# **Supporting Information**

# Cable-like Ru/WNO@C Nanowires for Simultaneously High-

# efficient Hydrogen Evolution and Low-energy Consumption Chlor-

# alkali Electrolysis

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Section	Page
Experimental Section and other Supplements	S2-S7
Supporting Figures	S8-S50
Supporting Tables	S51-S56
References	S57-S59

## **Table of contents**

## **Experimental Section and other Supplements**

#### Analysis of Energy Consumption in Chlor-alkali Industry

According to W=V×1000/(1.492× $\eta$ ), in which "W" represents the electricity consumption per ton of NaOH produced, "V" is referred to the cell voltage and " $\eta$ " is cathodic current efficiency, the tons of alkali electric consumption will be reduced by 67 kW·h/t<sub>NaOH</sub> for every 100 mV reduction of electrode overpotential. As a result, more than \$345 million would be saved annually around the world (the annual output of NaOH is calculated to be 70 million tons, the cost is calculated at \$ 0.074/kW·h electricity).

#### **Chemicals and Reagents**

Ruthenium trichloride (RuCl<sub>3</sub>), poly(vinylpyrrolidone) (PVP, MW  $\approx$  24000), Ru powder, Ru/C (5 wt%) and Nafion solution (5 wt%) are purchased from Aladdin. Pt/C (20 wt%), urea, tungsten hexachloride (WCl<sub>6</sub>), glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), potassium hydroxide (KOH), potassium sulfate (K<sub>2</sub>SO<sub>4</sub>), potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>), sodium chloride (NaCl), graphite powder, sodium hydroxide (NaOH) and anhydrous ethanol (EtOH) are purchased from Macklin. All chemicals and solvents are used without further purification. Water (18.2 M $\Omega$  cm, 25 °C) used throughout our experiments is treated with a Millipore system. W<sub>18</sub>O<sub>49</sub> nanowires used as precursor was synthesized according to a previous literature procedure. Both RuO<sub>2</sub>/IrO<sub>2</sub>-coated Ti-mesh and low carbon steel electrodes are purchased from Suzhou Shuertai industrial technology Co., LTD (China) [https://m.tb.cn/h.3paVNqX].

#### The preparation of precursor W<sub>18</sub>O<sub>49</sub> NWs

The precursor  $W_{18}O_{49}$  NWs were synthesized according to a modified reported method. A mixture of 0.001 g of PVP and 0.3 g of WCl<sub>6</sub> was dissolved in 400 mL of ethanol. The obtained solution was transferred into a Teflon-lined stainless steel autoclave and kept at 180 °C for 24 h. After the autoclave cooled to room temperature naturally,  $W_{18}O_{49}$  NWs were obtained by centrifugation and washed with deionized water and ethanol several times.

#### The preparation of control samples

In order to demonstrate the role of N-doped carbon shells in Ru/WNO@C (Ru wt%=3.37%) electrocatalyst, N doped carbon (labeled with N-C) and carbon (labeled with C) have been prepared.

#### Synthesis of N-C

Pure urea was heated to 500 °C for 2 h with a heating rate of 2 °C min<sup>-1</sup> in air, the asobtained  $C_3N_4$  powder was then heated to 800 °C for 6 h in N<sub>2</sub> atmosphere with a ramp rate of 5 °C min<sup>-1</sup>.

#### Synthesis of C

Carbon without nitrogen (C) is obtained by the pyrolysis of glucose ( $C_6H_{12}O_6$ ) at 800 °C for 6 h with a heating rate of 5 °C min<sup>-1</sup> in N<sub>2</sub>.

## Materials characterization

The morphologies of the samples were characterized using field-emission scanning electron microscopy (FESEM) on a Hitachi SU-8010 apparatus, transmission electron microscopy (TEM) on a JEOL-2100F instrument and high angle annular dark-field scanning TEM (HAADF-STEM) on a HF5000 at Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China. The powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku D/max-IIB X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda$ =1.5418Å). Raman spectrum was recorded on a Raman S3 spectrometer (JY, Labram HR 800). The element composition and valence states of samples were studied on an ESCALAB 250 spectrometer (Thermo Electron Corp.) with Al K $\alpha$  radiation (h $\nu$  = 1486.6 eV) as the excitation source. The interrelated energy dispersive X-ray detector (EDAX) spectra were achieved by using a SU8000 ESEM FEG microscope. The nitrogen sorption measurement was obtained on an ASAP 2020 (Micromeritics, USA). The ICP-AES elemental analyses were performed on a Prodigy Leeman ICP-AES spectrometer. The evolved gases during HER were detected by gas chromatograph (Shimadzu, GC-2014C with a thermal conductivity detector).

#### **Electrochemical measurements**

All electrochemical performance was measured using a CHI760E electrochemical workstation (CH Instruments, China). The electrochemical performance was firstly tested with a typical three-electrode system at room temperature. A modified glassy carbon electrode (GCE, d=3 mm) was used as the working electrode, a saturated calomel electrode was served as the reference electrode, and a carbon rod as the counter electrode. All potentials were referenced to a reversible hydrogen electrode (RHE) according to  $E_{RHE}=E_{SCE}+E^{\Theta}_{SCE}+0.059\times pH$ . The linear sweep voltammetry (LSV) measurements were tested with a scan rate of 5 mV s<sup>-1</sup>. All of the HER polarization curves were iR-corrected according to the following equation:  $E_{corrected} =$ 

