¹. The precursor annealed at 700 °C here is denoted as R- $Ni_{17}W_3/WO_2$.



Figure S7. Polarization curves of the as prepared WO₃·xH₂O, and P-500, P-600, P-700 and P-800 (annealed at 500 °C, 600 °C, 700 °C and 800 °C, respectively). Annealing condition: 5% H₂/Ar, 100 sccm, 0.1 MPa. The annealed temperatures were hold for 1 h, with the ramping rate of 10 °C min⁻¹. The precursor annealed at 700 °C here is denoted as P- Ni₁₇W₃/WO₂.



Figure S8. XRD patterns of R-Ni₁₇W₃/WO₂ (red line) on the Ni foam, annealed

by $Ni_4W_6O_{21}(OH)_2$ and P- $Ni_{17}W_3/WO_2$ (black line) on the Ni foam, annealed by $WO_3 \cdot xH_2O$.

To confirm Ni peak in **Figure S8**, the precursor powder obtained in the solution was annealed at the same condition and measured by XRD as shown in **Figure 2a**. No Ni particles was detected in both catalysts, and they only consist of $Ni_{17}W_3$ and WO_2 . It was inferred that the Ni peak is attributed to the Ni foam.



Figure S9. Elemental mapping results of (a) tested area, (b) O+Ni+W, (c) Ni, (d) O and (g) W of P-Ni₁₇W₃/WO₂.

Compared with W or O element, the intensity of Ni element is weak, which suggests the low amount of Ni atoms.



Figure S10. (a) SEM images and (b) XRD pattern of $R-Ni_{17}W_3/WO_2$ after 14 h duration test at the overpotential of -68 mV vs. RHE in 1 M KOH solution.



Figure S11. Electrochemically active surface area measurements of (a) R- $Ni_{17}W_3/WO_2$ and (b) P- $Ni_{17}W_3/WO_2$ in a potential window of 0.056 – 0.156 V vs. RHE with scan rate of 5, 20, 40, 60, 80 mV s⁻¹. (c) Turn over frequency (TOF) of $Ni_{17}W_3/WO_2$ samples calculated by ECSA.



Figure S12. XRD patterns of (a) carbon paper (CP) and Ni₄W₆O₂₁(OH)₂ precursor grown on CP, (b) Ni₁₇W₃/WO₂@CP and E-Ni₁₇W₃/WO₂@CP. (c) Polarization curves of Ni₁₇W₃/WO₂@CP and E-Ni₁₇W₃/WO₂@CP. The scan rate of polarization curve measurement is 5 mV s⁻¹. (d) Electrochemical impedance spectroscopy of Ni₁₇W₃/WO₂@CP and E-Ni₁₇W₃/WO₂@CP. The overpotential applied to the EIS measurements is -200 mV vs. RHE. Electrolyte is 1 M KOH solution. A Hg/HgO and graphitic electrode are as the reference and counter electrode, respectively.

 $Ni_4W_6O_{21}(OH)_2$ precursor on carbon paper (CP) was synthesized through the similar processes as the $Ni_4W_6O_{21}(OH)_2$ precursor on Ni foams, just by replacing the Ni foams with CP (**Figure S12**). Then the precursor was reduced with 5% H₂/Ar gas flow (100 sccm) at 700 °C at a ramping rate of 10 °C min⁻¹

for 1 h to obtain Ni₁₇W₃/WO₂@CP. To investigate the role of Ni₁₇W₃ in the HER activity, Ni₁₇W₃/WO₂@CP was immerged in 0.1 M H₂SO₄ for 12 h to etch the Ni₁₇W₃ particles. After etching, the obtained sample was expressed as E-Ni₁₇W₃/WO₂@CP, as **Figure S12b** shown. Electrochemical tests were applied to Ni₁₇W₃/WO₂@CP and E-Ni₁₇W₃/WO₂@CP. As **Figure S12c** shown, the activity of Ni₁₇W₃/WO₂@CP is lower than that of Ni₁₇W₃/WO₂ on Ni foam, which can be attributed to the conductivity of the substrate. In the other side, after the remove of Ni₁₇W₃, E-Ni₁₇W₃/WO₂@CP. The charge transfer resistance of E-Ni₁₇W₃/WO₂@CP is also larger than that of Ni₁₇W₃/WO₂@CP in **Figure S12d**, suggesting that Ni₁₇W₃ alloy nanoparticles and the metal-oxide interface play an important role in hydrogen evolution reaction.



