Supplementary Information for

Ultrathin Ru-Ni Nanounits as Hydrogen Oxidation Catalyst with Alkaline Electrolyte

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Chemicals. Potassium aquapenachloro-ruthenate (III) ($K_2RuCl_5 \cdot H_2O$) and potassium hydroxide (KOH) were purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai). Nafion and commercial Pt/C (20 $_{wt}$% of Pt) were purchased from Sinero Technology Co., Ltd (Suzhou). Nickel (II) formate dehydrate ($Ni(HCOO)_2 \cdot 2H_2O$), Polyvinyl pyrrolidone (PVP, MW = 58000), Sulfuric acid (H_2SO_4), Cupric sulfate ($CuSO_4$), Ethanol (CH_3CH_2OH), and acetone (CH_3COCH_3) were obtained from Macklin Biochemical Co., Ltd (Shanghai). All of the chemicals were used as received without further purification. The ultra-pure deionized water (18.2 MΩ cm^{-1}) was used in the experiments.

Characterization. Crystal phase structure of the samples was characterized by powder XRD on a Bruker D-8 Advanced diffractometer with Cu Kα (λ=1.5418 Å) radiation. The microstructures of the samples were checked by a (high-resolution) transmission electron microscope (HR-TEM, JEM-200CX). X-ray photoelectron spectra (XPS) were

carried out by using a PHI 5000 Versa-Probe photoelectron spectrometer with an Al Kα X-ray resource. The metal content in the catalyst were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, VARIAN VISTA-MPX). A spherical aberration electron microscope (FEI Titan G2 Cube) was also employed to check the sample. Fourier transform infrared spectra were collected on a Bruker VERTEX 70 spectrometer.

The working electrode. To prepare the catalysts ink, 2 mg of catalysts and 8 mg of acetylene black were dispersed in 1 mL solvent (which was prepared by mixing of 700 μL of ethanol, 270 μL of deionized water and 30 μL of 0.05 wt% Nafion solution), which was then ultrasonicated for 1 h to obtain a homogeneous mixture. The glass carbon electrode (GCE, 5 mm in diameter and disk area of 0.196 cm^2) was firstly polished with 0.05 μm of Al_2O_3 powder to acquire a bright surface. For HOR tests, 5 μL of the catalyst ink was drop-casted on GCE surface (with mass loading of 0.05 mg cm^{-2}_{geo}) and dried in air for 30 min. For HER tests, the preparation is similar to that of HOR except 15 μL of catalyst ink was used (with mass loading of 0.03 mg cm^{-2}_{geo}).

Estimation of the ECSA values. Cu-UPD method was used to evaluate the ECSA values for all catalysts. Briefly, the catalyst loaded working electrode was firstly cycled between 0.05 V to 0.7 V (*vs* RHE) at a scan rate of 10 mV s^{-1} in 0.1 M N_2-saturated H_2SO_4 to obtain a repeatable voltammetry curve served as the background. The electrode was then kept at 0.3 V (*vs* RHE) in 0.1 M N_2-saturated H_2SO_4 contained 0.2 mM $CuSO_4$ for 150 s to deposit a Cu layer on electrode surface. Then, copper oxidation polarization curves were collected in the range of 0.3-0.7 V (*vs* RHE) at a scan rate of 10 mV s^{-1}. The ECSA values were calculated via the following equation

$$ECSA = \frac{Q_{Cu}}{Q_s}$$

Where Q_{Cu} and Q_s represent the measured integral charge and surface charge density of 420 μC cm^{-2}_{metal} for monolayer adsorption of Cu-UPD stripping.

Table S1. ICP-AES analysis results for RuNi catalysts.

Samples	Ru:Ni atomic ratio
Ru_3Ni_7	1:2.22
Ru_5Ni_5	1:1.14
Ru_7Ni_3	1:0.42

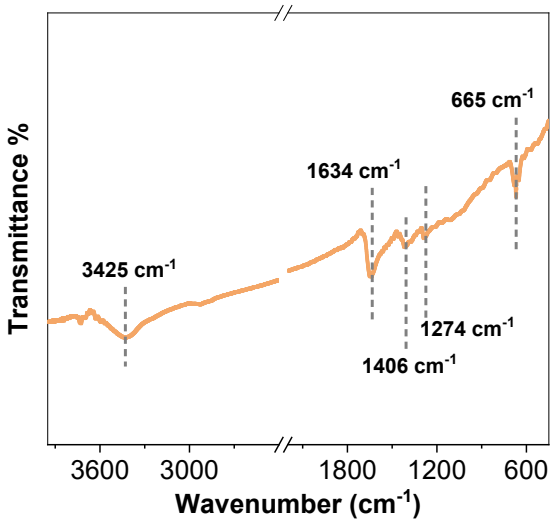

Fig. S1. FT-IR spectrum of the typical Ru_5Ni_5 sample.