E<sub>measured</sub> - iR<sub>s</sub>. Where E<sub>corrected</sub> is the iR-corrected potential, E<sub>measured</sub> and i are experimentally measured potential and current, respectively. The LSV curves were replotted as overpotential (n) versus the logarithm of the current density (log |i|) to determine Tafel plots according to Tafel equation  $\eta = b \log j + a$ . Electrochemical impedance spectra (EIS) tests were carried out over a frequency range from 0.01 to 100 kHz and an amplitude of 10 mV. The EIS spectra were fitted by the Z-SimpWin software. The electrochemical surface areas (ECSA) were obtained from cyclic voltammetry curves (CVs) recorded in a potential range with no faradic current at different scan rates from 25 to 200 mV s<sup>-1</sup>. The ECSA is evaluated by the doublelayer capacitance (Cdl) proportional to it. The value of Cdl was estimated by plotting the  $\Delta j (j_a - j_c)$  at a certain voltage against the scan rate, where the slope is twice Cdl. The range of voltage was from -1.1 to -0.9 V (vs. SCE, in 1 M KOH), -0.5 to -0.3 V (vs. SCE, in 1 M PBS) and -0.1 to 0.1 V (vs. SCE, in 0.5 M H<sub>2</sub>SO<sub>4</sub>), respectively. Electrochemical stability was measured using continuous cyclic voltammetric sweeps at 0.1 V s<sup>-1</sup> between -1.0 V and -1.2 V (vs. SCE) in 1 M KOH, between -0.6 V and -0.8 V (vs. SCE) in 1 M PBS, and between -0.2 V and -0.4 V (vs. SCE) in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The long-term I-T curves were measured under fixed overpotentials in different electrolytes. The activities of hydrogen evolution in chlor-alkali electrolysis were measured in simulated chlor-alkali industrial electrolyte (3 M NaCl + 3 M NaOH, pH = 14.4) at different temperature (20 °C to 90 °C). The simulated chloralkali process (overall sodium chloride solution electrolysis) was performed in a homemade two-electrode system with Ru/WNO@C (Ru wt%=3.37%) coated on carbon paper as the cathode for HER (hydrogen evolution reaction) and RuO<sub>2</sub>/IrO<sub>2</sub>coated Ti-plate as the anode catalyst for CIER (chlorine evolution reaction). For comparison, the 20% Pt/C coated on carbon paper, low carbon steel and bare carbon paper were also evaluated as reference cathodes. The long-term chronopotentiometric (CP) measurement was studied at a constant cathodic current density of 10 mA cm<sup>-2</sup> for 25 h. The electrolyte of the anode cell is supersaturated NaCl aqueous to ensure sufficient chlorine source with the continuous CIER process, and the electrolyte of the cathode cell is the aqueous solution of 3 M NaCl and 3 M NaOH. The two reaction cells are separated by a cation exchange membrane to ensure the passage of Na<sup>+</sup>. All the electrochemical measurements are represented with IR compensation.

## Preparation of the working electrodes

The working electrode was prepared as follows: 2 mg of catalyst was dispersed in 200  $\mu$ l of 0.5 wt% Nafion EtOH solution (the mass ratio of 5 wt% Nafion solution to EtOH is 1:9). After fully sonication for at least 2 h, 4  $\mu$ l of the homogeneous working electrode ink was dropped onto the surface of a glassy carbon electrode (GCE) with a diameter of 3 mm, leading to an approximate catalyst loading of 0.566 mg cm<sup>-2</sup>. The electrode was then dried in air.

Carbon paper (1 cm  $\times$  2 cm) was used as the support of catalysts when the twoelectrode system was performed to simulate the chlorine-alkali process. Carbon papers were sequentially degreased in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 0.5 h at 80 °C, cleaned thoroughly in DI water and absolute ethanol, respectively. Then 50 µl of the ink was drop cast onto the sides of carbon cloth (2  $\times$  1 cm  $\times$  0.3 cm = 0.6 cm<sup>2</sup>) after dried in air at ambient temperature, the catalyst loading is 0.833 mg cm<sup>-2</sup>. Finally, the carbon paper was dried naturally in air.

## **Preparation of electrolytes**

0.5 M H<sub>2</sub>SO<sub>4</sub> (pH = 0.30), 0.05 M H<sub>2</sub>SO<sub>4</sub> + 0.45 M Na<sub>2</sub>SO<sub>4</sub> (pH = 1.24), 5 mM H<sub>2</sub>SO<sub>4</sub> + 0.49 M Na<sub>2</sub>SO<sub>4</sub> (pH = 2.77), 0.5 mM H<sub>2</sub>SO<sub>4</sub> + 0.49 M Na<sub>2</sub>SO<sub>4</sub> (pH = 3.83), 0.05 mM H<sub>2</sub>SO<sub>4</sub> + 0.49 M Na<sub>2</sub>SO<sub>4</sub> (pH = 4.93), 5  $\mu$ M H<sub>2</sub>SO<sub>4</sub> + 0.49 M Na<sub>2</sub>SO<sub>4</sub> (pH = 5.80), 0.5 $\mu$ M H<sub>2</sub>SO<sub>4</sub> + 0.49 M Na<sub>2</sub>SO<sub>4</sub> (pH = 6.25), 1 M KOH (pH = 14.00), 0.1 M KOH + 0.6 M K<sub>2</sub>SO<sub>4</sub> (pH = 12.76), 0.01 M KOH + 0.66 M K<sub>2</sub>SO<sub>4</sub> (pH = 11.6), 1 mM KOH + 0.66 M K<sub>2</sub>SO<sub>4</sub> (pH = 10.46), 0.1 mM KOH + 0.66 M K<sub>2</sub>SO<sub>4</sub> (pH = 9.77), 0.01 mM KOH + 0.66 M K<sub>2</sub>SO<sub>4</sub> (pH = 9.25), 1  $\mu$ M KOH + 0.66 M K<sub>2</sub>SO<sub>4</sub> (pH = 8.9). 1 M PBS was prepared by dissolving 1.361 g KH<sub>2</sub>PO<sub>4</sub> in 10 mL deionized water, and the pH of the mixture was adjusted to 7.00 with 1 M KOH.

