

## Supplementary Information

### Reversible hydrogen spillover in Ru-WO<sub>3-x</sub> enhances hydrogen evolution activity in neutral pH water splitting

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## Supplementary Notes

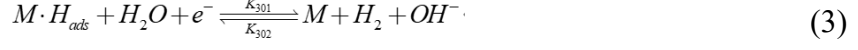
### Supplementary Note 1. Microkinetic modelling of HER on Ru/C and Ru-WO<sub>3-x</sub>.

In alkaline/neutral environment, Markovic et al. proposed that H<sub>2</sub>O rather than H<sup>+</sup> is the reactant of HER, which directly dissociates on the surface of HER catalyst<sup>1</sup>. However, not all water molecules at the catalyst/electrolyte interface are able to participate in HER. It was suggested that the noncovalent interactions between the oxophilic sites on the surface of catalyst and the water molecules could promote the activity of HER. Furthermore, Wang et al. found that the hydrated alkali cations could adsorb in the catalyst's double layer, which *in-situ* activated the H-OH bond through the hydration effect, promoting dissociation of water molecules<sup>2</sup>. Therefore, it is deduced that water molecules need to be activated (H<sub>2</sub>O<sub>act,ads</sub>) before they can participate in the HER in alkaline/neutral environment.

With consideration of H<sub>2</sub>O activation, a microkinetic model for HER in neutral environment was constructed as shown in Supplementary Table 1. The kinetics parameters were obtained by fitting the model with steady-state internal resistance (IR) corrected polarization curves using a global optimization method, which composes of a random search using genetic algorithm and a local optimization employing trust-region-reflective algorithm. All simulations were performed using a commercial software package (MATLAB R2010b, the MathWorks Inc.). The relative error tolerance for the initial value problem of ordinary differential equations was set as 10<sup>-6</sup>.

Supplementary Tables 1 and 2 list the elementary reaction steps and the enrolled reaction rate equations of HER in neutral electrolyte, where  $r$  is the elementary reaction rate [ $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ],  $K$  is the reaction rate constant [ $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ],  $c$  is the concentration [ $\text{mol}\cdot\text{m}^{-3}$ ],  $\theta$  is the coverage,  $\alpha$  is the symmetry coefficient,  $\eta$  is the overpotential [V],  $R$  is the gas constant [ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ],  $T$  is the temperature [K],  $\theta$  subscripts  $\text{H}_2\text{O}_{\text{act,ads}}$  and  $\text{H}_{\text{ads}}$  represent the activated water molecule and adsorbed H intermediate, respectively.

**Supplementary Table 1.** Elementary reaction steps of HER in neutral medium.



$$r_1 = K_{101} \cdot (1 - \theta_{H_2O_{act,ads}} - \theta_{H_{ads}}) \quad (4)$$

$$r_{-1} = K_{102} \cdot \theta_{H_2O_{act,ads}} \quad (5)$$

$$r_2 = K_{201} \cdot \theta_{H_2O_{act,ads}} \cdot \exp\left(\frac{\alpha F \eta}{RT}\right) \quad (6)$$

$$r_{-2} = K_{202} \cdot \theta_{H_{ads}} \cdot \left(\frac{c_{OH^-}}{c^\ominus}\right) \cdot \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right) \quad (7)$$

$$r_3 = K_{301} \cdot \theta_{H_{ads}} \cdot \exp\left(\frac{\alpha F \eta}{RT}\right) \quad (8)$$

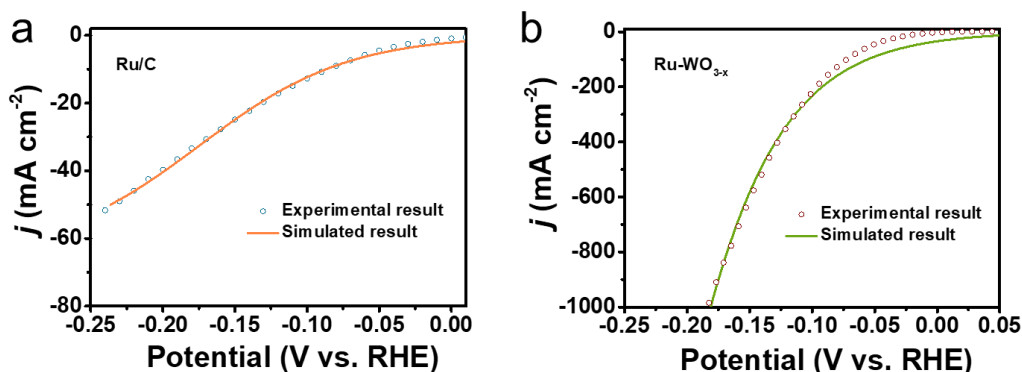
$$r_{-3} = K_{302} \cdot (1 - \theta_{H_2O_{act,ads}} - \theta_{H_{ads}}) \cdot \left(\frac{c_{OH^-}}{c^\ominus}\right) \cdot \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right) \quad (9)$$

**Supplementary Table 2.** Reaction rate equations for HER in neutral medium.

$$C_{H_2O_{act,ads}} \frac{d\theta_{H_2O_{act,ads}}}{dt} = r_1 - r_{-1} - r_2 + r_{-2} \quad (10)$$

$$C_{H_{ads}} \frac{d\theta_{H_{ads}}}{dt} = r_2 - r_{-2} - r_3 + r_{-3} \quad (11)$$

$$C_{dl} \frac{dE}{dt} = j(t) - [(r_2 - r_{-2}) + (r_3 - r_{-3})] \cdot F/n \quad (12)$$



**Supplementary Figure 1.** Simulated and experimental polarization curves. (a) Comparison of experimental HER polarization curve on Ru/C with the simulated polarization curve. (b) Comparison of experimental HER polarization curve on Ru-WO<sub>3-x</sub> with the simulated polarization curve.

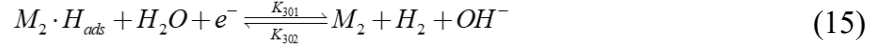
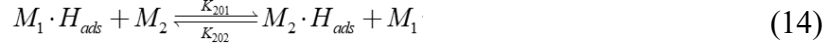
Supplementary Figure 1 displays the comparison of the experimental HER performance of Ru/C and Ru-WO<sub>3-x</sub> with the simulated results. It can be observed that the three-step mechanism can well reproduce the experimental data.

**Supplementary Table 3.** The rate constants of HER on Ru/C and Ru-WO<sub>3-x</sub> at 40 mA cm<sup>-2</sup>.

Reaction rate constant	Ru/C (mol·s <sup>-1</sup> ·m <sup>-2</sup> )	Ru-WO <sub>3-x</sub> (mol·s <sup>-1</sup> ·m <sup>-2</sup> )
$K_{101}$	$3.37 \times 10^{-3}$	$6.56 \times 10^4$
$K_{201}$	$1.48 \times 10^4$	6.41
$K_{201} \cdot \exp\left(\frac{\alpha F \eta}{RT}\right)$	$2.37 \times 10^4$	$8.86 \times 10^{-3}$
$K_{202} \cdot \exp\left(-\frac{(1-\alpha)F\eta}{RT}\right)$	$4.94 \times 10^2$	$2.04 \times 10^{-3}$
$K_{301} \cdot \exp\left(\frac{\alpha F \eta}{RT}\right)$	$4.78 \times 10^4$	$1.21 \times 10^{-1}$
$K_{302} \cdot \exp\left(-\frac{(1-\alpha)F\eta}{RT}\right)$	$4.93 \times 10^2$	$2.03 \times 10^{-3}$

Supplementary Table 3 lists the rate constants of HER on Ru/C and Ru-WO<sub>3-x</sub> at 40 mA cm<sup>-2</sup>. It is clear to see that the HER rate determining step (RDS) on Ru/C and Ru-WO<sub>3-x</sub> are obviously different. On Ru/C in neutral pH medium, the HER is rate-limited at the water activation step, while the RDS changes to hydrogen recombination on Ru-WO<sub>3-x</sub>. As a result, a new microkinetic model without the consideration of water activation, but instead taking hydrogen spillover from WO<sub>3-x</sub> to Ru into consideration was built to simulate the H coverage on Ru-WO<sub>3-x</sub> (Supplementary Table 4).  $\theta$  subscripts H<sub>1,ads</sub> and H<sub>2,ads</sub> represent the adsorbed H on WO<sub>3-x</sub> and Ru, respectively. The simulation results are displayed in Supplementary Figure 2.

