Supporting Information

Accelerating Neutral Hydrogen Evolution with Tungsten Modulated Amorphous Metal Hydroxides

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Experimental Section

Materials. Ni foam (thickness: 1.5 mm, bulk density: 0.23 g cm⁻³) was purchased from Heze Tianyu Technology Development Co., Ltd. Carbon paper (TGP-H-060) was purchased from Alfa Aesar. Cobalt sulphate heptahydrate (CoSO₄·7H₂O), nickel sulfate hexahydrate (NiSO₄·6H₂O), sodium tungstate dehydrate (Na₂WO₄·2H₂O), boric acid (H₃BO₃), sodium gluconate (C₆H₁₁NaO₇), sodium chloride (NaCl), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), nitric acid (HNO₃), hydrogen peroxide (H₂O₂, 30 wt. %), dipotassium hydrogen phosphate (K₂HPO₄), potassium dihydrogen phosphate (KH₂PO₄), and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion (5 wt. % in a mixture of lower aliphatic alcohols and water) was purchased from Sigma-Aldrich. Pt/C (platinum, 5% on carbon, dry) was purchased from Alfa Aesar. All chemicals were used as received without further purification and all aqueous solutions were prepared with ultrapure water (>18.25 MΩ cm) obtained from Millipore system.

Preparation of CoW(OH)_x. Ni foam (2 cm \times 0.5 cm) and carbon paper (2 cm \times 0.5 cm) were used as substrates for the electrodeposition. Before electrodeposition, the Ni foam was cleaned by ultrasonication in 3 M HCl for 15 min to remove the surface oxide layer, then washed with water and acetone many times, finally dried in air. The carbon paper was treated with concentrated HNO₃ at $100 \square$ for 12 h, then washed with water and ethanol many times, finally dried in air. Electrodeposition was carried out in a two-electrode cell (100 mL beaker). Ni foam or carbon paper was used as the cathode and carbon rod was used as the anode. A CHI 660E electrochemistry workstation was used to control the applied current density. The deposition electrolyte of $CoW(OH)_x$ was prepared as follows: 0.562 g CoSO₄·7H₂O (2 mmol), 1.319 g Na₂WO₄·2H₂O (4 mmol), 2.4 g H₃BO₃, 6.6 g C₆H₁₁NaO₇, and 1.8 g NaCl were dissolved and mixed in the beaker with 60 mL ultrapure water. The pH of electrolyte was adjusted to 6.0 by the addition of either NaOH or H₂SO₄. The deposition current of -0.33 A cm⁻² was held for 1 h at room temperature. The sample was then rinsed with water and ethanol many times, finally dried in air. We also prepared a series of deposition electrolytes with different Co:W molar ratio (5:1, 4:2, 3:3, 2:4, 1:5) to prepare various CoW(OH)_x samples. The HER performance of each sample is shown in Figure S21. Except the data shown in Figure S21, all other data were obtained by using the sample prepared in the electrolyte with a 2:4 Co:W molar ratio.

Preparation of Co(OH)_x. The preparation of Co(OH)_x was similar to that of CoW(OH)_x, except that 0.562 g CoSO₄·7H₂O and 1.319 g Na₂WO₄·2H₂O were replaced by 1.687 g CoSO₄·7H₂O (6 mmol).

Preparation of W(OH)_x. The W(OH)_x was prepared according to the reported procedures with some modifications.¹ Typically, the deposition was performed in a three-electrode cell (100 mL beaker) using carbon rod, Ag/AgCl electrode (3.5 M KCl), and Ni foam or carbon paper as counter electrode, reference electrode, and working electrode, respectively. The deposition electrolyte was prepared as follows: 0.495 g Na₂WO₄·2H₂O (1.5 mmol) was dissolved in the beaker with 60 mL

ultrapure water. Then 0.204 g H_2O_2 (30 wt. %) was added into the solution. The pH of the resulting solution was adjusted to 0.8 by adding HNO₃. The deposition potential of -0.47 V vs Ag/AgCl was held for 1 h at room temperature. The sample was then rinsed with water and ethanol many times, finally dried in air.

Preparation of NiW(OH)_x. The preparation of NiW(OH)_x was similar to that of CoW(OH)_x, except that $0.562 \text{ g } \text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was replaced by $0.526 \text{ g } \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (2 mmol).