The simulated chlor-alkali industrial electrolyte (3 M NaCl + 3 M NaOH): 120 g NaOH and 175.5 g NaCl were dissolved in deionized water, and the total volume of the solution is 1000 mL (pH = 14.4).

# **Supporting Figures**



Fig. S1 (a) PXRD pattern and (b) TEM image of precursor  $W_{18}O_{49}$  NWs.



**Fig. S2** (a)-(b) TEM images of WNO@C; (c)-(d) TEM images of Ru/WNO@C (Ru wt%=0.46%); (e)-(f) TEM images of Ru/WNO@C (Ru wt%=1.01%).



**Fig. S3** (a)-(b) TEM images of Ru/WNO@C (Ru wt%=2.37%); (c)-(d) TEM images of Ru/WNO@C (Ru wt%=3.85%); (e)-(f) TEM images of Ru/WNO@C (Ru wt%=6.69%).



Fig. S4 PXRD patterns of WNO@C and series of Ru/WNO@C with different Ru mass loading.



Fig. S5 PXRD pattern of Ru NPs@C. The average grain size of Ru NPs@C was calculated to be 38.34 nm using Debye-Scherrer method.



**Fig. S6** (a) TEM and (b) HRTEM images of Ru NPs@C. The measured average size of Ru NPs@C was similar to the value calculated from PXRD results. The lattice spacing of 0.2 nm was well matched with the (101) crystal plane of hexagonal Ru in HRTEM image, and the lattice spacing of 0.34 nm observed outside the Ru nanoparticle corresponded to the typical layer distance of graphite-like carbon. The core-shell structure of Ru NPs@C was succesfully demonstrated.



Fig. S7 EDAX spectra of (a) WNO@C, (b)-(g) series of Ru/WNO@C with different Ru mass loading and (h) Ru NPs@C.



Fig. S8 XPS full-scan spectrum of Ru/WNO@C (Ru wt%=3.37%).



Fig. S9 XPS full-scan spectra of Ru NPs@C and WNO@C.



**Fig. S10** The high-resolution (a) N 1s and (b) C 1s spectra of Ru NPs@C. The high-resolution N 1s spectrum shows three peaks at 398.17, 400.02 and 401.05 eV, corresponding to pyridinic N, pyrrolic N and graphitic N, respectively; The high-resolution C 1s and Ru 3d spectrum dispalys two peaks at 280.40 and 284.49 eV, which can be assigned to Ru  $3d_{5/2}$  and Ru  $3d_{3/2}$ , respectively. The peaks at 284.48 and 285.33 eV are attributed to C=C/C-C and C-N bonds, respectively. These XPS data clearly prove that there is N doping in the carbon layers of Ru NPs@C.



Fig. S11 The high-resolution C 1s spectrum of WNO@C. The peaks located at 284.44, 284.96, 285.94 and 288.56 eV are attributed to C=C/C-C, C-N, C-O and C=O,



respectively. The existence of C-N demonstrates the N doping in carbon.

Fig. S12 (a) W 4f, (b) N 1s and (c) O 1s high-resolution spectra of Ru/WNO@C (Ru wt%=3.37%) and WNO@C; (d) Ru 3p spectra of Ru/WNO@C (Ru wt%=3.37%), RuCl<sub>3</sub> and Ru NPs@C.



**Fig. S13** the N<sub>2</sub> adsorption-desorption isotherms of Ru/WNO@C (Ru wt%=3.37%) and WNO@C. Ru/WNO@C (Ru wt%=3.37%) exhibits similar BET surface area with WNO@C, proving that the introduction of ruthenium did not cause obvious agglomeration. The typical IV hysteresis-loop of Ru/WNO@C (Ru wt%=3.37%) demonstrates the mesoporous structure. Such a mesoporous structure could expose more catalytic active sites and promote the infiltration of reactants and electrolyte.<sup>S1</sup>



Fig. S14 Fourier transform infrared (FTIR) spectrum of Ru/WNO@C (Ru wt%=3.37%) shows stretching vibrations of O-H ( $3157.96 \text{ cm}^{-1}$ ), C=O ( $1598.8 \text{ cm}^{-1}$ ) and C=C ( $1399.14 \text{ cm}^{-1}$ ) functional groups, indicating the presence of hydrophilic groups (-COOH and -OH) on the surface of catalyst.<sup>S2</sup>



Fig. S15 Raman spectrum of Ru/WNO@C (Ru wt%=3.37%). The peaks located at

251, 684 and 796 cm<sup>-1</sup> are ascribed to the WNO phase.<sup>S3-S4</sup>



Fig. S16 The LSV curves of Ru/WNO@C (Ru wt%=3.37%) in 1 M KOH with and

without iR-compensation.



**Fig. S17** I-T curves of Ru/WNO@C (Ru wt%=3.37%) (overpotential = 23 mV) and WNO@C (overpotential = 365 mV) before and after the addition of SCN<sup>-</sup> ions in 1 M KOH. As depicted in Fig. S17, both the current densities of Ru/WNO@C (Ru wt%=3.37%) and WNO@C in the IT-curves exhibit decline obviously after the addition of 10 mmol SCN<sup>-</sup> at t = 200 s. The current density of Ru/WNO@C (Ru wt%=3.37%) decreases from 30.31 to 8.24 mA cm<sup>-2</sup> (the decline of current density is 72.81%), and the current density of WNO@C decreases from 28.8 to 25.3 mA cm<sup>-2</sup> (the decline of current density is 12.15%). These results strongly proved that the Rucenter of Ru nanoclusters and the W-center of WNO nanowires together act as the active sites in Ru/WNO@C. DFT calculations also help us to further understand the interaction between Ru nanoclusters and WNO nanowires. As displayed in the charge density difference (CDD) diagram (Fig. 4b), the charge density at the interface of Ru<sub>13</sub> cluster and WNO increases significantly, which demonstrates the strong electron