**Supplementary Table 4.** Elementary reaction steps of HER in neutral medium on Ru-  
WO<sub>3-x</sub>.



$$r_1 = K_{101} \cdot (1 - \theta_{H_{1,ads}}) \cdot \exp\left(\frac{\alpha F \eta}{RT}\right) \quad (16)$$

$$r_{-1} = K_{102} \cdot \theta_{H_{1,ads}} \cdot \left(\frac{c_{OH^-}}{c^{\ominus}}\right) \cdot \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right) \quad (17)$$

$$r_2 = K_{201} \cdot \theta_{H_{1,ads}} \cdot (1 - \theta_{H_{2,ads}}) \quad (18)$$

$$r_{-2} = K_{202} \cdot \theta_{H_{2,ads}} \cdot (1 - \theta_{H_{1,ads}}) \quad (19)$$

$$r_3 = K_{301} \cdot \theta_{H_{2,ads}} \cdot \exp\left(\frac{\alpha F \eta}{RT}\right) \quad (20)$$

$$r_{-3} = K_{302} \cdot (1 - \theta_{H_{2,ads}}) \cdot \left(\frac{c_{OH^-}}{c^{\ominus}}\right) \cdot \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right) \quad (21)$$

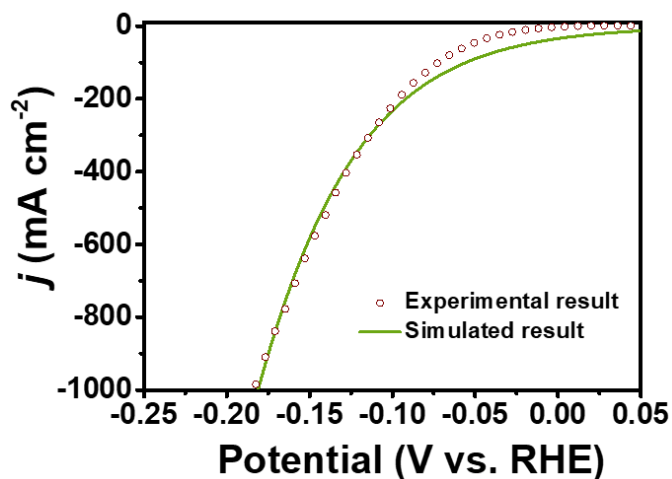
**Supplementary Table 5.** Reaction rate equations for HER in neutral medium on Ru-  
WO<sub>3-x</sub>.

$$C_{H_{1,ads}} \frac{d\theta_{H_{1,ads}}}{dt} = r_1 - r_{-1} - r_2 + r_{-2} \quad (22)$$

$$C_{H_{2,ads}} \frac{d\theta_{H_{2,ads}}}{dt} = r_2 - r_{-2} - r_3 + r_{-3} \quad (23)$$

$$C_{dl} \frac{dE}{dt} = j(t) - [(r_1 - r_{-1}) + (r_3 - r_{-3})] \cdot F/n \quad (24)$$





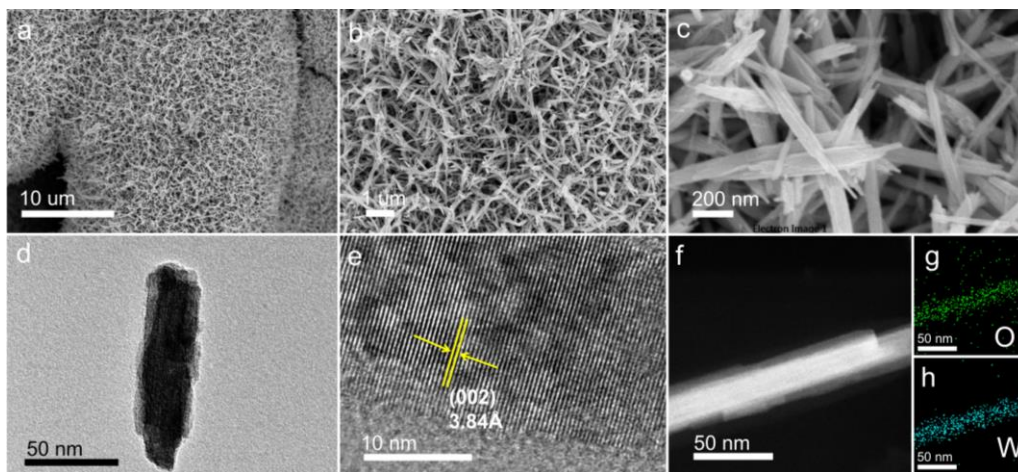
**Supplementary Figure 2.** Simulated and experimental polarization curves. Comparison of experimental HER polarization curve on Ru-WO<sub>3-x</sub> with the simulated polarization curve.

**Supplementary Table 6.** The rate constants of HER on Ru-WO<sub>3-x</sub> at 40 mA cm<sup>-2</sup>.

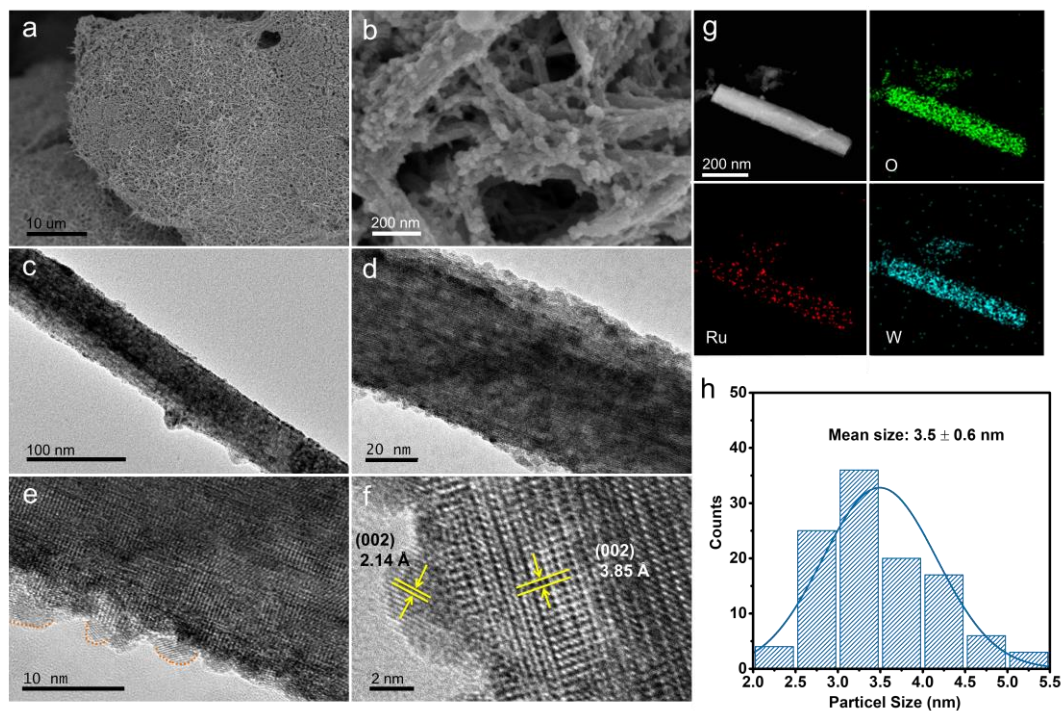
Reaction rate constant	Ru-WO <sub>3-x</sub> (mol·s <sup>-1</sup> ·m <sup>-2</sup> )
$K_{201} \cdot \exp\left(\frac{\alpha F \eta}{RT}\right)$	$1.46 \times 10^{-1}$
$K_{202} \cdot \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right)$	4.34
$K_{201}$	$3.67 \times 10^{-1}$
$K_{202}$	$2.48 \times 10^{-2}$
$K_{301} \cdot \exp\left(\frac{\alpha F \eta}{RT}\right)$	$2.09 \times 10^{-3}$
$K_{302} \cdot \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right)$	$1.29 \times 10^1$

**Supplementary Note 2.** The deuterium isotopic substitution experiment.

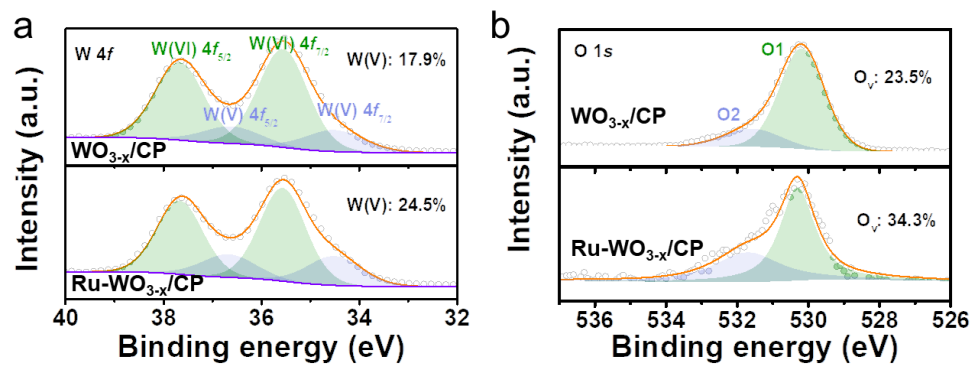
Fig. 4b shows the *in-situ* Raman results on Ru-WO<sub>3-x</sub>/CP recorded in 1.0 M PBS (prepared using D<sub>2</sub>O) saturated with N<sub>2</sub>. It could be observed that the peak at around 878 cm<sup>-1</sup> shifted to around 611 cm<sup>-1</sup>. For Ru-H vibration, the corresponding Raman frequency downward shift ratio ( $\gamma$ ) in the isotopic experiment can be analyzed by:  $\gamma = \nu(\text{RuD})/\nu(\text{RuH}) = \frac{\sqrt{m(\text{Ru})+m(\text{D})}}{\sqrt{m(\text{Ru})\times m(\text{D})}} \div \frac{\sqrt{m(\text{Ru})+m(\text{H})}}{\sqrt{m(\text{Ru})\times m(\text{H})}} = \frac{\sqrt{101.07+2}}{\sqrt{101.07\times 2}} \div \frac{\sqrt{101.07+1}}{\sqrt{101.07\times 1}} = 71.06\%$ . As a consequence, the Raman peak at around 878 cm<sup>-1</sup> should shift to 878 × 71.06% = 623.9 cm<sup>-1</sup> in the isotopic experiment. Under the actual experimental condition, water solvent effect should be considered and thus the Ru-H vibration can be influenced by the interfacial water molecules, which may exist as RuH-H<sub>2</sub>O state through forming hydrogen bond. As a result, in comparison with the calculated result, the Raman frequency of Ru-H can be shifted more obviously in the actual isotopic experiment.