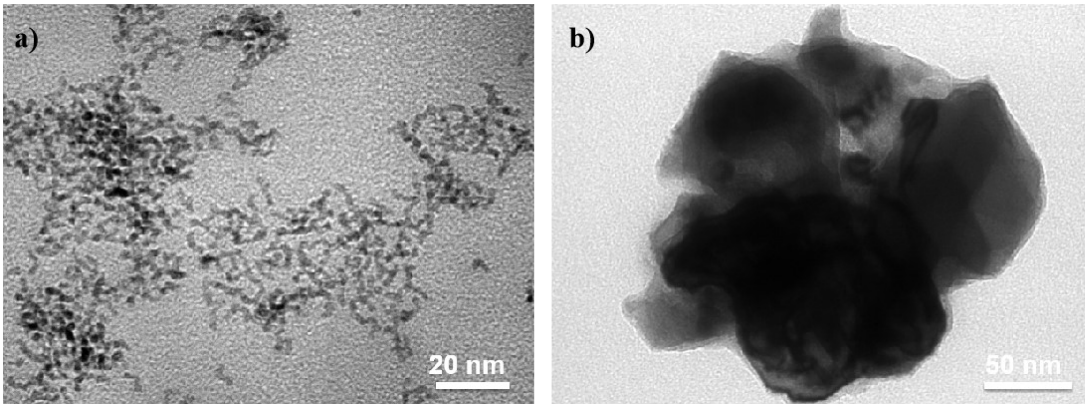

Fig. S2. TEM images of a) Ru and b) Ni NPs.

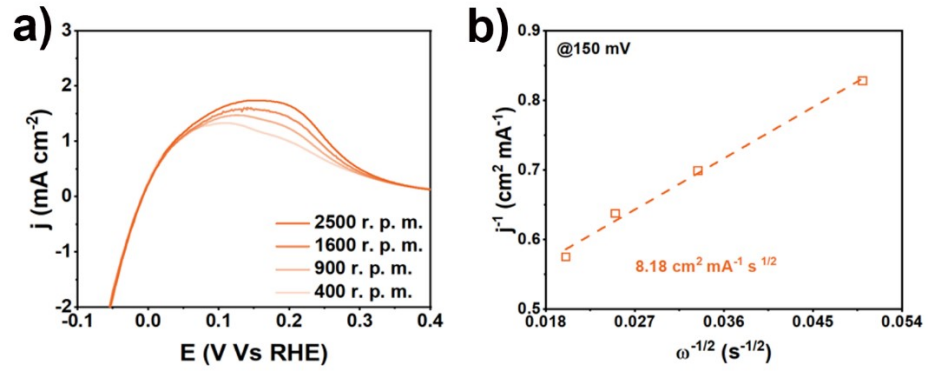

Fig. S3. a) HOR polarization curves of Ru in 0.1 M H_2-saturated KOH at various rotating speeds. b) Corresponding Koutecky-Levich plots at 0.15 V.

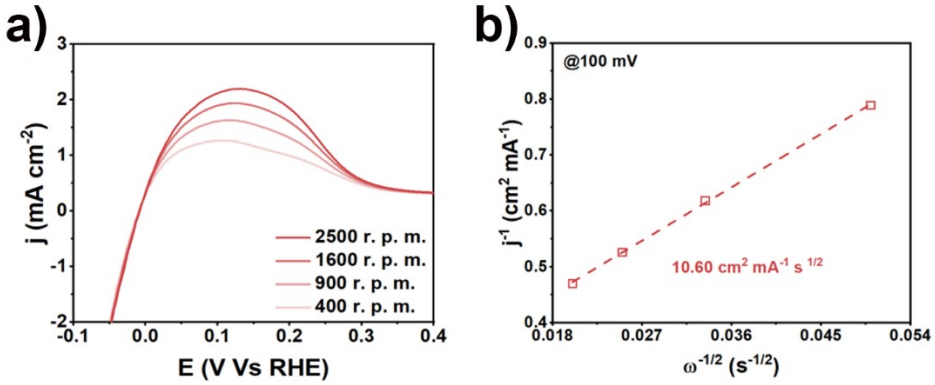

Fig. S4. a) HOR polarization curves of Ru_7Ni_3 in 0.1 M H_2-saturated KOH at various rotating speeds. b) Corresponding Koutecky-Levich plots at 0.1 V.