interaction between Ru and WNO in the composite electrocatalyst. Combined with the experimental results and DFT calculation, we infer that the interaction at the interface between WNO and Ru nanocluster optimizes the electronic property and produces synergistic effect, which endows the Ru/WNO@C with suitable adsorbed free energy of hydrogen ( $\Delta G_H$ \*) and low barrier of water dissociation ( $\Delta G_B$ ), as well as fast electron transfer ability. Moreover, the current density of Ru/WNO@C (Ru wt%=3.37%) reduces to 8.24 mA cm<sup>-2</sup> after the addition of SCN<sup>-</sup>, indicating that the carbon and nitrogen elements might also contribute to the HER activity besides Ru and W-center. The HER performance of carbon (C) and nitrogen-doped carbon (N-C) in 1 M KOH has been tested to verify this speculation in Fig S19 in supporting information.



**Fig. S18** PXRD patterns of C and N-C. The PXRD patterns of N-C and C show similar characteristic peaks of graphite carbon.



**Fig. S19** LSV plots of C, N-C and Ru/WNO@C (Ru wt%=3.37%) in 1 M KOH. As shown in Fig. S19, the hydrogen production activity of Ru/WNO@C (Ru wt%=3.37%) is much higher than those of N-C and C, which indicates that the WNO nanowires and ultra-small Ru nanoclusters are the primary active sites in the composite catalysts Ru/WNO@C. Furthermore, N-C shows higher HER performance than that of C, confirming the effect of nitrogen doping on improving the HER activities of electrocatalysts, which may be due to the effect of the accumulating proton of nitrogen element. Take into account the results shown in Fig. S17-S19, the main active sites in the composite catalyst of Ru/WNO@C should be mainly the interfaces between ultra-small Ru nanoclusters and WNO nanowires, and the outer N-doped carbon shells also contribute to the excellent HER performance.



**Fig. S20** (a) HER polarization curves of WNO@C and Ru/WNO@C (different Ru content) in 1 M KOH; (b) corresponding Tafel plots of Ru/WNO@C (different Ru content) in 1 M KOH; (c) mass activities of Ru/WNO@C (different Ru content) in 1 M KOH; (d) specific activities and mass activities of Ru/WNO@C (different Ru content) at overpotential of 50 mV in 1 M KOH.



**Fig. S21** Powder XRD patterns of (a) Ru/WO<sub>x</sub>@C-500, (b) Ru/WNO@C-600, (c) Ru/WNO@C-700 and (d) Ru/WC/W<sub>2</sub>C/WNO@C-900. When pyrolysis temperature is 500 °C,  $W_{18}O_{49}$  can not be converted into WNO, and the composite of amorphous carbon and WO<sub>x</sub> was obtained. WNO could be obtained when pyrolysis temperature rises to 600 and 700 °C, Ru/WNO@C-700 shows better crystallinity than Ru/WNO@C-600. The pyrolysis temperature rising to 900 °C leads to the partially carbonization of  $W_{18}O_{49}$ , resulting in the composite of WC,  $W_2C$  and WNO. The Ru/RuO<sub>x</sub> peak was not found in the PXRD patterns of all these catalysts pyrolyzed at different temperatures.



Fig. S22 EDAX spectra of (a)  $Ru/WO_x@C-500$ , (b) Ru/WNO@C-600, (c) Ru/WNO@C-700 and (d)  $Ru/WC/W_2C/WNO@C-900$ .



**Fig. S23** (a) SEM image and (b) TEM image of Ru/WO<sub>x</sub>@C-500; (c)-(h) STEM image and EDAX elemental mapping of (d) Ru, (e) W, (f) N, (g) O and (h) C in Ru/WO<sub>x</sub>@C-500. The Ru/WO<sub>x</sub>@C-500 does not exhibit the nanowire morphology of the precursor, which is due to the presence of a large amount of carbon due to the relatively low pyrolysis temperature.



Fig. S24 (a) SEM image and (b) TEM image of Ru/WNO@C-600; (c)-(h) STEM image and EDAX elemental mapping of (d) Ru, (e) W, (f) N, (g) O and (h) C in Ru/WNO@C-600.



**Fig. S25** (a) SEM image and (b) TEM image of Ru/WNO@C-700; (c)-(h) STEM image and EDAX elemental mapping of (d) Ru, (e) W, (f) N, (g) O and (h) C in Ru/WNO@C-700. As shown in Fig. S24-S25, Ru/WNO@C-600 and Ru/WNO@C-700 exhibit nanowire morphology.



Fig. S26 (a) SEM image and (b) TEM image of Ru/WC/W<sub>2</sub>C/WNO@C-900; (c)-(h) STEM image and EDAX elemental mapping of (d) Ru, (e) W, (f) N, (g) O and (h) C in Ru/WC/W<sub>2</sub>C/WNO@C-900. The Ru/WC/W<sub>2</sub>C/WNO@C-900 failed to retain well the nanowire morphology while exists partially agglomeration when the pyrolysis temperature rises to 900 °C.



Fig. S27 (a) HER polarization curves of Ru/WO<sub>x</sub>@C-500, Ru/WNO@C-600, Ru/WNO@C-700, Ru/WNO@C-800 (Ru wt%=3.37%) and Ru/WC/W<sub>2</sub>C/WNO@C-900 and (b) corresponding Tafel plots in 1 M KOH. These experimental results show that 800 °C is the optimal pyrolysis temperature.