Preparation of Ni(OH)_x. The preparation of Ni(OH)_x was similar to that of CoW(OH)_x, except that 0.562 g CoSO₄·7H₂O and 1.319 g Na₂WO₄·2H₂O were replaced by 1.577 g NiSO₄·6H₂O (6 mmol).

Preparation of Pt/C decorated Ni foam electrode (Pt/C). 20 mg Pt/C and 80 μ L Nafion were dispersed in 2 mL of water-ethanol solution with a volume ratio of 4:1 by at least 30 min ultrasonication to form a homogeneous solution. The cleaned Ni foam was immersed in the solution for 5 min and then dried in air at room temperature.

Characterizations. The morphologies and structures were characterized by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEM 2100, 200 kV). The crystal structure was determined by X-ray diffraction (XRD, D/max2550V). The surface composition and valence state were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250), and the binding energy of C 1s peak at 284.8 eV was taken as an internal standard. The metal element content was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian 710ES). The samples for XPS and ICP-AES were rinsed with ultrapure water and ethanol many times.

Electrochemical measurements. The electrochemical measurements were performed with a CHI660E electrochemistry workstation in a three-electrode system using a carbon rod and an Ag/AgCl electrode (3.5 M KCl) as counter electrode and reference electrode, respectively. The CoW(OH)_x, Co(OH)_x, W(OH)_x, NiW(OH)_x, Ni(OH)_x, Pt/C, and blank Ni foam were directly used as working electrode. 1.0 M PBS (pH = 7, 145 mL) and 1.0 M KOH (pH = 13.6, 145 mL) were used as electrolyte. All potentials measured were calibrated to the reversible hydrogen electrode (RHE) using the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.205$. The current density was calculated by normalizing the current to the corresponding geometric surface area. The linear sweep voltammetry (LSV) was tested at a sweep rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurement was carried out in the frequency range of 10⁵ to 0.001 Hz at the overpotential of -100 or -200 mV and the magnitude of the modulation signal was 5 mV. For stability tests, galvanostatic measurements were performed at a constant current density of -20 or -500 mA cm⁻², cyclic voltammetric (CV) cycles were tested for 10000 cycles from -0.6 to 0.0 V vs RHE at 50 mV s⁻¹. All LSV curves and galvanostatic curves were *IR*-compensated with *R*_s obtained from EIS measurements.

Electrochemically active surface area (ECSA) calculation. The ECSA was estimated from the electrochemical double-layer capacitance $(C_{\rm dl})$.²⁻⁴ First, a series of cyclic voltammetry (CV) curves were measured at different scan rates (40, 80, 120, 160, 240, and 320 mV s⁻¹) in a non-Faradaic region (+0.723 to +0.823 V vs RHE). Then plotting the half of the difference in current density between the anodic and cathodic sweeps ($(j_a - j_c)/2$) at +0.773 V vs RHE as a function of scan rates yielded a straight line with slope equal to $C_{\rm dl}$ (Figure S7). The specific capacitance ($C_{\rm s}$) value $C_{\rm s} = 0.040$ mF cm⁻² was adopted for the estimation of ECSA. The ECSA can be calculated as below:

$$ECSA = \frac{C_{dl-catalyst}}{C_s}$$



Figure S1. (a, b) SEM images of blank Ni foam at different magnifications.



Figure S2. (a, b) SEM and (c-f) corresponding elemental mapping images of $CoW(OH)_x$. (g) SEM-EDX spectrum of $CoW(OH)_x$. EDX reveals a 3.09:1 Co:W atomic ratio, which is close to the 3.12:1 Co:W atomic ratio confirmed by ICP-AES.



Figure S3. (a) TEM image of $CoW(OH)_x$. (b, c) SAED patterns and (d, e) HRTEM images of $CoW(OH)_x$ at different regions marked in (a). (f-i) TEM-EDX elemental mapping images of $CoW(OH)_x$. (j) Line-scanning profiles of Co, W, and O along the white dash arrow in (f). The elemental mapping and line-scanning profiles demonstrate the homogeneous distribution of Co, W, and O.



Figure S4. (a, b) SEM and (c-e) corresponding elemental mapping images of $Co(OH)_x$



Figure S5. (a, b) SEM and (c-e) corresponding elemental mapping images of W(OH)_x.



Figure S6. XRD patterns of $CoW(OH)_x$, $Co(OH)_x$, and $W(OH)_x$. The three sharp diffraction peaks in all XRD patterns originate from the Ni foam substrate.



