

## Electronic Supplementary Information

# Element Immiscibility Assisted Ru@Ni<sub>3</sub>B as An Efficient Electrocatalyst toward Alkaline and Acidic Hydrogen Evolution Reaction

Yin'an Zhu, Jia Yao, Xu Zhong, Tao Lu, Ye Pan\*

*School of Materials Science and Engineering, Jiangsu Key Laboratory of Advanced  
Metallic Materials, Southeast University, Nanjing 211189, China.*

\* Correspondent Author: Ye Pan, e-mail: [panye@seu.edu.cn](mailto:panye@seu.edu.cn)

### Experimental Details

#### Materials

Metal/Non-metal particles including Ni, Al, Ru, and B ( $\geq 99.5\%$ ) were purchased from Beijing China New Metal Co., Ltd. H<sub>2</sub>SO<sub>4</sub> (98%) and KOH were brought from Aladdin Chemistry Co. Ltd.

#### Preparation of dealloying precursors

Dealloying precursors Ni<sub>73-x</sub>Al<sub>4</sub>B<sub>23</sub>Ru<sub>x</sub> (x=0, 0.2, 0.5, 1.0) were synthesized by a melting-spinning method. Typically, metal and non-metal particles with a certain ratio were mixed and put into a copper crucible under an Ar atmosphere. Alloy ingots were then obtained by a high-temperature arc. To reach a uniform composition, each ingot should be melted at least four times. After breaking the ingot into small particles, it was melted again and injected onto a rotating copper roller. Alloy ribbons with 30  $\mu\text{m}$  in thickness and 2 mm in width.

#### Preparation of Ru@Ni<sub>3</sub>B

Alloy ribbon was cut and dealloyed in 5M H<sub>2</sub>SO<sub>4</sub> at 70°C for 10 hours. After dealloying, the dealloyed products were washed with water and ethanol to remove the attached

corrosive agent. It then died at room temperature. The corresponding dealloyed products were denoted as xRu@Ni<sub>3</sub>B (x=0, 0.2, 0.5, 1.0).

### **Electrochemical measurements**

Electrocatalytic performance of xRu@Ni<sub>3</sub>B (x=0, 0.2, 0.5, 1.0) was conducted by a conventional three-electrode system. Graphite rod and Ag/AgCl electrode were employed as counter electrode and reference electrode, respectively. The dealloyed ribbons directly work as the working electrode. 0.5M H<sub>2</sub>SO<sub>4</sub> and 1M KOH were chosen as catalytic electrolytes. All the obtained potentials were transformed to reversible hydrogen electrode (RHE) via the formula of  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \cdot \text{pH} + 0.197$ . The so-called overpotential ( $\eta$ ) was calculated to be the absolute value of  $E_{\text{RHE}}$ . Electrocatalytic performance of the dealloyed products was estimated by the polarization curve, which was measured at a scan rate of 1 mV/s with 90% IR compensation. To compare the actual electrochemical active surface area (ECSA) of the tested electrocatalysts, a cyclic voltammogram (non-Faradaic interval) was carried out with scan rates from 20 to 120 mV/s. Double-layer capacitance ( $C_{\text{dl}}$ ) of tested catalysts was fitted from the slope of  $\Delta J = 0.5 \cdot (J_{\text{a}} - J_{\text{c}})$  against the scan rates. Then ECSA could be estimated by the formula of  $\text{ECSA} = C_{\text{dl}} / C_{\text{s}}$  ( $C_{\text{s}}$  is the specific capacitance of the smooth planar surface of electrode per unit area in different electrolytes, 0.035 and 0.04 mF/cm<sup>2</sup> for 0.5M H<sub>2</sub>SO<sub>4</sub> and 1M KOH, respectively). Stability test of the dealloyed products was performed under the constant current density of -10 mA/cm<sup>2</sup> for 24 hours. Lastly, Nyquist plots of dealloyed products were measured at -0.1 and -0.02 V (vs RHE) for alkaline and acidic electrolyte, respectively.