**Fig. S28** CV curves of (a) Ru/WNO@C (Ru wt%=3.37%), (c) Ru NPs@C and (e) WNO@C with different scan rates from 25 to 200 mV dec<sup>-1</sup> in 1 M KOH, the corresponding capacitive current at 0.175 V as a function of the scan rate for (b) Ru/WNO@C (Ru wt%=3.37%), (d) Ru NPs@C and (f) WNO@C.



**Fig. S29** Electrochemical impedance spectra (EIS) of Ru/WNO@C (Ru wt%=3.37%) measured with overpotentials from 50 to 250 mV in 1 M KOH. Inset: two-time-constant model equivalent circuit used for data fitting of EIS spectra.



Fig. S30 I-T curve of Ru/WNO@C (Ru wt%=3.37%) at a fixed overpotential of 5 mV.



**Fig. S31** I-T curves of Ru/WNO@C (Ru wt%=3.37%) (overpotential = 6 mV), Ru powder (overpotential = 75 mV), 5% Ru/C (overpotential = 150 mV) and Ru NPs@C (overpotential = 160 mV). The current densities of Ru powder and 5% Ru/C dropped over 80% within about 1 and 2.5 hours, respectively. On the contrary, the Ru/WNO@C (Ru wt%=3.37%) and Ru NPs@C exhibit significantly enhanced electrochemical stability, further confirming that the presence of N-doped carbon shell can protect the catalyst from loss and corrosion in strong alkaline electrolyte.



**Fig. S32** The (a) PXRD pattern and (b) EDAX spectrum of Ru/WNO@C (Ru wt%=3.37%) after electrochemical stability test in 1 M KOH. These results reveal that the composition and structure of Ru/WNO@C (Ru wt%=3.37%) could be remained after long-term (100 h) test.



Fig. S33 XPS spectra of Ru/WNO@C (Ru wt%=3.37%) after electrochemical stability test (100 h) in 1 M KOH. (a) XPS full-scan spectra, high-resolution (b) Ru 3p, (c) C 1s + Ru 3d, (d) W 4f, (e) N 1s and (f) O 1s spectra.



**Fig. S34** TEM image of Ru/WNO@C (Ru wt%=3.37%) after long-term (100 h) electrochemical stability test in 1 M KOH. The image demonstrates that the morphology of Ru/WNO@C (Ru wt%=3.37%) catalyst shows negligible change after electrochemical test.



**Fig. S35** Illustration of the optimized model ( $2 \times 2$  supercell) with Ru<sub>13</sub>, WNO, and carbon layer included. The model with carbon layer adsorbed upon the Ru<sub>13</sub>/WNO which interacted through the Ru side (a) was computed to 1.60 eV more stable than that down to the WNO side (b). Color code: W (light blue), N (yellow), Ru (purple), O (red), and C (gray).



Fig. S36 (a) HER polarization curves of Ru/WNO@C (Ru wt%=3.37%), WNO@C, Ru NPs@C, commercial 20 wt% Pt/C, Ru powder, 5 wt% Ru/C and bare GCE in 0.5 M H<sub>2</sub>SO<sub>4</sub>; (b) corresponding Tafel plots in 0.5 M H<sub>2</sub>SO<sub>4</sub>; (c) overpotentials at 10 mA cm<sup>-2</sup> of 20 wt% Pt/C, Ru/WNO@C (Ru wt%=3.37%), Ru powder, 5 wt% Ru/C, WNO@C and Ru NPs@C in 0.5 M H<sub>2</sub>SO<sub>4</sub>; (d) the accelerated durability tests of Ru/WNO@C (Ru wt%=3.37%) in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Inset: I-T curve of Ru/WNO@C (Ru wt%=3.37%) at a fixed overpotential of 55 mV in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The Ru/WNO@C (Ru wt%=3.37%) catalyst only requires small overpotential of 37 mV to reach 10 mA cm<sup>-2</sup>, which is only 3 mV higher than that of 20% Pt/C (34 mV). Pleasingly, the cathodic current density of Ru/WNO@C (Ru wt%=3.37%) surpasses that of 20% Pt/C when the potential is more negative than 75 mV. As displayed in Fig. S36b, the

corresponding Tafel slope is calculated to be 41 mV dec<sup>-1</sup>, which is slightly higher than that of 20% Pt/C, suggesting the HER process occurred via the Volmer-Heyrovsky mechanism. The overpotentials at 10 mA cm<sup>-2</sup> of 20% Pt/C, Ru/WNO@C (Ru wt%=3.37%), Ru powder, 5% Ru/C, WNO@C and Ru NPs@C in 0.5 M H<sub>2</sub>SO<sub>4</sub> have been summarized in Fig. S36c, the  $\eta_{10}$  of Ru/WNO@C (Ru wt%=3.37%) is only slightly higher than that of 20% Pt/C, while much lower than those of the other catalysts, demonstrating the satisfactory electrocatalytic activity of Ru/WNO@C (Ru wt%=3.37%) in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The accelerated durability tests and long-term I-T tests of Ru/WNO@C (Ru wt%=3.37%) in 0.5 M H<sub>2</sub>SO<sub>4</sub> were also performed (Fig. S36d), and the results reveal that the composite catalyst possesses remarkable durability in acidic media.



S36

**Fig. S37** (a) CV curves of Ru/WNO@C (Ru wt%=3.37%) with different scan rates from 25 to 200 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>; (b) the corresponding capacitive current at 0.25 V as a function of the scan rate for Ru/WNO@C (Ru wt%=3.37%); (c) electrochemical impedance spectra (EIS) of Ru/WNO@C (Ru wt%=3.37%) measured with overpotentials from 50 to 250 mV in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Inset: two-time-constant model equivalent circuit used for data fitting of EIS spectra; (d) faradaic efficiency of Ru/WNO@C (Ru wt%=3.37%) towards HER in 0.5 M H<sub>2</sub>SO<sub>4</sub> at several overpotentials. The Ru/WNO@C (Ru wt%=3.37%) possesses large Cdl value of 69 mF cm<sup>-2</sup>, low electrochemical impedance of 8.20 Ω at overpotential of 150 mV and high Faraday Efficiency close to 100% in 0.5 M H<sub>2</sub>SO<sub>4</sub>, proving the excellent kinetics of Ru/WNO@C (Ru wt%=3.37%) in acid electrolyte.