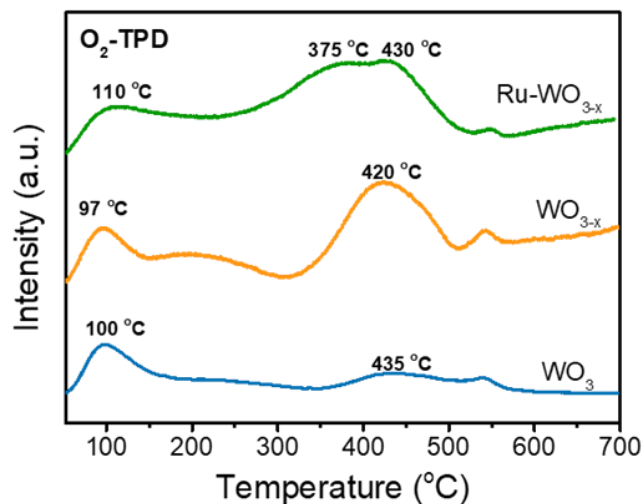
**Supplementary Figure 3.** Morphological characterization of  $\text{WO}_3/\text{CP}$ . (a-c) SEM images. (d) TEM image. (e) HRTEM image. (f-h) HAADF-STEM image and the corresponding EDX elemental mappings.



**Supplementary Figure 4.** Morphological characterization of Ru-WO<sub>3-x</sub>/CP. (a & b) SEM images. (c-e) TEM images. (f) HRTEM image. (g) HAADF-STEM image and the corresponding EDX elemental mappings. (h) Size distribution profiles of Ru NPS on Ru-WO<sub>3-x</sub>/CP.

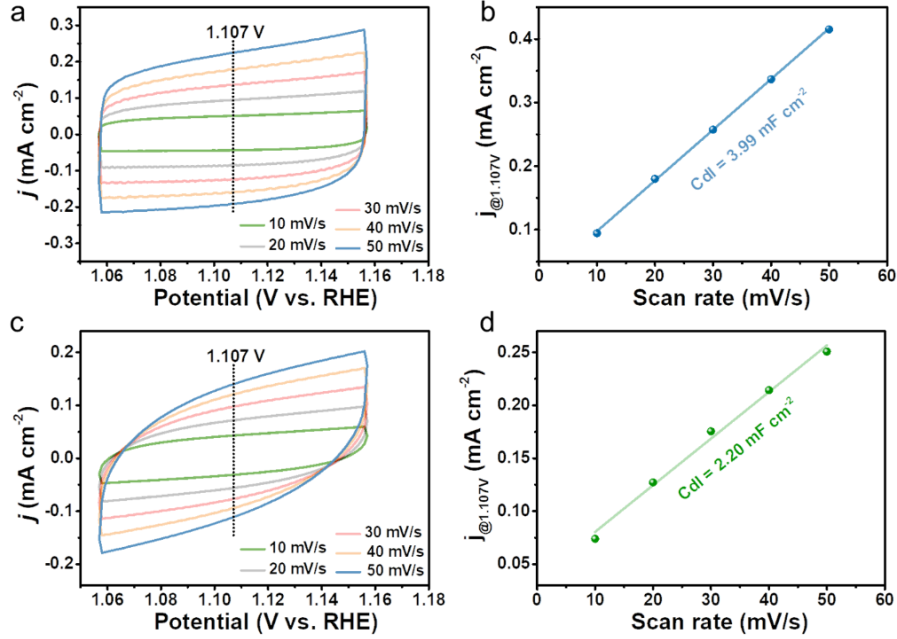


**Supplementary Figure 5.** XPS spectra of  $\text{WO}_{3-x}/\text{CP}$  and  $\text{Ru-WO}_{3-x}/\text{CP}$ . (a) W 4f spectra. (b) O 1s spectra.



**Supplementary Figure 6.** O<sub>2</sub>-TPD profiles of Ru-WO<sub>3-x</sub>, WO<sub>3-x</sub> and WO<sub>3</sub>.

To further investigate oxygen vacancies in Ru-WO<sub>3-x</sub>, we conducted O<sub>2</sub>-temperature programmed desorption (O<sub>2</sub>-TPD). Generally, the desorption peak at low temperature (< 200 °C) is associated to desorption of physically adsorbed oxygen species. The desorption peaks at 200-600 °C correspond to desorption of chemisorbed oxygen species, and the peak above 700 °C is attributed to the release of lattice oxygen<sup>3,4</sup>. As shown in Figure R3, compared with WO<sub>3</sub>, Ru-WO<sub>3-x</sub> and WO<sub>3-x</sub> present shifts of desorption peaks of chemisorbed oxygen species to lower temperatures with much higher intensities of desorption peaks at around 400 °C, which should be related to the chemically adsorbed oxygen adjacent to oxygen vacancies. This result reveals oxygen vacancies in WO<sub>3-x</sub> and Ru-WO<sub>3-x</sub>, which matches well with the EPR and O 1s XPS results.

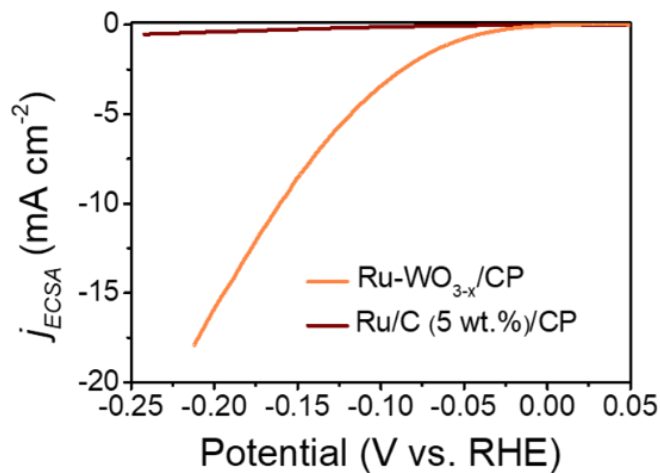


**Supplementary Figure 7.** CV curves and capacitive currents plotted as the function of scan rates for the calculation of double-layer capacitance. (a) CV curves of Ru/C (5 wt.%) recorded at various scan rates. (b) The capacitive current measured at 1.107 V (vs. RHE) plotted as a function of scan rate of Ru/C (5 wt.%). (c) CV curves of Ru-WO<sub>3-x</sub> recorded at various scan rates. (d) The capacitive current measured at 1.107 V (vs. RHE) plotted as a function of scan rate of Ru-WO<sub>3-x</sub>.

Firstly, we calculated the roughness factor ( $R_f$ ) based on the double layer capacitance ( $C_{dl}$ ) by the following equation:

$$R_f = \frac{C_{dl}}{0.04}$$

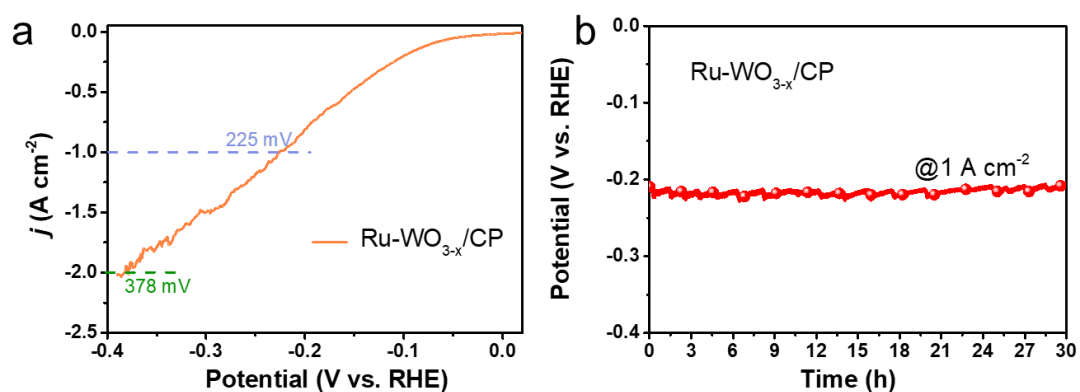
where the  $C_{dl}$  (F/g) is the double-layer capacitance of catalysts (Figure R1), and 0.04 (mF/cm<sup>2</sup>) is the general double-layer capacitance for a smooth surface for metal oxides<sup>5</sup>. The  $R_f$  of Ru/C (5 wt.%) and Ru-WO<sub>3-x</sub> is calculated to be 100 and 55, respectively. The  $R_f$  of Ru-WO<sub>3-x</sub> is only 55% of Ru/C, indicating that roughness factor should not be a decisive factor in significantly increasing HER activity.



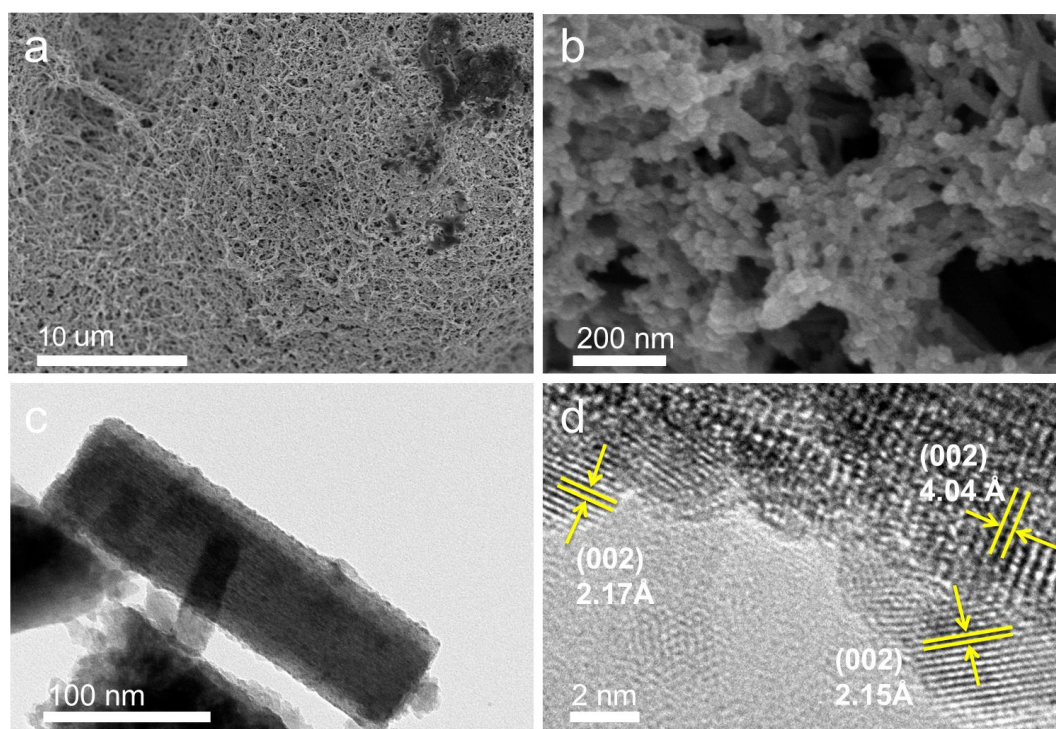
**Supplementary Figure 8.** LSV curves normalized by ECSA of Ru-WO<sub>3-x</sub>/CP and Ru/C (5 wt.)/CP.