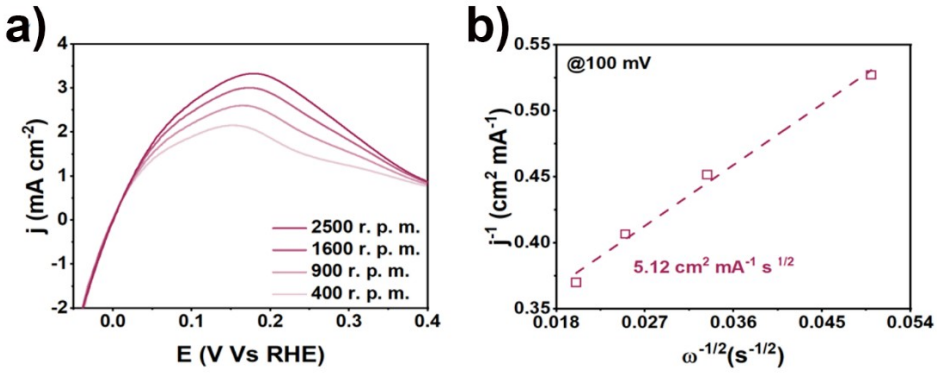

Fig. S5. a) HOR polarization curves of Ru_5Ni_5 in 0.1 M H_2-saturated KOH at various rotating speeds. b) Corresponding Koutecky-Levich plots at 0.1 V.

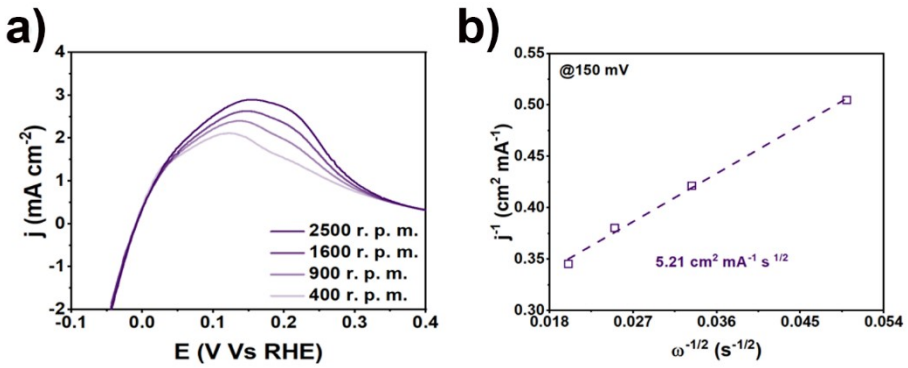

Fig. S6. a) HOR polarization curves of Ru_3Ni_7 in 0.1 M H_2-saturated KOH at various rotating speeds. b) Corresponding Koutecky-Levich plots at 0.15 V.

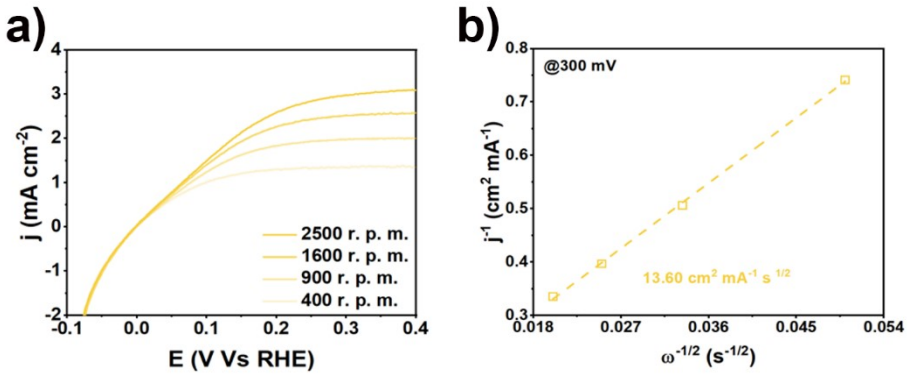

Fig. S7. a) HOR polarization curves of Pt/C in 0.1 M H_2-saturated KOH at various rotating speeds. b) Corresponding Koutecky-Levich plots at 0.3 V.