**Fig. S38** (a) HER polarization curves of Ru/WNO@C (Ru wt%=3.37%), WNO@C, Ru NPs@C, commercial 20 wt% Pt/C, Ru powder, 5 wt% Ru/C and bare GCE in 1 M PBS; (b) corresponding Tafel plots in 1 M PBS; (c) overpotentials at 10 mA cm<sup>-2</sup> of 20 wt% Pt/C, Ru/WNO@C (Ru wt%=3.37%), Ru powder, 5 wt% Ru/C, WNO@C and Ru NPs@C in 1 M PBS; (d) the accelerated durability tests of Ru/WNO@C (Ru wt%=3.37%) in 1 M PBS. Inset: I-T curve of Ru/WNO@C (Ru wt%=3.37%) at a fixed overpotential of 65 mV in 1 M PBS. In 1 M PBS, it only take Ru/WNO@C (Ru wt%=3.37%) a low overpotential of 56 mV to attain cathodic current density of 10 mA cm<sup>-2</sup>, 13 mV lower than that of 20% Pt/C (69 mV), and much lower than those of other catalysts (Fig. S38a). Ru/WNO@C (Ru wt%=3.37%) shows the lowest Tafel slope of 78 mV dec<sup>-1</sup> among all of the samples (Fig. S38b). In addition, the accelerated durability tests and long-term I-T tests of Ru/WNO@C (Ru wt%=3.37%) in 1 M PBS were also performed (Fig. S38d), and the results reveal that the composite catalyst possesses remarkable durability in neutral media.



**Fig. S39** The HER polarization plots of Ru/WNO@C (Ru wt%=3.37%), 20% Pt/C, Ru powder and 5% Ru/C in pH (a) 1.24 and (b) 2.77 electrolytes. The Ru/WNO@C

(Ru wt%=3.37%) catalyst requires 109 mV to achieve current density of 10 mA cm<sup>-2</sup> in pH 1.24 electrolyte (Fig. S39a), which is slightly larger than that of 20% Pt/C (87 mV). Similar to the phenomenon in 0.5 M H<sub>2</sub>SO<sub>4</sub>, the current density of Ru/WNO@C (Ru wt%=3.37%) would outperform 20% Pt/C when the potential is higher than 315 mV. In 2.77 pH electrolyte (Fig. S39b), although 20% Pt/C shows a smaller onset potential than Ru/WNO@C (Ru wt%=3.37%), the current density of 20% Pt/C remains constant at 8 mA cm<sup>-2</sup> while Ru/WNO@C (Ru wt%=3.37%) could reach 12 mA cm<sup>-2</sup>.



**Fig. S40** The HER polarization plots of Ru/WNO@C (Ru wt%=3.37%), 20% Pt/C, Ru powder and 5% Ru/C in pH (a) 3.83, (b) 4.93 (c) 5.8 and (d) 6.25 electrolytes.



**Fig. S41** The HER polarization plots of Ru/WNO@C (Ru wt%=3.37%), 20% Pt/C, Ru powder and 5% Ru/C in pH (a) 8.9, (b) 9.25, (c) 9.77, (d) 10.46, (e) 11.6 and (f) 12.76 electrolytes.



**Fig. S42** The variation of mass activities of Ru/WNO@C (Ru wt%=3.37%) and 20 wt% Pt/C at the same overpotential of 50 mV with the pH values of 1-13. As shown in Fig. S36-S37 and S39, Ru/WNO@C (Ru wt%=3.37%) possesses specific HER activities really close to 20% Pt/C under small potential and better activities than 20% Pt/C at high potential condition in 0-3 pH electrolytes. As for pH>3 electrolytes (Fig. S38 and Fig. S40-S41), the specific HER activities of Ru/WNO@C (Ru wt%=3.37%) are much higher than those of 20% Pt/C over all the potential range (The two catalysts exhibit similar specific HER activities at pH = 8.9). Considering the difference in noble metal loading between Ru/WNO@C (Ru wt%=3.37%) and 20% Pt/C, Ru/WNO@C (Ru wt%=3.37%) exhibits superior mass activity than 20% Pt/C over the entire pH range.



**Fig. S43** (a) HER LSV curves and corresponding (b) Tafel plots of Ru/WNO@C (Ru wt%=3.37%) in simulated chlorine-alkali electrolyte (3 M NaCl + 3 M NaOH) and 1 M KOH; (c) HER LSV curves and corresponding (d) Tafel plots of commercial 20% Pt/C in simulated chlorine-alkali electrolyte (3 M NaCl + 3 M NaOH) and 1 M KOH. The polarization curves of Ru/WNO@C (Ru wt%=3.37%) and 20% Pt/C in simulated chlorine-alkali electrolyte exhibit the consistent slight increase of onset potentials, tiny decrease of Tafel slopes and enhancement in current densities compared with those of in 1 M KOH. This phenomenon can be understood as follows: (1) With the increase of alkaline concentration, it becomes more difficult to trigger HER due to the competition between  $H_2O$  and  $OH^-$  adsorption on the electrode surface, which results in the increase of onset potentials; (2) The decreased Tafel slopes and increased

current densities should be attributed to the accelerated ion transfer rate derived from the proper increase of concentration of supporting electrolyte.