Then, we calculated the electrochemically active surface area (ECSA) based on the  $R_f$  and obtained the LSV curves normalized by the ECSA. As displayed in Figure R2, Ru-WO<sub>3-x</sub>/CP still shows much better HER activity than Ru/C (5 wt.)/CP and the current density of Ru-WO<sub>3-x</sub>/CP is enhanced by a factor of 34 as compared to the Ru/C (5 wt.)/CP at the potential of -0.150 V vs. RHE.

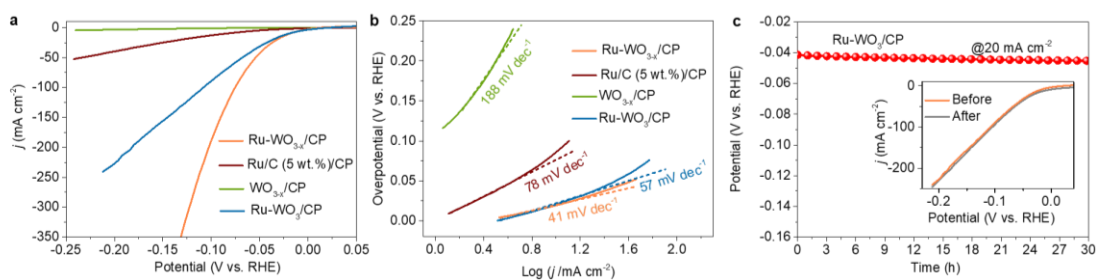




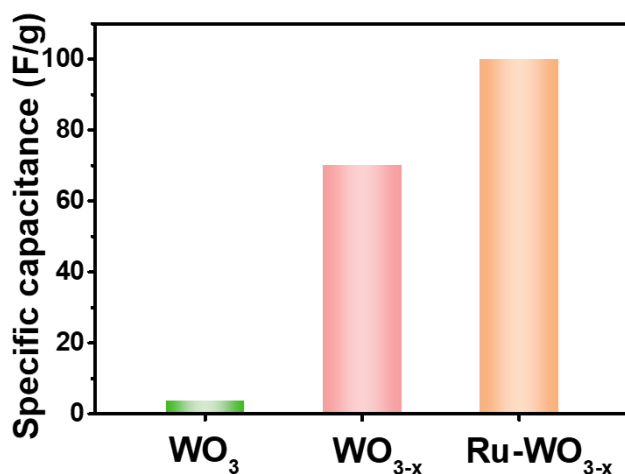
**Supplementary Figure 9.** HER activity and stability test of Ru-WO<sub>3-x</sub>/CP in 1.0 M PBS. (a) LSV curve of Ru-WO<sub>3-x</sub>/CP recorded in 1.0 M PBS. (b) Chronopotentiometric stability of Ru-WO<sub>3-x</sub>/CP under constant current density of 1 A cm<sup>-2</sup> in 1.0 M PBS.



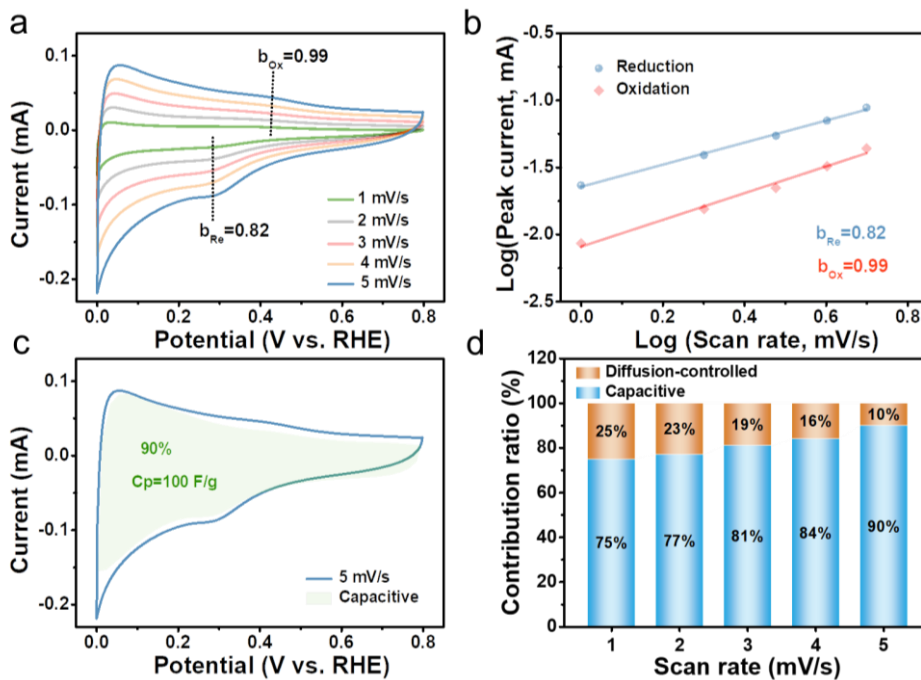
**Supplementary Figure 10.** Morphological characterization of Ru-WO<sub>3-x</sub>/CP after stability test. (a & b) SEM images. (c) TEM image. (d) HRTEM image.



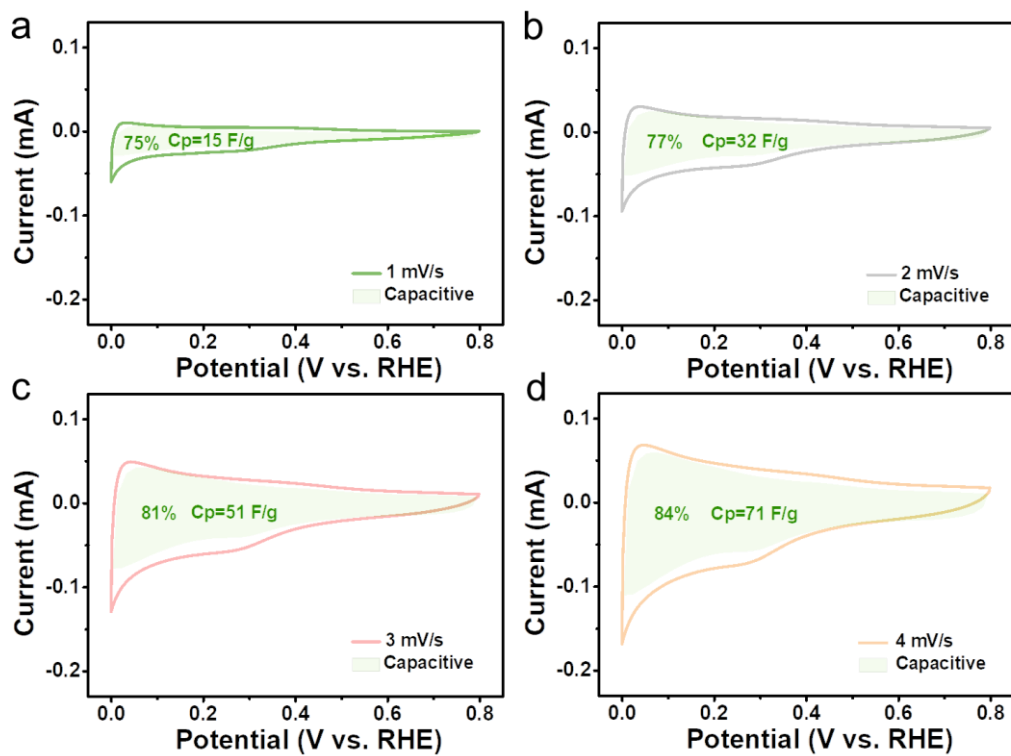
**Supplementary Figure 11.** HER activity of Ru-WO<sub>3</sub>/CP and other catalysts in 1.0 M PBS. (a) LSV curves in 1.0 M PBS. (b) The corresponding Tafel plots. (c) Chronopotentiometric curve recorded at a constant cathodic current density of 20 mA cm<sup>-2</sup>. Inset compares the LSV curve before and after the stability test.



**Supplementary Figure 12.** Comparison of the capacity for storing protons by specific capacitance. Specific Capacitance of WO<sub>3</sub>, WO<sub>3-x</sub> and Ru-WO<sub>3-x</sub>.