Figure S7. Cyclic voltammetry curves at different scan rates (40-320 mV s⁻¹) in a non-Faradaic region of +0.723 to +0.823 V vs RHE in 1.0 M PBS for (a) CoW(OH)_x, (b) Co(OH)_x, (c) W(OH)_x, (d) Pt/C, and (e) blank Ni foam, respectively. (f) Plots used for the calculations of the C_{dl} for CoW(OH)_x, Co(OH)_x, W(OH)_x, Pt/C, and blank Ni foam. The linear slope is equivalent to the C_{dl} .



Figure S8. XRD patterns of $CoW(OH)_x$ before and after 24 h galvanostatic measurement at the current density of -20 mA cm⁻² in 1.0 M PBS.



Figure S9. (a, b) SEM images of $CoW(OH)_x$ before HER measurement. (c, d) SEM images and (e-h) corresponding elemental mapping images of $CoW(OH)_x$ after 24 h galvanostatic measurement at the current density of -20 mA cm⁻² in 1.0 M PBS.



Figure S10. (a) Polarization curves of $CoW(OH)_x$ before and after 10000 CV cycles in 1.0 M PBS. (b) Galvanostatic curve of $CoW(OH)_x$ at the current density of -500 mA cm⁻² in 1.0 M PBS.



Figure S11. P 2p XPS spectra of $CoW(OH)_x$ before and after 1 h, 2 h, as well as 4 h galvanostatic measurements at the current density of -20 mA cm⁻² in 1.0 M PBS, respectively.



Figure S12. (a) Co 2p, (b) O 1s, and (c) P 2p XPS spectra of $Co(OH)_x$ before and after 2 h galvanostatic measurement at the current density of -20 mA cm⁻² in 1.0 M PBS.



Figure S13. (a) W 4f, (b) O 1s, and (c) P 2p XPS spectra of $W(OH)_x$ before and after 2 h galvanostatic measurement at the current density of -20 mA cm⁻² in 1.0 M PBS.



Figure S14. (a) Polarization curves of $CoW(OH)_x$, $Co(OH)_x$, and $W(OH)_x$ before and after 2 h galvanostatic measurements in 1.0 M PBS. (b) Corresponding galvanostatic curves at the current density of -20 mA cm⁻² in 1.0 M PBS.



Figure S15. (a, b) SEM and (c-f) corresponding elemental mapping images of CoW(OH)_x/CP. CP represents carbon paper.



Figure S16. (a, b) SEM and (c-e) corresponding elemental mapping images of Co(OH)_x/CP.



Figure S17. (a, b) SEM and (c-e) corresponding elemental mapping images of W(OH)_x/CP.



Figure S18. Polarization curves of $CoW(OH)_x/CP$, $Co(OH)_x/CP$, $W(OH)_x/CP$, Pt/C/CP, and blank carbon paper in 1.0 M PBS.



Figure S19. (a) Activity comparison of $CoW(OH)_x$ in 1.0 M PBS and 1.0 M KOH, respectively. (b) Nyquist plots of $CoW(OH)_x$ at -200 mV overpotential in 1.0 M PBS and 1.0 M KOH, respectively.

As shown in Figure S19, at a relative high overpotential of -200 mV, a clear Warburg impedance can be observed in low frequency region in the plot of 1.0 M PBS, suggesting the critical role of mass transport in neutral buffered solution. On the contrary, the absence of Warburg impedance in the plot of 1.0 M KOH implies the fast mass transport process in alkaline solution. According to the previous study,⁵ the slow mass transport process is the major cause of low HER activity in near-neutral pH buffered solutions.



Figure S20. (a) Digital image showing that after immersing $CoW(OH)_x$ in 0.5 M H₂SO₄ for 10 min, the color of the solution changed from colorless to light red. (b, c) SEM images of $CoW(OH)_x$ after 10 min immersion in 0.5 M H₂SO₄. SEM images reveal that the $CoW(OH)_x$ layer on Ni foam substrate disappeared after 10 min immersion in 0.5 M H₂SO₄.

As shown in Figure S20a, after immersing $CoW(OH)_x$ in 0.5 M H₂SO₄ for 10 min, the color of the solution changed from colorless to light red. Noting that the color of aqueous solution containing Co^{2+} is red, the $CoW(OH)_x$ suffers from the corrosion in acidic media. The SEM images of $CoW(OH)_x$ after 10 min immersion in 0.5 M H₂SO₄ (Figure S20b and S20c) reveal that the $CoW(OH)_x$ layer on Ni foam substrate disappeared. Thus, this material is unstable in acidic environments.