**Fig. S44** (a) CV curves of Ru/WNO@C (Ru wt%=3.37%) with different scan rates from 25 to 200 mV s<sup>-1</sup> in simulated chlorine-alkali electrolyte (3 M NaCl + 3 M NaOH). Inset (the bottom right corner): corresponding capacitive current at 0.21 V as a function of the scan rate for Ru/WNO@C (Ru wt%=3.37%). The Cdl value of Ru/WNO@C (Ru wt%=3.37%) in simulated chlorine-alkali electrolyte is calculated to be 110 mF cm<sup>-2</sup>, implying the large electrochemical surface areas (ECSA); (b) electrochemical impedance spectra (EIS) of Ru/WNO@C (Ru wt%=3.37%) measured with overpotentials from 50 to 250 mV in simulated chlorine-alkali electrolyte. Inset: two-time-constant model equivalent circuit used for data fitting of EIS spectra.



**Fig. S45** HER polarization curves for Ru/WNO@C (Ru wt%=3.37%) in simulated chlorine-alkali electrolyte at temperatures from 20 to 90 °C. As shown in Fig. S45, the onset overpotential and the current density increases gradually with the increase of temperature. The increase of the overpotential is due to the fact that the rate of hydrogen production increases with the increase of temperature, and the concentration of hydroxide in the solution increases, which leads to the hindrance of water adsorption. The increase of current density should be attributed to the increase of the migration rate of ions at high temperature.



Fig. S46 HER polarization curves for (a) 20% Pt/C and (b) low carbon steel in simulated chlorine-alkali electrolyte at temperatures from 20 to 90 °C. As shown in S44

the Fig. S46, the overpotential of low carbon steel and 20% Pt/C catalysts does not change obviously with the increase of temperature, indicating the slow rates of  $H^+$  consumption, further proving the relatively poor intrinsic hydrogen production activity of low carbon steel and 20% Pt/C.



Fig. S47 CIER polarization curve of RuO<sub>2</sub>/IrO<sub>2</sub>-coated Ti-mesh in saturated sodium chloride solution at 20 °C. The electrochemical formation of chlorine gas at the anode occurs according to the following reaction:  $2CI^{-} - 2e^{-} \rightarrow Cl_{2}$ , with an associated equilibrium potential of  $E^{\Theta} = 1.358$  V versus SHE. The RuO<sub>2</sub>/IrO<sub>2</sub>-coated Ti-mesh requires overpotential of 298 mV to reach 10 mA cm<sup>-2</sup>.



**Fig. S48** (a) PXRD and (b) TEM patterns of Ru/WNO@C (Ru wt%=3.37%) after chronopotentiometric test in simulated chlorine-alkali electrolyte. As shown in Fig. S48 a, the characteristic peaks located at 37.62°, 43.72°, 63.54°, 76.23° and 80.27° are indexed to the (111), (200), (220), (311) and (222) facets of  $W_{0.62}(N_{0.62}O_{0.38})$  (JCPDF No.25-1254). The TEM image in Fig. S48b displays the cable-like morphology of catalyst after durability test in simulated chlorine-alkali electrolyte, further indicating the structural robustness of Ru/WNO@C (Ru wt%=3.37%).



**Fig. S49** XPS spectra of Ru/WNO@C (Ru wt%=3.37%) after chronopotentiometric test in simulated chlorine-alkali electrolyte. (a) XPS full-scan spectra, (b) Ru 3p, (c) C 1s + Ru 3d, (d) W 4f, (e) N 1s and (f) O 1s. These results demonstrate that the element composition and the valence states of Ru/WNO@C (Ru wt%=3.37%) show negligible changes after durability test in simulated chlorine-alkali electrolyte.



**Fig. S50** PXRD pattern of S-0.92 (sample-0.92). In the preparation of Ru/WNO@C (with different Ru mass loading), the mass of urea and  $W_{18}O_{49}$  NWs added was 10 g and 0.1 g, respectively. While the mass of RuCl<sub>3</sub> aqueous solution (1%) was 0.115, 0.23, 0.575, 0.92, 1.15 and 1.725 g, respectively. The series obtained solids with different ruthenium mass loading were denoted as S-0.115, S-0.23, S-0.575, S-0.92, S-1.15 and S-1.725, respectively. Take the S-0.92 of the optimal electrocatalyst Ru/WNO@C (Ru wt%=3.37%) as an example, the PXRD pattern only exhibits strong

diffraction peaks of urea, while the peaks of  $W_{18}O_{49}$  and  $RuCl_3$  are very weak, which is due to the relatively low content of  $W_{18}O_{49}$  and  $RuCl_3$  in the S-0.92.



Fig. S51 PXRD patterns of S-0.115, S-0.23, S-0.575, S-0.92, S-1.15 and S-1.725.



Fig. S52 EDAX spectra of (a) S-0.115, (b) S-0.23, (c) S-0.575, (d) S-0.92, (e) S-1.15 and (f) S-1.725.



Fig. S53 (a) PXRD pattern and (b) SEM image of 3.37% Ru/C.

# **Supporting Tables**

Table S1. The ICP and EDAX results of WNO@C and Ru/WNO@C (different Ru mass loading).