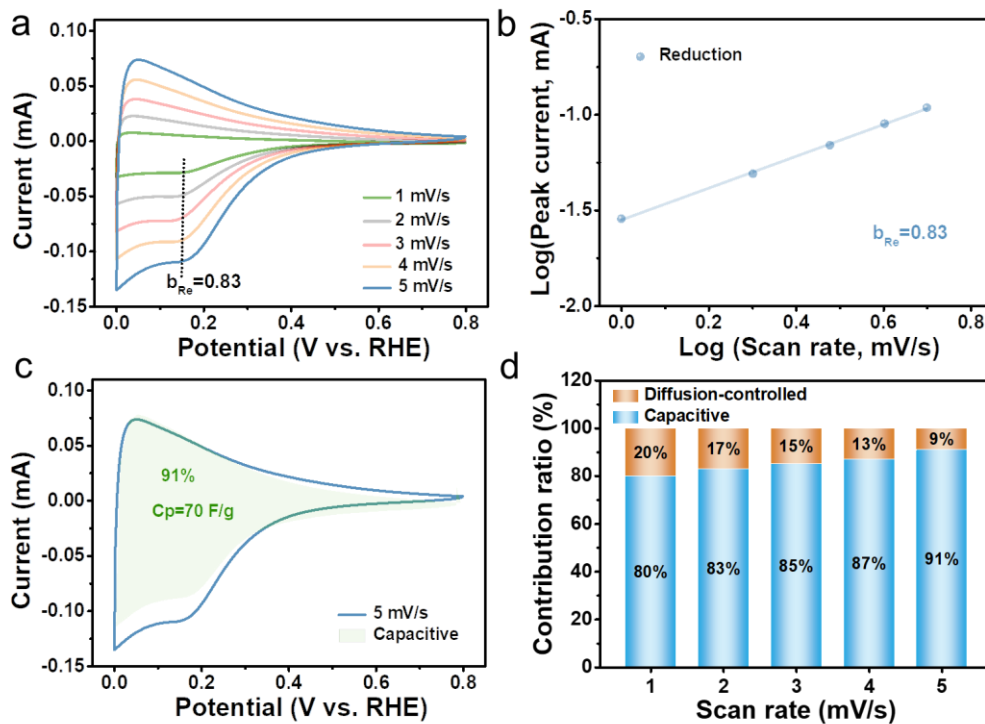


**Supplementary Figure 13.** Capacitance analysis of Ru-WO<sub>3-x</sub>. (a) CV curves recorded at various scan rates with calculated  $b$  values. Scan rates vary from 1 to 5 mV/s. (b) Analysis of  $b$  value for reduction and oxidation peaks. (c) Capacitive contribution at 5 mV/s. (d) Capacitive contribution at various scan rates.

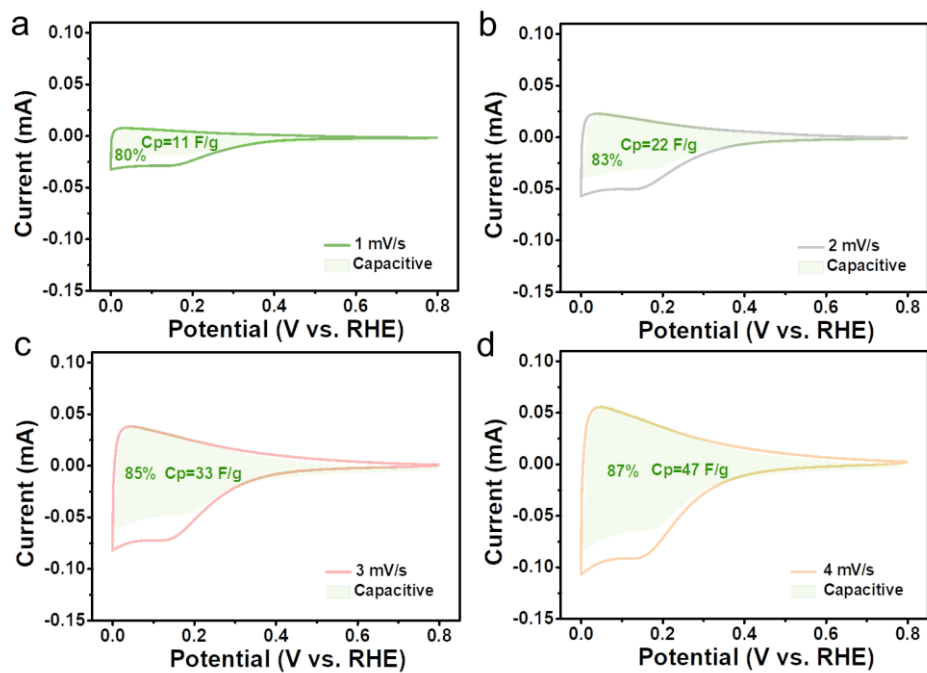


**Supplementary Figure 14.** Capacitive contribution of Ru-WO<sub>3-x</sub> at various scan rates.

(a) 1 mV/s. (b) 2 mV/s. (c) 3 mV/s. (d) 4 mV/s.

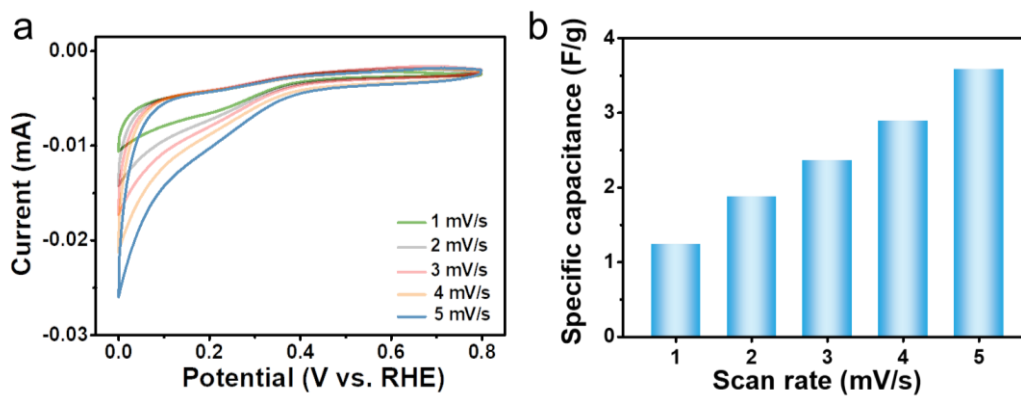


**Supplementary Figure 15.** Capacitance analysis of  $\text{WO}_{3-x}$ . (a) CV curves recorded at various scan rates with calculated  $b$  values. Scan rates vary from 1 to 5 mV/s. (b) Analysis of  $b$  value for reduction peak. (c) Capacitive contribution at 5 mV/s. (d) Capacitive contribution at various scan rates.

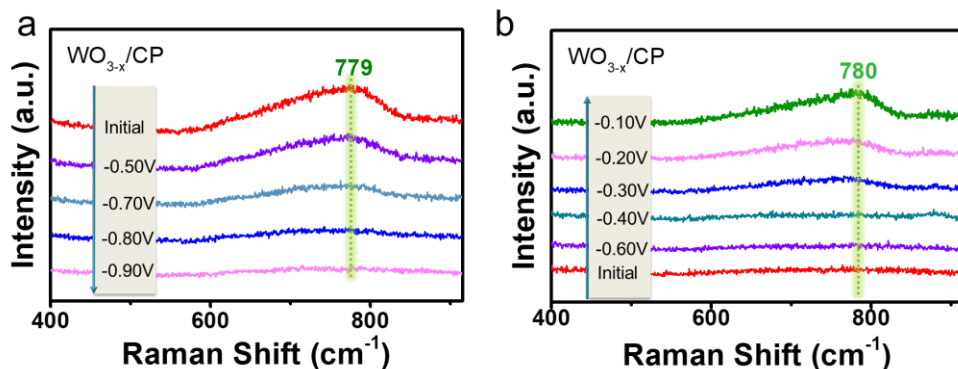


**Supplementary Figure 16.** Capacitive contribution of  $\text{WO}_{3-x}$  at various scan rates. (a)

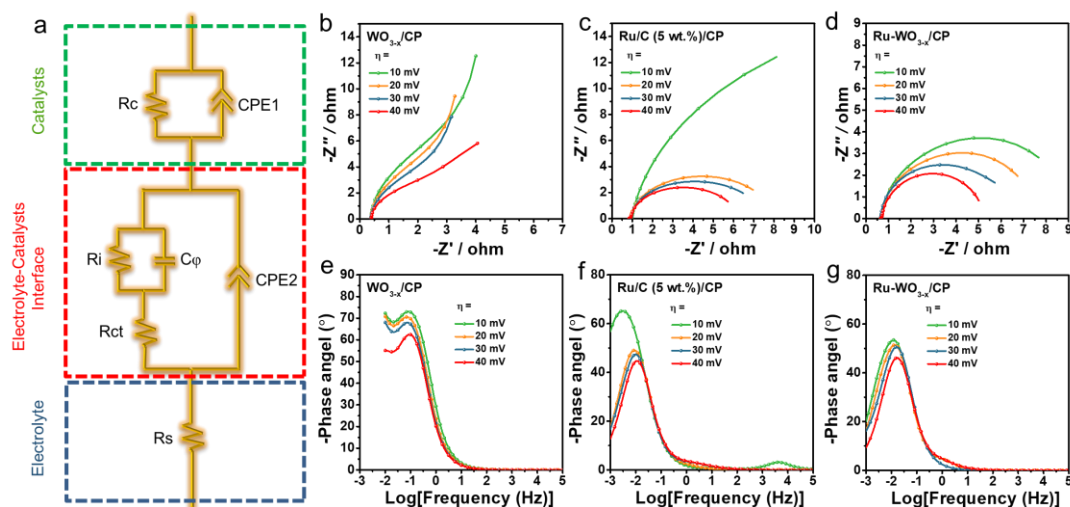
1 mV/s. (b) 2 mV/s. (c) 3 mV/s. (d) 4 mV/s.



**Supplementary Figure 17.** Capacitance analysis of  $\text{WO}_3$ . (a) CV curves recorded at various scan rates. Scan rates vary from 1 to 5 mV/s. (b) Specific capacitance at various scan rates.