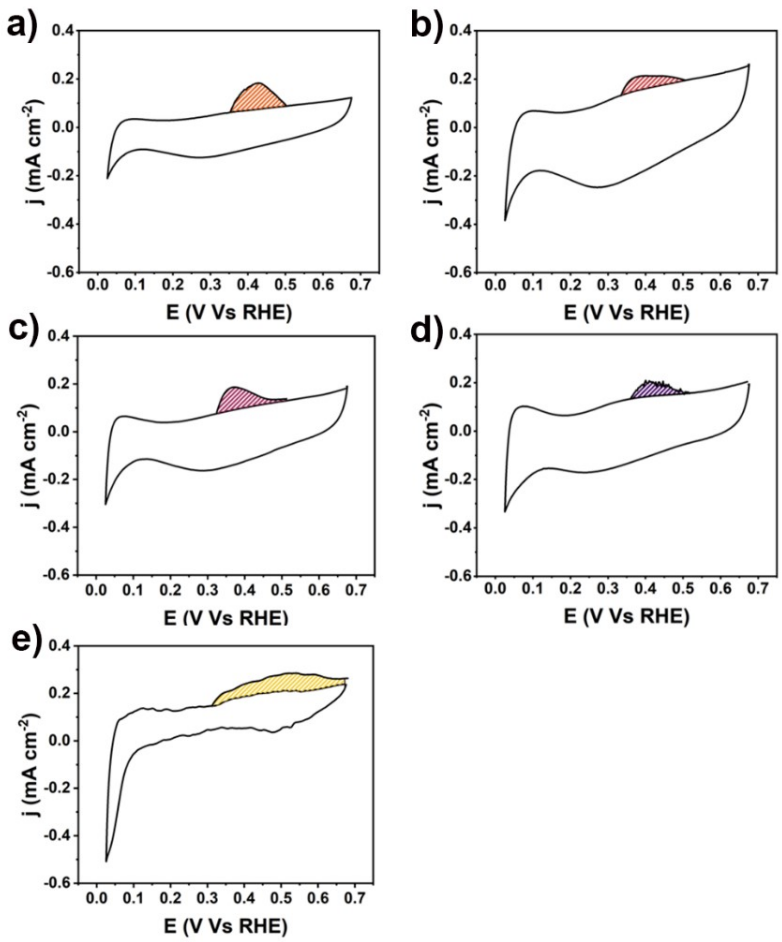

Fig. S8. CVs of catalysts collected with 0.5 M Ar-saturated H_2SO_4 contained 5mM $CuSO_4$ and the corresponding Cu-UPD stripping voltammograms of a) Ru, b) Ru_7Ni_3, c) Ru_5Ni_5, d) Ru_3Ni_7 and e) Pt/C. 10 mV s^{-1} was applied for all ECSA evaluation.

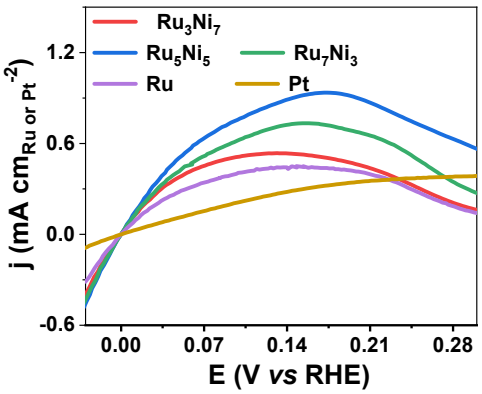

Fig. S9. HOR polarization curves of the typical samples normalized by the estimated Ru or Pt electrochemical active specific surface area, further suggesting the excellent catalytic activity of RuNi products.

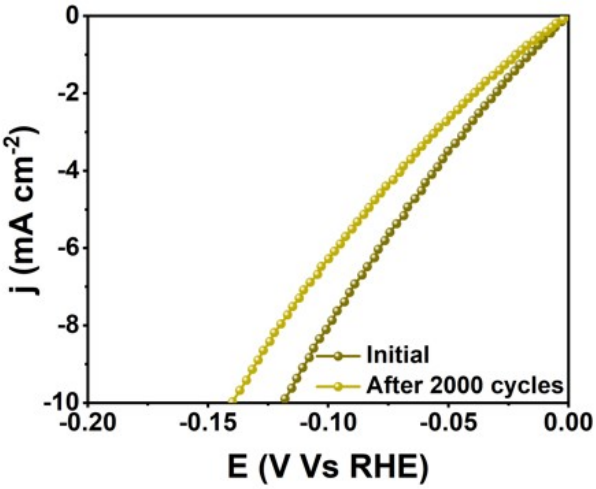

Fig. S10. HER polarization curves of Ru_5Ni_5 before and after stability evaluation in 0.1 M N_2-saturated KOH at the rotating speed of 1600 rpm.