### **Characterizations**

The phase structure of ribbons was measured by the D8 Bruker X-ray diffraction equipped with Cu K $\alpha$  radiation. The surface chemical valence of the dealloyed ribbons was characterized by an ESCALab 250XI X-ray photoelectron spectrometer and all the binding energies were calibrated at C 1s 284.8 eV. Morphologies details of the dealloyed ribbons were filmed by Navo Nano SEM450 and Talos F200X.

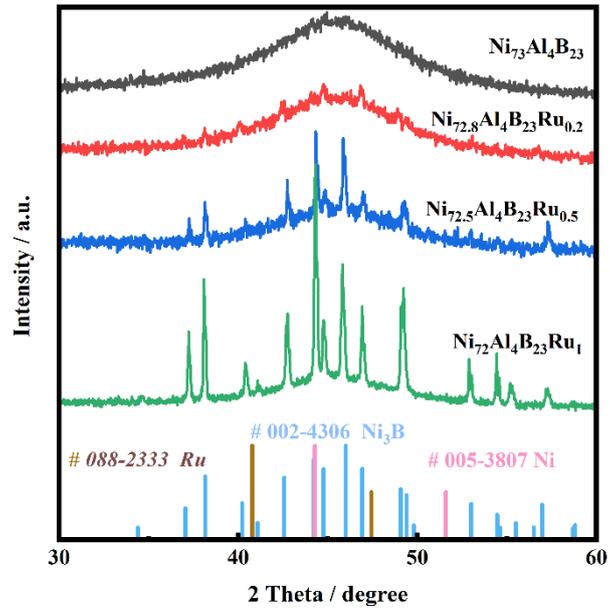


Fig.S1 XRD patterns of the dealloying precursors.

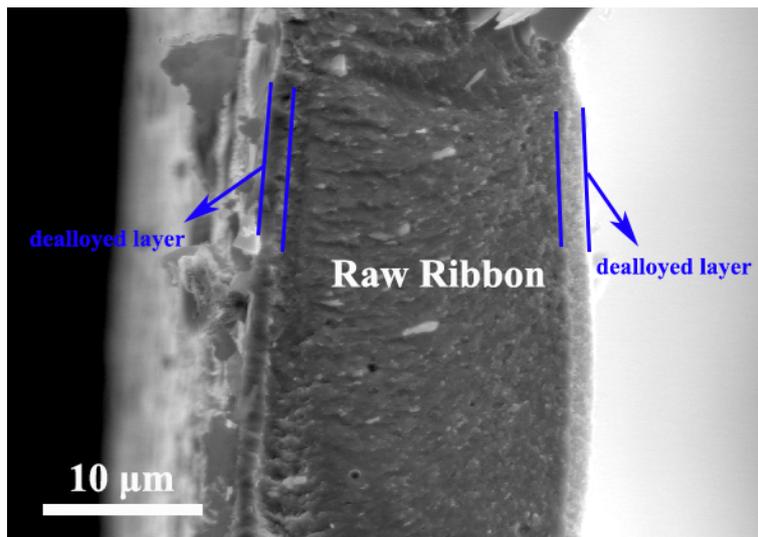


Fig. S2 Section SEM image of 1.0Ru@ $\text{Ni}_3\text{B}$ .