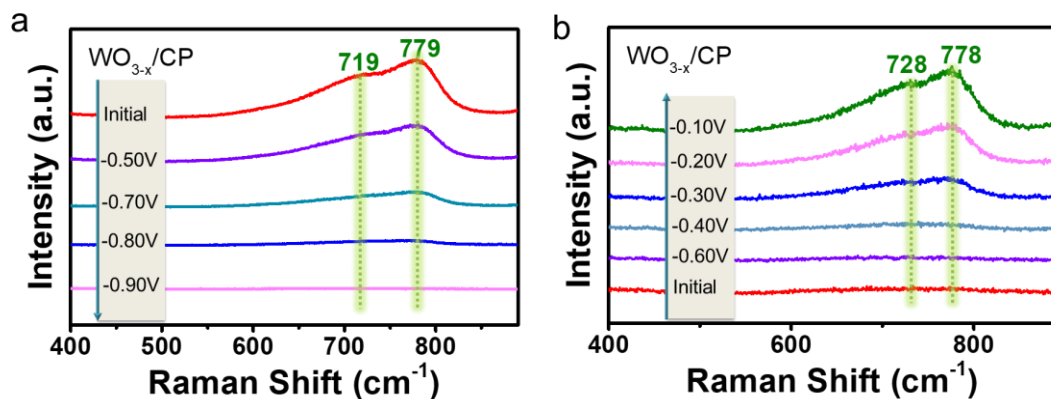


**Supplementary Figure 18.** *In-situ* Raman analysis of  $\text{WO}_{3-x}/\text{CP}$  in deuterium isotopic substitution experiment. *In-situ* Raman spectra of  $\text{WO}_{3-x}/\text{CP}$  recorded in 1.0 M PBS from -0.5 to -0.9 V vs. Ag/AgCl (a) and sweep back from -0.6 to -0.1 V vs. Ag/AgCl (b).

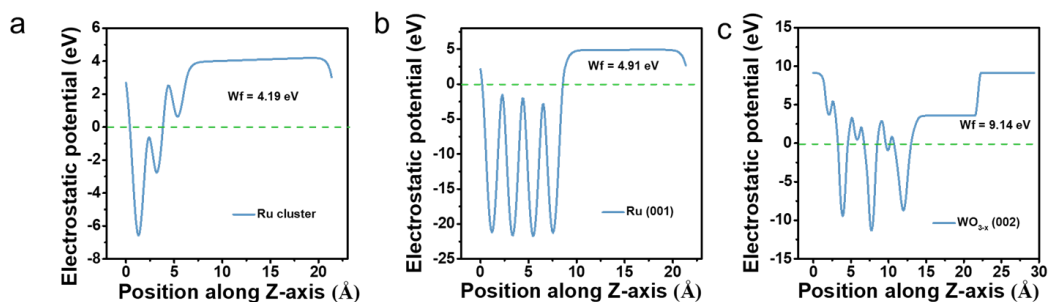


**Supplementary Figure 19.** Nyquist plots and the corresponding Bode plots at various overpotentials. (a) Schematic diagram of the electrode structure and the equivalent circuit model. (b-d) Nyquist plots of (b)  $\text{WO}_{3-x}/\text{CP}$ , (c) Ru/C (5 wt.%)/CP and (d) Ru- $\text{WO}_{3-x}/\text{CP}$ . (e-g) Bode plots of (e)  $\text{WO}_{3-x}/\text{CP}$ , (f) Ru/C (5 wt.%)/CP and (g) Ru- $\text{WO}_{3-x}/\text{CP}$ .

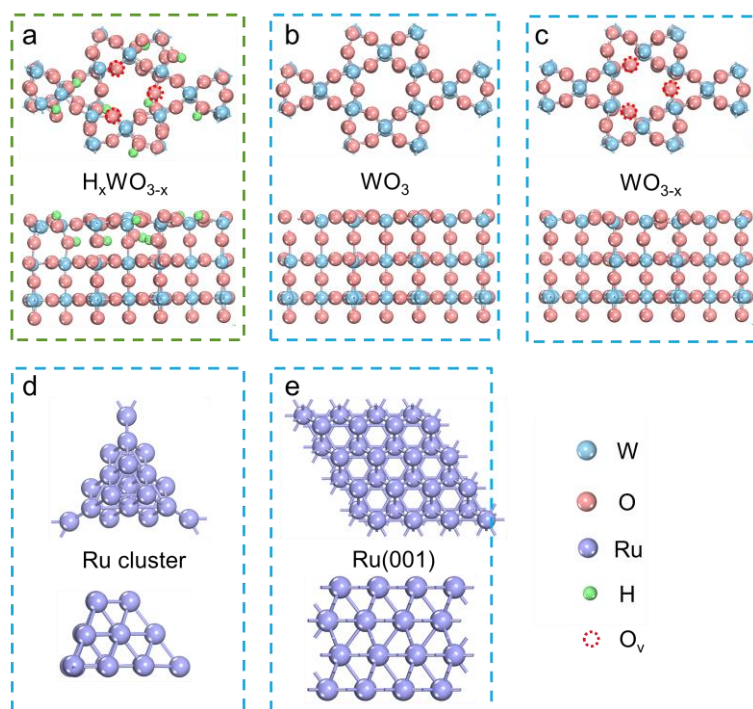




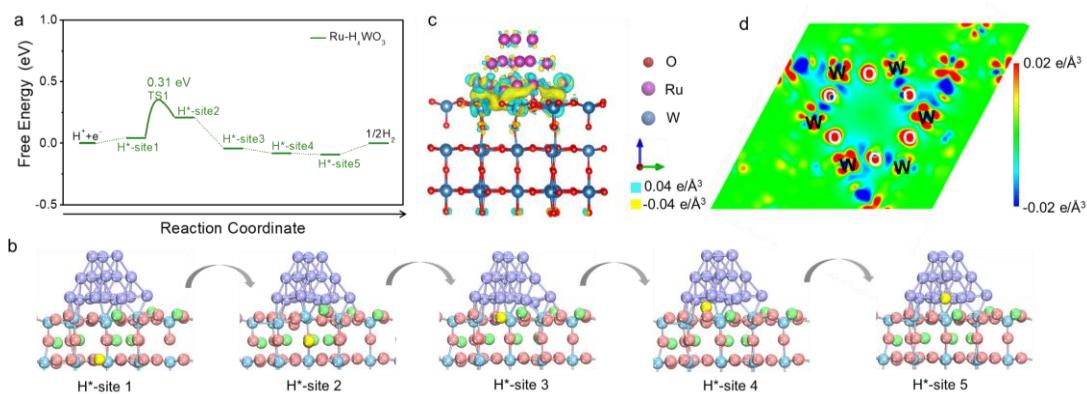
**Supplementary Figure 20.** *In-situ* Raman analysis of  $\text{WO}_{3-x}/\text{CP}$ . *In-situ* Raman spectra of  $\text{WO}_{3-x}/\text{CP}$  recorded in 1.0 M PBS from -0.5 to -0.9 V vs. Ag/AgCl (a) and sweep back from -0.6 to -0.1 V vs. Ag/AgCl (b).



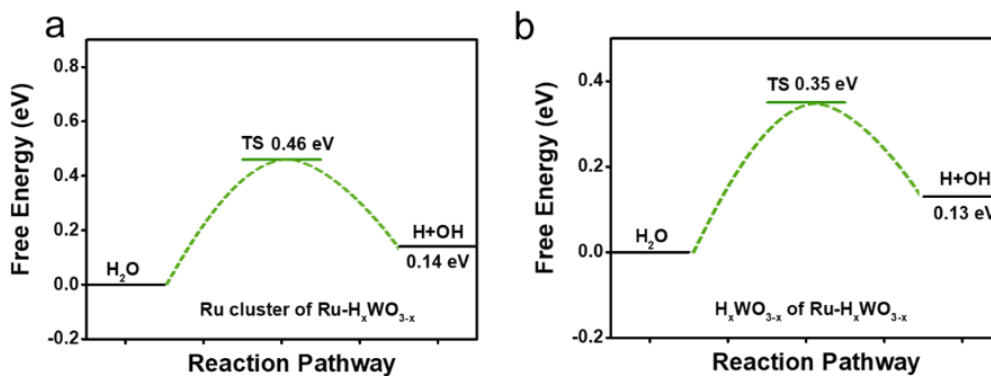
**Supplementary Figure 21.** Work function estimation. The work function estimated for (a) Ru cluster, and (b) Ru (001) (c)  $\text{WO}_{3-x}$  (002).



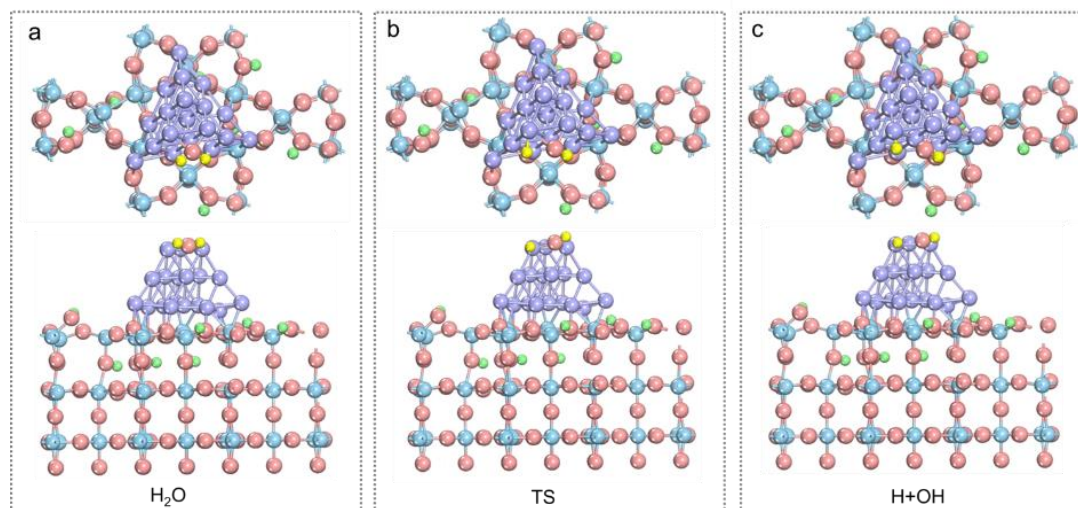
**Supplementary Figure 22.** Side and top view illustrations of DFT models used for the work function calculation. (a)  $H_xWO_{3-x}$  (002). (b)  $WO_3$  (002). (c)  $WO_{3-x}$  (002). (d) Ru cluster. (e) Ru (001).