Catalysts Ru content (wt%) Characterization methods	ІСР	EDAX
WNO@C	0	0
Ru/WNO@C (Ru wt%=0.46%)	0.46	0.37
Ru/WNO@C (Ru wt%=1.01%)	1.01	0.79
Ru/WNO@C (Ru wt%=2.37%)	2.37	1.71
Ru/WNO@C (Ru wt%=3.37%)	3.37	3.33
Ru/WNO@C (Ru wt%=3.85%)	3.85	3.76
Ru/WNO@C (Ru wt%=6.69%)	6.69	4.13

Catalyst	$\eta_{10}$	<b>Tafel Slope</b>	Ref.
	(mV)	(mV dec <sup>-1</sup> )	
Ru/WNO@C (Ru			
wt%=3.37%)	2	33	This work
Co <sub>1</sub> /PCN	89	52	S2
S-RP/C	17	34	S5
Ru@CN	32	53	S6
Mo <sub>2</sub> N-Mo <sub>2</sub> C/HGr	154	152	S7
Co-substituted Ru	13	29	S8
RuCoP	23	37	S9
Rh NP/C	7	19	S10
Pt <sub>3</sub> Ni <sub>3</sub>	15	~	S11
Ru@C <sub>2</sub> N	17	38	S12
NP-MoS <sub>2</sub> /CC	78	51.6	S13
FePSe <sub>3</sub> /NC	118.5	88	S14
Mo <sub>2</sub> C@NC@Pt	47	57	S15
NiO/Ru@Ni	39	75	S16
Ni-Ni <sub>0.19</sub>	42	125	S17
Ir@CON	13.5	29	S18
NC/Vo-WON	16	33	S19
FeCoNi-HNTAs	58	37.5	S20

**Table S2.** Comparison of HER performance in 1 M KOH for Ru/WNO@C (Ru wt%=3.37%) with other HER electrocatalysts.

Catalyst	η <sub>10</sub> (mV)	Mass Activity <sup>a</sup> (mA mg <sup>-1</sup> )	Tafel Slope (mV dec <sup>-1</sup> )	j₀ <sup>b</sup> (mA cm <sup>-2</sup> )
Ru/WNO@C (Ru wt%=3.37%)	2	4095.6	33	9.09
WNO@C	310	~	131	0.04
Ru NPs@C	143	6.3	97	0.65
20% Pt/C	27	145.3	42	3.95
5% Ru/C	137	45.8	91	0.46
Ru powder	61	14.6	72	2.25
3.37% Ru/C	202	37.8	122	0.21

**Table S3.** The electrochemical parameters of Ru/WNO@C (Ru wt%=3.37%) and other control electrocatalysts for HER in 1 M KOH.

<sup>a</sup>The current densities at overpotential of 50 mV. <sup>b</sup>Exchange current densities

 $(j_{\theta})$  are obtained from Tafel curves by using extrapolation method.

**Table S4.** The values of charge transfer resistance ( $R_{ct}$ ) and the series resistance ( $R_s$ ) for Ru/WNO@C (Ru wt%=3.37%) with overpotentials from 50 to 250 mV in 1 M KOH.

Overpotential (mV vs.	Ru/WNO@C (Ru wt%=3.37%)		
RHE)	$R_{ct}(\Omega)$	$R_{s}\left(\Omega ight)$	
50	10.38	8.71	
100	5.62	8.80	
150	4.4	8.78	
200	3.8	8.75	
250	3.20	8.70	

**Table S5.** The values of charge transfer resistance ( $R_{ct}$ ) and a series resistance ( $R_s$ ) for Ru/WNO@C (Ru wt%=3.37%) with overpotentials from 50 to 250 mV in simulated chlorine-alkali electrolyte.

Overpotential	Ru/WNO@C (Ru wt%=3.37%)		
(mV vs. RHE)	$R_{ct}(\Omega)$	$R_{s}(\Omega)$	
50	8.34	8.80	
100	2.86	8.84	
150	2.37	8.92	
200	1.86	8.91	
250	1.69	8.79	

Catalyst	Electrolyte	Т (°С)	<sup>a</sup> η <sub>(current</sub> density) (mV)	Tafel slope (mV dec <sup>-1</sup> )	Ref.
Ru/WNO@C (Ru	3 M NaOH+3	90	108	30	This
wt%=3.37%)	M NaCl	90 10	100(500)	50	work
Ni-Sn/copper	1 М КОН	room	~	121	S21
Ni-Fe-C/steel	NaCl 3.5%	90	70(120)	~	S22
NiMn/graphite	NaOH 30%	25	141 <sub>(100)</sub>	130	S23
NiCoZn/copper	1 M KOH	25	140(100)	81	S24
Ni-CeO <sub>2</sub> /mild steel	1 M NaOH	25	~	157	S25
$Co_{90}W_{10}$	1 M NaOH	25	326(250)	102	S26
Fe <sub>82</sub> B <sub>18</sub>	1 М КОН	25	430(300)	113	S27
Ni-P/mild steel	NaOH 32%	30	340(250)	147	S28
Pt	8 M KOH	85	460(100)	390	S29
Nano-Zr <sub>67</sub> Ni <sub>33</sub>	6 M KOH	25	1530(50)	121	S30

**Table S6.** Comparison of HER performance in simulated chlor-alkali electrolyte forRu/WNO@C (Ru wt%=3.37%) with other reported cathode elecrocatalysts.

 $^{a}\eta$  (current density): the overpotentials at different current densities (mA cm<sup>-2</sup>).

Couple	Cell voltage at 10 mA cm <sup>-2</sup> (V)
Ru/WNO@C (Ru wt%=3.37%)//RuO <sub>2</sub> /IrO <sub>2</sub> - coated Ti-mesh	2.48
20% Pt/C//RuO <sub>2</sub> /IrO <sub>2</sub> -coated Ti-mesh	2.52
low carbon steel//RuO <sub>2</sub> /IrO <sub>2</sub> -coated Ti-mesh	2.8
bare carbon paper//RuO <sub>2</sub> /IrO <sub>2</sub> -coated Ti- mesh	3.1

TableS7.The electrochemical parameters of Ru/WNO@C (Ruwt%=3.37%)//RuO<sub>2</sub>/IrO<sub>2</sub>-coated Ti-mesh and other control couples.

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