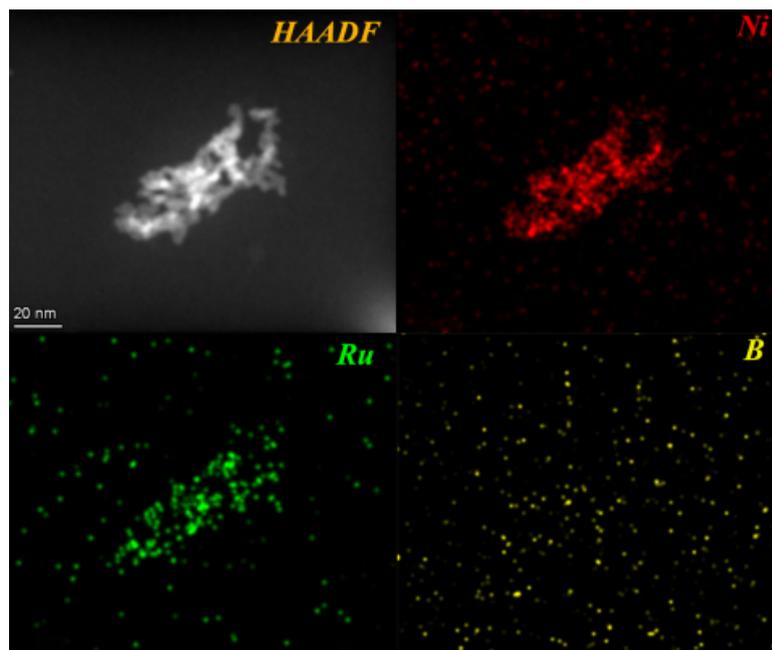


Fig.S3 HAADF-STEM image and the corresponding EDX mapping of 1.0Ru@Ni<sub>3</sub>B.

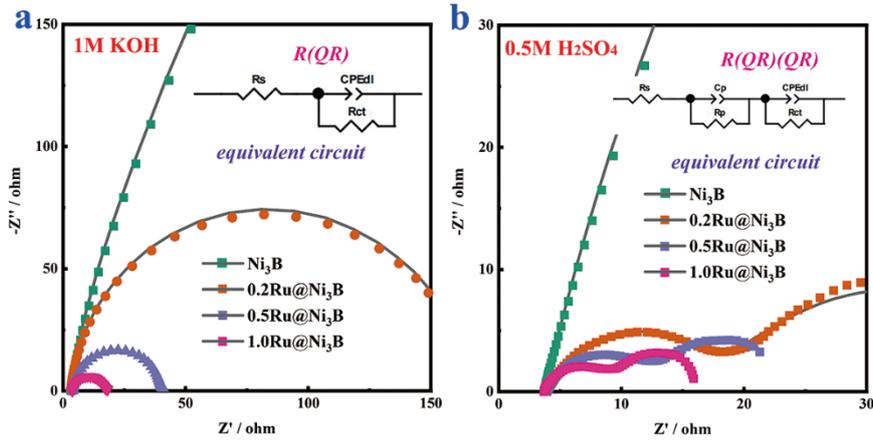


Fig.S4 The tested and fitted Nyquist plots of  $x\text{Ru}@ \text{Ni}_3\text{B}$  ( $x=0, 0.2, 0.5, 1.0$ ) in (a) 1M KOH and (b) 0.5M  $\text{H}_2\text{SO}_4$ , respectively. The insert maps are the corresponding equivalent circuits.

Table S1 The fitted  $R_{ct}$  of  $x\text{Ru}@ \text{Ni}_3\text{B}$  ( $x=0, 0.2, 0.5, 1.0$ ) in different electrolytes, respectively.

samples	$R_{ct}$ in 1M KOH / $\Omega$	$R_{ct}$ in 0.5M $\text{H}_2\text{SO}_4$ / $\Omega$
$\text{Ni}_3\text{B}$	$5570 \pm 115$	$520.6 \pm 4.8$
$0.2\text{Ru}@ \text{Ni}_3\text{B}$	$158.3 \pm 5.5$	$25.5 \pm 2.0$
$0.5\text{Ru}@ \text{Ni}_3\text{B}$	$35.7 \pm 1.5$	$12.1 \pm 1.9$
$1.0\text{Ru}@ \text{Ni}_3\text{B}$	$13.4 \pm 0.4$	$7.1 \pm 0.7$