Figure S21. Polarization curves of various $CoW(OH)_x$ samples prepared in a series of electrodeposition electrolytes with different Co:W molar ratio (5:1, 4:2, 3:3, 2:4, 1:5), along with pure $Co(OH)_x$ and $W(OH)_x$ for comparison. Note: except the data shown in Figure S21, all other data were obtained by using the sample prepared in the electrolyte with a 2:4 Co:W molar ratio.



Figure S22. (a, b) SEM and (c-f) corresponding elemental mapping images of NiW(OH)_x.



Figure S23. (a, b) SEM and (c-e) corresponding elemental mapping images of Ni(OH)_x.



Figure S24. (a) Ni 2p, (b) W 4f, and (c) O 1s XPS spectra of $NiW(OH)_x$ and $Ni(OH)_x$.



Figure S25. Polarization curves of $NiW(OH)_x$, $Ni(OH)_x$, $W(OH)_x$, Pt/C, and blank Ni foam in 1.0 M PBS.

Table S1. Atomic percentages of elements in each sample before and after 1 h, 2 h, as well as 4 h galvanostatic measurements obtained from XPS.

Samples	Atomi	Co:W				
after HER	Со	W	0	Р	С	atomic ratio
0 h	15.85	3.5	48.26	1.15	31.23	4.53:1
1 h	18.86	1.27	55.58	7.18	17.11	14.85:1
2 h	19.69	1.46	54.51	4.17	20.17	13.49:1
4 h	21.72	1.43	55.23	2.25	19.26	15.19:1

Notes: The current density in each galvanostatic measurement was -20 mA cm^{-2} . The electrolyte was 1.0 M PBS. The volume of the electrolyte was kept at 145 mL in each galvanostatic measurement.

Table S2. The contents of leached Co^{2+} and W^{6+} in the electrolyte after 1 h, 2 h, and 4 h galvanostatic measurements obtained from ICP-AES.

Electrolytes after HER	Co ²⁺ concentration (µg/mL)	W ⁶⁺ concentration (µg/mL)
1 h	1.94	2.38
2 h	2.77	2.92
4 h	1.83	3.10

Notes: The current density in each galvanostatic measurement was -20 mA cm⁻². The electrolyte was 1.0 M PBS. The volume of the electrolyte was kept at 145 mL in each galvanostatic measurement.

 Table S3. Comparison of some recently reported HER catalysts tested in neutral solution.

Catalysts	Electrolyte	η at $j = -10$ mA cm ⁻²	Reference	
CoW(OH) _x	1 M PBS	73.6 ± 1	This work	
NiW(OH) _x	1 M PBS	76.2 ± 1	This work	
Co-doped NiSe	1 M PBS	82	Adv. Mater. 2017, 29, 1606521	
Zn _{0.3} Co _{2.7} S ₄	0.1M PBS	90	J. Am. Chem. Soc. 2016 , 138, 1359-1365	
Ni-C-N NSs	1 M PBS	92.1	J. Am. Chem. Soc. 2016 , 138, 14546-14549	
FeP/Ti	1 M PBS	102	ACS Nano 2015 , 8, 11101-11107	
CoP@BCN	1 M PBS	122	Adv. Energy Mater. 2017, 7, 1601671	
Co ₂ P@NPG	1 M PBS	130	Nano Lett. 2016 , 16, 4691-4698	
Mo ₂ C@NC	1 M PBS	156	Angew. Chem. Int. Ed. 2015 , 54, 10752-10757	
Ni ₃ S ₂ /NF	1 M PBS	170	J. Am. Chem. Soc. 2015 , 137, 14023-14026	
Co-S films	1 M PBS	180	J. Am. Chem. Soc. 2013 , 135, 17699-17702	
NiMoZn	0.1 M PBS	187	Proc. Natl. Acad. Sci. U. S. A. 2015, 112, 2337-2342	
CoP/CC	1 M PBS	200	J. Am. Chem. Soc. 2014 , 136, 7587-7590	
Mo ₂ C	1 M PBS	204	Nanoscale 2017, 9, 7260-7267	
Co/CoO _x /CN	1 M PBS	280	J. Am. Chem. Soc. 2015 , 137, 2688-2694	

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