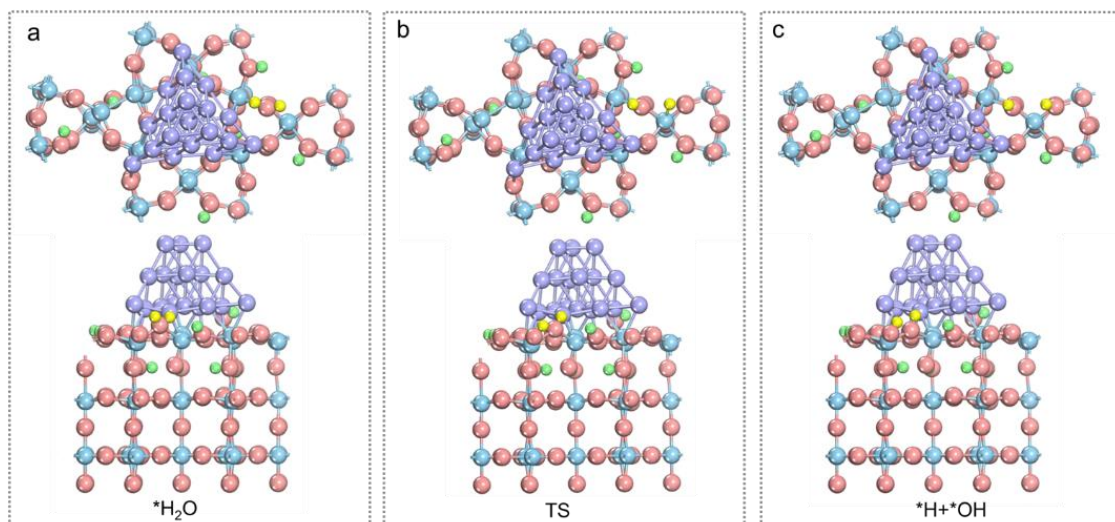
**Supplementary Figure 23.** DFT calculations of Ru- $H_x$ WO $_3$ . (a) Calculated free energy diagram for HER on Ru- $H_x$ WO $_3$ . (b) The optimized H\* adsorption structure on various sites of Ru- $H_x$ WO $_3$ . (c) Electron density difference plot across the Ru-WO $_{3-x}$  interface. Electron accumulation and depletion are indicated in yellow and blue, respectively. (d) The differential charge density maps of Ru-WO $_3$ . From aquamarine to orange indicates the transition from electron depletion to accumulation.



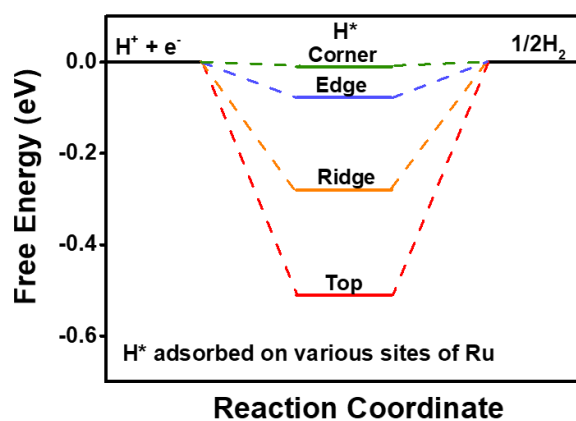
**Supplementary Figure 24.** Energy barrier of water dissociation process on Ru of Ru-H<sub>x</sub>WO<sub>3-x</sub> (a) and WO<sub>3-x</sub> of Ru- H<sub>x</sub>WO<sub>3-x</sub> (b). (TS represent the transition states).



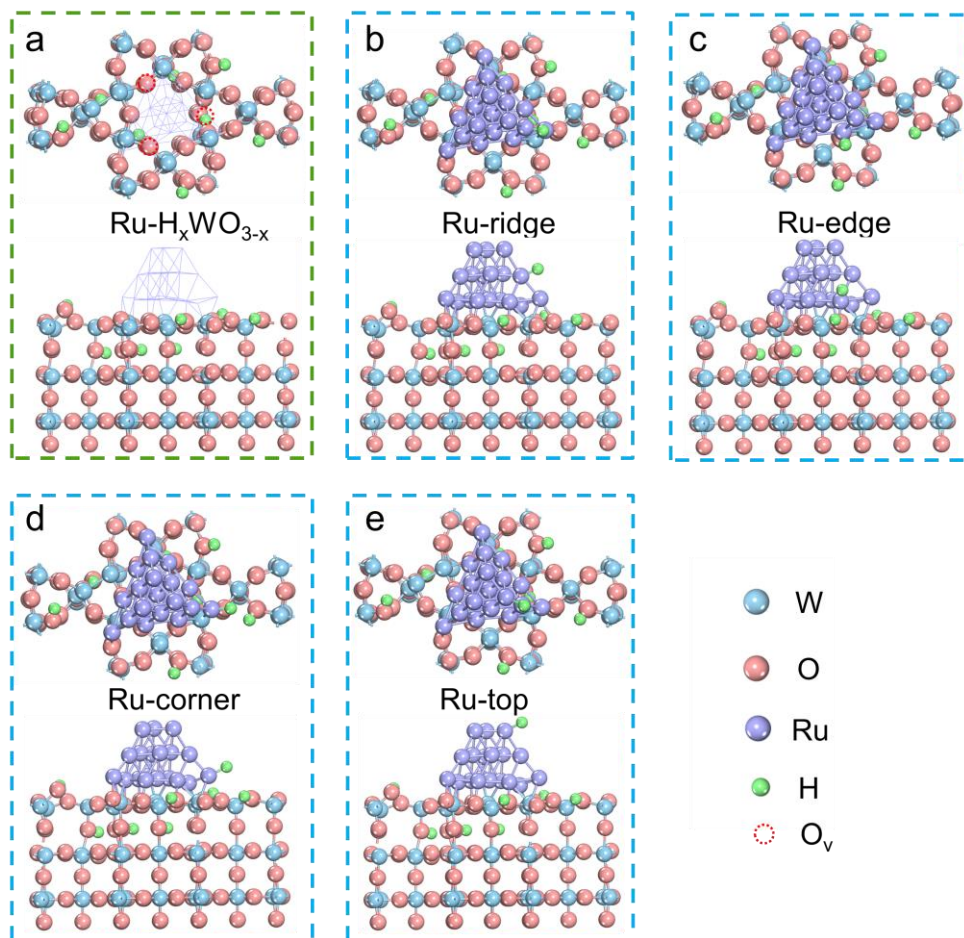
**Supplementary Figure 25.** Side and top view illustrations of DFT models used for calculating the energy barrier of water dissociation process on Ru of Ru-H<sub>x</sub>WO<sub>3-x</sub>. (a) Initial state. (b) Transition state. (c) Final state. The blue, red and purple balls represent W, O and Ru atoms. The green and yellow balls represent the H atoms inserted into WO<sub>3-x</sub> and the H atoms involved in HER.



**Supplementary Figure 26.** Side and top view illustrations of DFT models used for calculating the energy barrier of water dissociation process on  $\text{WO}_{3-x}$  of  $\text{Ru-H}_x\text{WO}_{3-x}$ . (a) Initial state. (b) Transition state. (c) Final state. The blue, red and purple balls represent W, O and Ru atoms. The green and yellow balls represent the H atoms inserted into  $\text{WO}_{3-x}$  and the H atoms involved in HER.

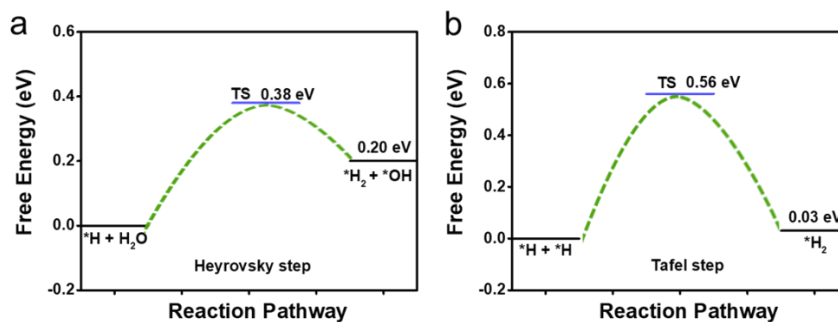


**Supplementary Figure 27.** Comparison of the hydrogen adsorption on various active sites. Free energy of hydrogen adsorption on  $\text{Ru-H}_x\text{WO}_{3-x}$ .