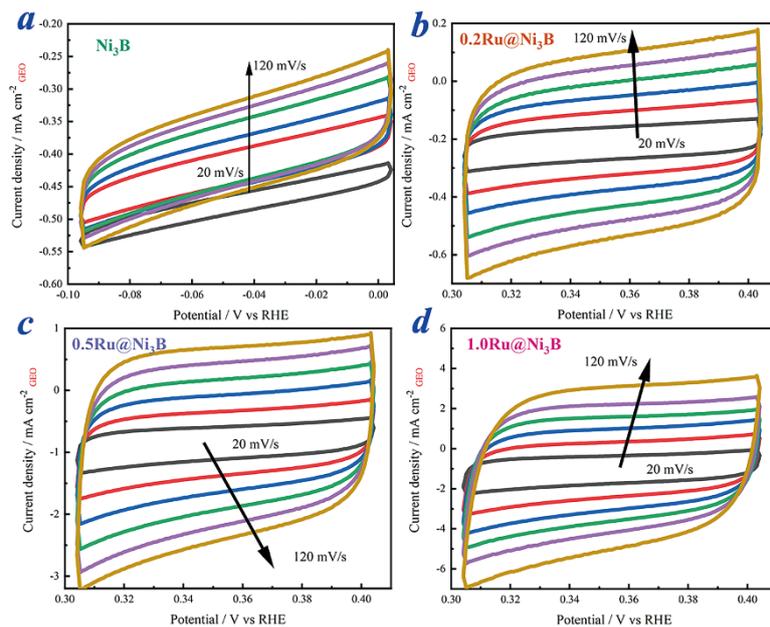


Fig.S5 CVs of  $x\text{Ru}@Ni_3B$  ( $x = 0, 0.2, 0.5, 1.0$ ) in 1M KOH.

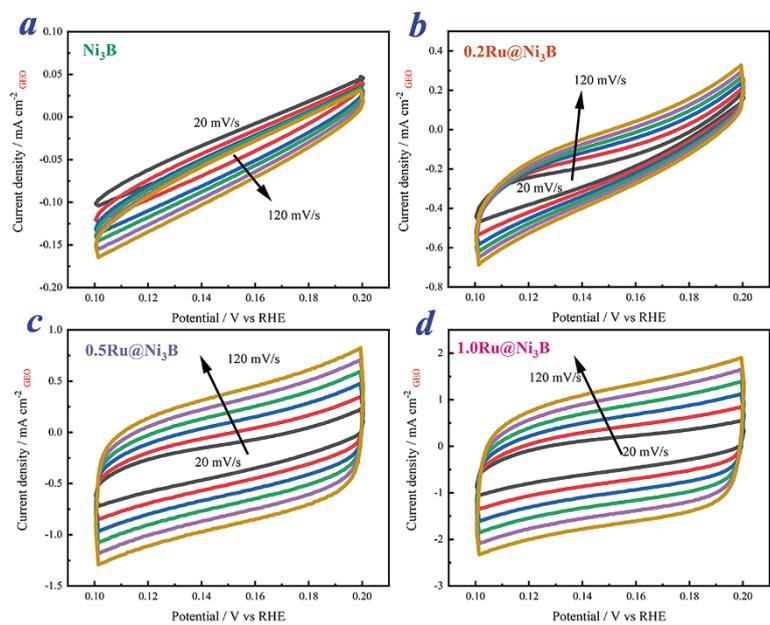


Fig.S6 CVs of  $x\text{Ru}@Ni_3B$  ( $x = 0, 0.2, 0.5, 1.0$ ) in 0.5M  $H_2SO_4$ .

Table S2 Element content of the  $x\text{Ru}@Ni_3B$  ( $x=0, 0.2, 0.5, 1.0$ ) via EDX.

Samples	Ni / at%	Ru / at%	B / at%	Al / at%	O / at%
$Ni_3B$	94.40	0	_*	5.60	0
$0.2@Ni_3B$	86.26	2.54	-	5.27	5.92
$0.5@Ni_3B$	73.82	7.51	-	3.15	15.52
$1.0@Ni_3B$	66.48	15.35	-	1.16	17.01

\* Due to the inherent instrumental limitation, the signal of B is difficult to be detected.

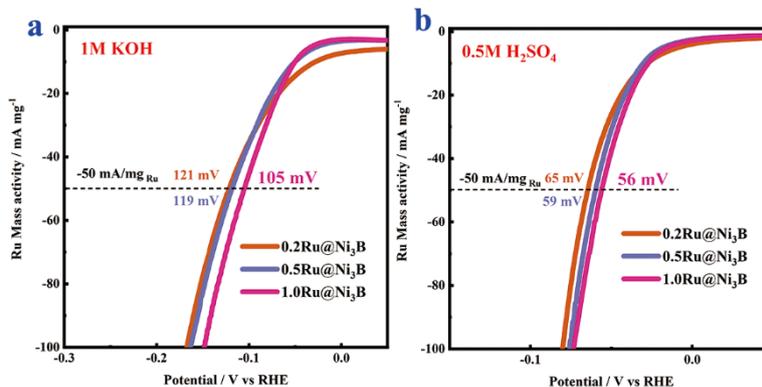


Fig.S7 Linear sweep voltammetry curves of  $x\text{Ru}@Ni_3B$  ( $x=0.2, 0.5, 1.0$ ) normalized by Ru Mass.