Figure S13. XRD patterns of R-800 and P-800 samples.

R-800 and P-800 were obtained by annealing the Ni₄W₆O₂₁(OH)₂ and WO₃• xH_2O precursor at 800 °C, respectively. Compared with R-Ni₁₇W₃/WO₂ and P-

 $Ni_{17}W_3/WO_2$ XRD patterns of the catalyst R-800 and P-800 indicated the WO_2 totally transformed into W metal, which suggested that the disappearance of metal-oxide interface.



Figure S14. XPS spectra of (a) Ni $2p_{3/2}$, (b) W 4f, and (c) O 1s of R-Ni₁₇W₃/WO₂

under different cathodic potential of chronoamperometric measurement.



Figure S15. XPS spectra of (a) Ni $2p_{3/2}$, (b) W 4f, and (c) O 1s of P-Ni₁₇W₃/WO₂

under different cathodic potential by chronoamperometric measurement.



Figure S16. Comparative XPS spectra (a) Ni $2p_{3/2}$, (b) W 4f and (c) O 1s of R-Ni₁₇W₃/WO₂ samples dipped in H₂O and 1 M KOH aqueous solution for 30 min, respectively. No potential was applied on the samples.

In Figure S16, the R-Ni₁₇W₃/WO₂ samples were dipped in both DI water and 1 M KOH aqueous solution for 30 min, respectively. Seen in Figure S16a and b, Ni⁰ and W⁰ was oxidized after dipped in water and 1 M KOH aqueous solution. Moreover, it can be seen that the ratio of Ni²⁺/Ni_{total} of the catalyst in the KOH solution was higher than that in the DI water, and both of them were higher than the Ni²⁺/Ni_{total} ratio of as prepared sample. It is speculated that the concentration of OH⁻ in the water or electrolyte is one of the crucial factors to affect chemical oxidation.

Table S1. Transition metal composites for Hydrogen Evolution Reaction

Sample	Tafel slope	Potential	TOF	Electrolyte	Paper
	(mV dec ⁻¹)	@ 10mA	(s⁻¹)		
		cm⁻² (mV)			
Ni ₁₇ W ₃ /WO ₂ @NF	33	48	0.09@50 mV	1М КОН	our
			0.62@100 mV		work
MoO₂@NF	66	55		1М КОН	2
WO₂@NF	43	48		1М КОН	3
MoNi₄/MoO₂@NF	30	15	0.4@15 mV	1M KOH	4
W/WO₂@CP	74.5	297		0.5M	5
				H ₂ SO ₄	
NiWO₄@TM	51	100		1M KOH	6
Ni/NiO@NF	72	145		1M KOH	7
NiO/Ni@CNT	_	135		0.1M KOH	8
NiO _x @BCNTs	119	79		1М КОН	9
MoNi₄/MoO _{3-x} @NF	36	17		1М КОН	10
MoO ₂ -Ni	36.6	58.4		1М КОН	11
Ni-Mo	_	_	0.05@100 mV	2М КОН	12

Mo/MoO ₂	34.4	_	0.004@100	0.5M	13
			mV	H ₂ SO ₄	
Ni ₄ Mo/GNS	66.4	69	0.11@100 mV	1М КОН	14
NiCoP	63.3	102	0.024@100	1М КОН	15
			mV		
NiCo ₂ O ₄	120	185	0.17@100 mV	1М КОН	16
Co-Mo₅N ₆	29	19	0.25@150 mV	1М КОН	17
Pt	30		100@36 mV	0.5M	18
				H ₂ SO ₄	

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