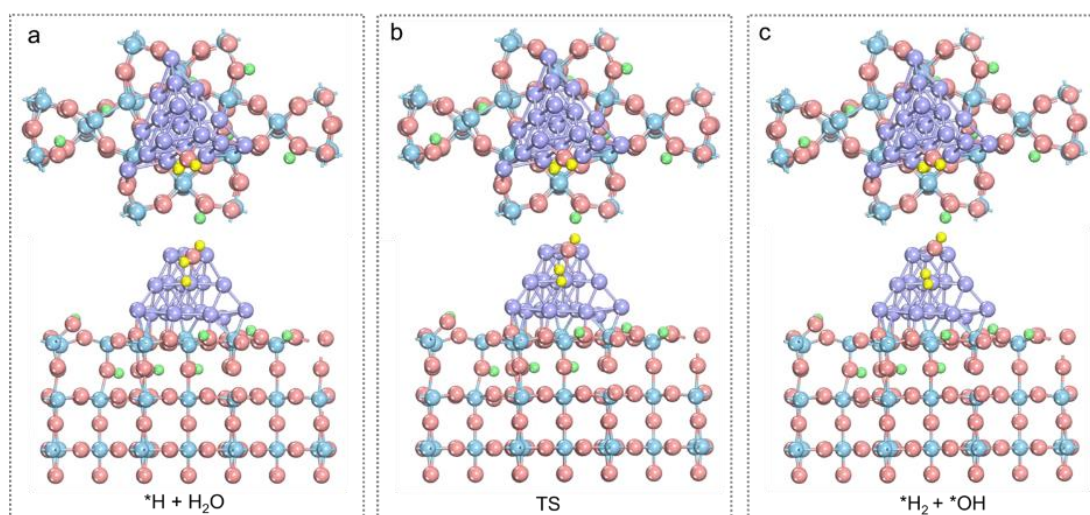


**Supplementary Figure 28.** Top and side views of DFT models used for calculating the hydrogen adsorption energy of Ru-H<sub>x</sub>WO<sub>3</sub>. (a) Ru-H<sub>x</sub>WO<sub>3</sub>. (b) Ridge site of Ru on Ru-H<sub>x</sub>WO<sub>3</sub>. (c) Edge site of Ru on Ru-H<sub>x</sub>WO<sub>3</sub>. (d) Corner site of Ru on Ru-H<sub>x</sub>WO<sub>3</sub>. (e) Top site of Ru on Ru-H<sub>x</sub>WO<sub>3</sub>.

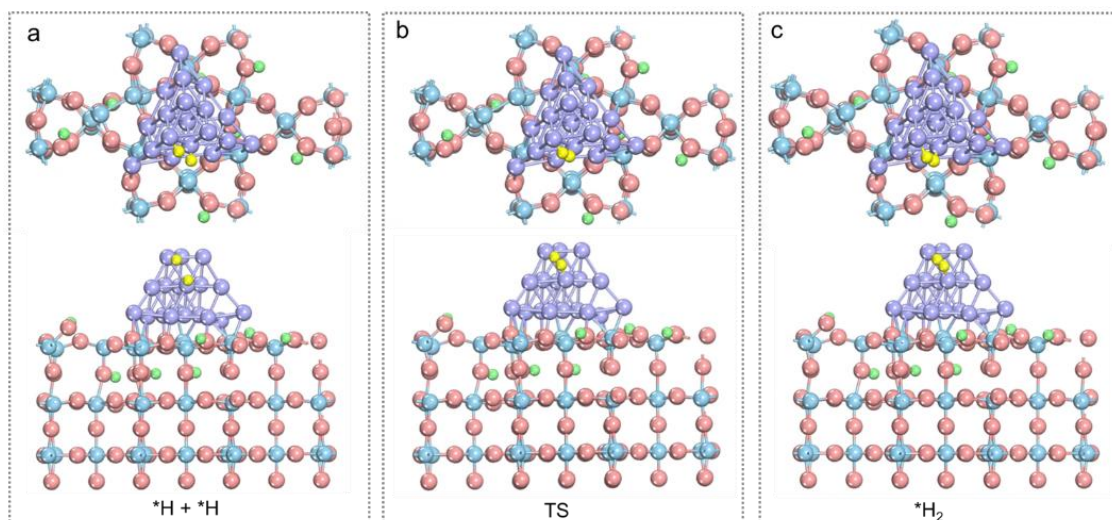




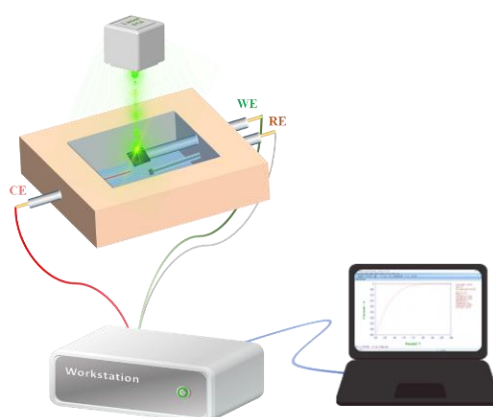
**Supplementary Figure 29.** Energy barrier of Heyrovsky step (a) and Tafel step (b) on Ru of Ru- $H_x$ WO $_{3-x}$ . (TS represent the transition states).



**Supplementary Figure 30.** Side and top view illustrations of DFT models used for calculating the energy barrier of Heyrovsky step on Ru clusters of Ru- $H_x$ WO $_{3-x}$ . (a) Initial state. (b) Transition state. (c) Final state. The blue, red and purple balls represent W, O and Ru atoms. The green and yellow balls represent the H atoms inserted into WO $_{3-x}$  and the H atoms involved in HER.



**Supplementary Figure 31.** Side and top view illustrations of DFT models used for calculating the energy barrier of Tafel step on Ru clusters of Ru-H<sub>x</sub>WO<sub>3-x</sub>. (a) Initial state. (b) Transition state. (c) Final state. The blue, red and purple balls represent W, O and Ru atoms. The green and yellow balls represent the H atoms inserted into WO<sub>3-x</sub> and the H atoms involved in HER.



**Supplementary Figure 32.** Test setup used for Raman in this work. The illustration of in situ Raman spectroscopy setup.



**Supplementary Table 7.** Ru wt.% determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Samples	Ru wt. %	Ru wt. % after stability test
Ru-WO <sub>3-x</sub> /CP	5.103	4.981
Ru-WO <sub>3</sub> /CP	6.320	6.111
Ru/C(5 wt. %)/CP	4.849	/

**Supplementary Table 8.** Comparison of HER performance in 1.0 M PBS for Ru-WO<sub>3-x</sub>/CP and the state-of-the-art HER electrocatalysts.

Catalyst	Electrolyte	Tafel slope (mV dec <sup>-1</sup> )	Overpotential (mV) @ j=10 mA cm <sup>2</sup>	Reference
<b>Ru-WO<sub>3-x</sub>/CP</b>	<b>1.0 M PBS</b>	<b>41</b>	<b>19</b>	<b>This work</b>
N-Ni	1.0 M PBS	106	64	Ref. <sup>6</sup>
Pt/np-Co <sub>0.85</sub> Se	1.0 M PBS	35	55	Ref. <sup>7</sup>
PtSA-NT-NF	1.0 M PBS	30	24	Ref. <sup>8</sup>
np-Co <sub>9</sub> S <sub>4</sub> P <sub>4</sub>	1.0 M PBS	51	87	Ref. <sup>9</sup>
CoP/Co-MOF	1.0 M PBS	63	49	Ref. <sup>10</sup>
MoP700	1.0 M PBS	79	196	Ref. <sup>11</sup>
Ni <sub>0.1</sub> Co <sub>0.9</sub> P	1.0 M PBS	103	125	Ref. <sup>12</sup>
NiCo <sub>2</sub> P <sub>x</sub>	1.0 M PBS	63.3	63	Ref. <sup>13</sup>
Ni <sub>0.89</sub> Co <sub>0.11</sub> Se <sub>2</sub>	1.0 M PBS	78	82	Ref. <sup>14</sup>

Mn-Co-P/Ti	1.0 M PBS	82	86	Ref. <sup>15</sup>
Co <sub>0.6</sub> Fe <sub>0.4</sub> P/CN T	1.0 M PBS	80	105	Ref. <sup>16</sup>
Cu <sub>0.08</sub> Co <sub>0.92</sub> P NAs/CP	1.0 M PBS	83.5	81	Ref. <sup>17</sup>
Fe-O-P NRs/CC	1.0 M PBS	47	96	Ref. <sup>18</sup>
MoP NA/CC	1.0 M PBS	94	187	Ref. <sup>19</sup>
N-Co <sub>2</sub> P/CC	1.0 M PBS	68	42	Ref. <sup>20</sup>
Karst NF	1.0 M PBS	99	110	Ref. <sup>21</sup>
CoS <sub>x</sub> -(0.2- 0.02)-12	1.0 M PBS	76	168	Ref. <sup>22</sup>
SiO <sub>2</sub> /PPy NTs- CFs	1.0 M PBS	100.2	192	Ref. <sup>23</sup>
Hollow Ni(S <sub>0.5</sub> Se <sub>0.5</sub> ) <sub>2</sub>	1.0 M PBS	81	124	Ref. <sup>24</sup>
MoP/MoS <sub>2</sub>	1.0 M PBS	48	96	Ref. <sup>25</sup>
Co-HNP/CC	1.0 M PBS	38	85	Ref. <sup>26</sup>

**Supplementary Table 9.** Fitted data of EIS Nyquist plots by the equivalent circuit for Ru-WO<sub>3-x</sub>/CP, WO<sub>3-x</sub>/CP and Ru/C (5 wt.%)/CP.

Catalyst	$\eta$ (mV)	R <sub>s</sub>	CPE <sub>1</sub>	R <sub>ct</sub>	C <sub><math>\phi</math></sub> (F)	R <sub>i</sub>	CPE <sub>2</sub>	R <sub>c</sub>
<b>WO<sub>3-x</sub>/CP</b>	10	0.21	0.719	16.83	0.705	17.9	0.009	37.2
	20	0.39	0.931	12.45	0.973	10.84	2.461	35.6
	30	0.39	1.893	10.52	1.680	7.05	2.820	35.1
	40	0.40	1.075	6.132	2.258	1.05	0.007	36.1
<b>Ru/C(5 wt.%)/CP</b>	10	0.63	2.059	1.052	2.140	6.454	0.001	6.62
	20	0.66	0.269	0.091	4.422	4.051	9.165	7.02
	30	0.65	1.928	0.083	8.371	1.564	10.98	6.22
	40	0.65	1.990	0.074	10.75	0.283	9.066	7.08
<b>Ru-WO<sub>3-x</sub>/CP</b>	10	0.84	0.004	0.906	1.660	7.028	6.547	3.648
	20	0.82	0.359	0.506	8.067	5.571	0.002	3.585
	30	0.86	1.629	0.125	24.91	3.337	10.58	3.163
	40	0.83	1.639	0.116	57.98	1.223	7.521	4.029

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