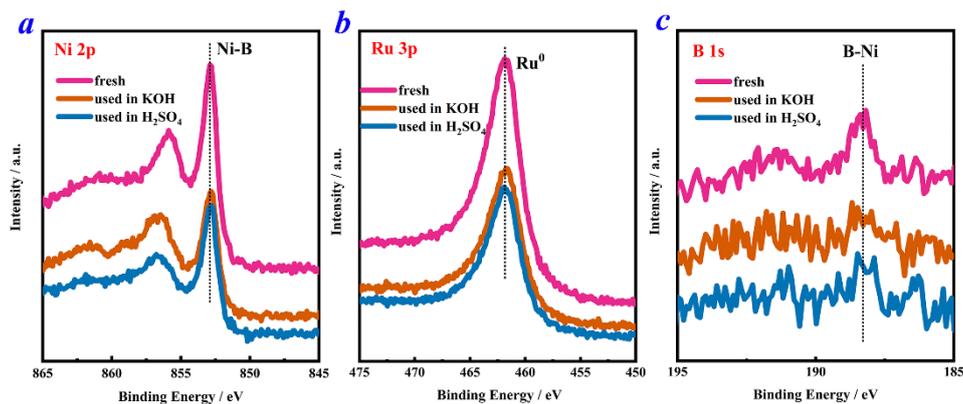


Fig. S8 XPS spectra of  $1.0\text{Ru}@Ni_3B$  before and after stability test.

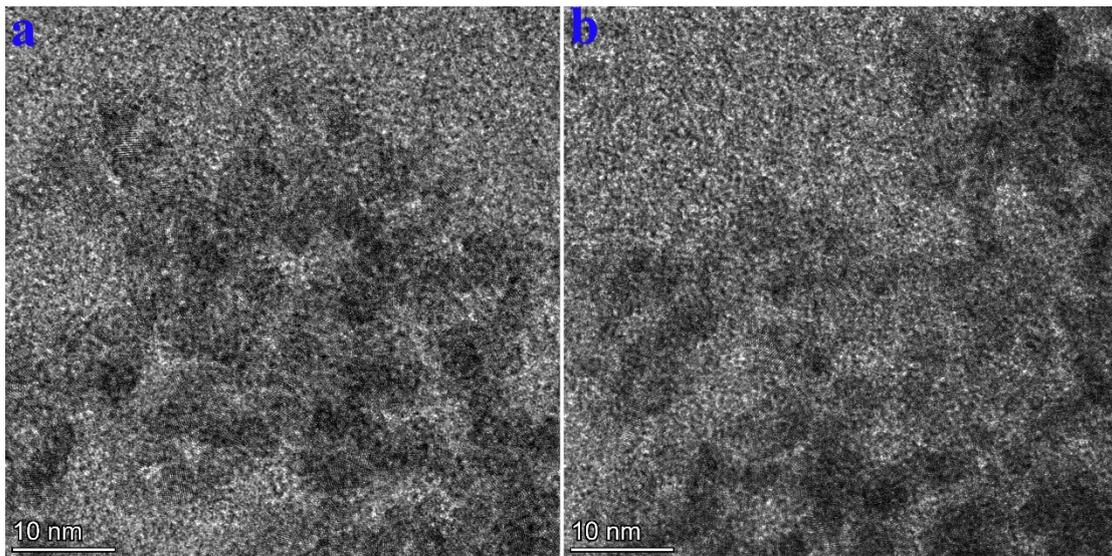


Fig. S9 HRTEM images of 1.0Ru@Ni<sub>3</sub>B after stability test in (a) 1M KOH and (b) 0.5M H<sub>2</sub>SO<sub>4</sub>.