Electronic Supplementary Information

Synergy of Ni single atom and RuNi alloy nanocluster enables

boosted hydrogen evolution at industrial current densities

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1. Experimental section

1.1 Chemical reagents

All solvents and chemicals were used as bought without further purification. 2methylimidazole and $Zn(NO_3)_2 \cdot 6H_2O$ were purchased from Aladdin. Methanol and isopropyl alcohol were purchased from Xilong Science. Ni(acac)₂ and Nafion solution (5 wt%) were purchased from Sigma Aldrich. Ultrapure water (R=18.25 M Ω) provided by a Millipore Milli-Q Lab apparatus was used in our experiments.

1.2 Synthesis of N-C support

The N-C support was synthesized by directly carbonized zeolitic imidazolate frameworks (ZIF-8). Typically, 6.5 g 2-methylimidazole was stirred and dissolved in 80 mL methanol. 3 g $Zn(NO_3)_2 \cdot 6H_2O$ was stirred and dissolved in 40 mL methanol. The latter was added to the former and stirred violently at room temperature for 24 h. The obtained product was centrifuged with ethanol for more than 3 times and dried at 60 °C. The dried product was placed in a quartz boat and then pyrolyzed at 950 °C for 1 h in Ar/H₂ (10% H₂). After cooling to room temperature, the N-C support was obtained.

1.3 Synthesis of Ni-N₄-C

The Ni-N₄-C was synthesized by directly carbonized zeolitic imidazolate frameworks (Ni-ZIF-8). Typically, 6.5 g 2-methylimidazole and 0.1455g Ni(acac)₂ were stirred and dissolved in 80 mL methanol. 3 g $Zn(NO_3)_2 \cdot 6H_2O$ was stirred and dissolved in 40 mL methanol. The latter was added to the former and stirred violently at room temperature for 24 h. The obtained product was centrifuged with ethanol for more than 3 times and dried at 60 °C. The dried product was placed in a quartz boat and then pyrolyzed at 950 °C for 1 h in Ar/H₂ (10% H₂). After cooling to room temperature, the Ni-N₄-C was obtained.

1.4 Synthesis of Ru-N-C

The Ru-N-C was synthesized by pyrolysis of Ru-adsorbed N-C support. Typically, 60 mg N-C, 15 mL water and 15 mL isopropyl alcohol were added to the beaker and ultrasonic treatment for 30 min. Then 3.3 mL RuCl₃ solution (1 mg_{Ru}/mL in isopropanol) was added. After stirring at room temperature overnight, the mixture was dried at 110 °C. The obtained product was firstly heat-treated at 150 °C for 1 h in Ar/H₂

 $(10\% H_2)$ in a tube furnace, and then heated up to 900 °C for 1 h.

1.5 Synthesis of Ni-N-C

The Ni-N-C was synthesized by pyrolysis of Ni-adsorbed N-C support. Typically, 60 mg N-C, 15 mL water and 15 mL isopropyl alcohol were added to the beaker and ultrasonic treatment for 30 min. Then 0.694 mL Ni(acac)₂ solution (1 mg_{Ni}/mL in isopropanol) was added. After stirring at room temperature overnight, the mixture was dried at 110 °C. The obtained product was firstly heat-treated at 150 °C for 1 h in Ar/H₂ (10% H₂) in a tube furnace, and then heated up to 900 °C for 1 h.

1.4 Synthesis of RuNi₂-N-C, RuNi-N-C, Ru₃Ni-N-C and Ru₅Ni-N-C

The Ru₃Ni-N-C was synthesized by pyrolysis of Ru,Ni-adsorbed N-C support. Typically, 60 mg N-C, 15 mL water and 15 mL isopropyl alcohol were added to the beaker and ultrasonic treatment for 30 min. 3.3 mL RuCl₃ solution (1 mg_{Ru}/mL in isopropanol) and 0.694 mL Ni(acac)₂ solution (1 mg_{Ni}/mL in isopropanol) were added. After stirring at room temperature overnight, the mixture was dried at 110 °C. The obtained product was firstly heat-treated at 150 °C for 1 h in Ar/H₂ (10% H₂) in a tube furnace, and then heated up to 900 °C for 1 h. RuNi₂-N-C, RuNi-N-C and Ru₅Ni-N-C was obtained by ensuring that the molar ratios of Ru, Ni were 1:2, 1:1, 5:1 respectively.

1.5 Synthesis of Ru/C

The Ru/C was synthesized by reducing RuCl₃ with NaBH₄. Typically, 95 mg Vulcan XC-72 was dispersed in 30 mL water by ultrasonic treatment for 30 min. Then, 5 mL of RuCl₃ solution (1 mg_{Ru}/mL in H₂O) was added under stirring. After 2 h, 10 mL NaBH₄ solution (50 mg/mL) was added drop by drop. After stirring for another 2 h at room temperature, the mixture was centrifugally washed and dried at 60 °C.

2. Materials Characterization and Measurements

2.1 Instruments characterization

Scanning electron microscopy (SEM) measurements were performed with an XL 30 ESEM FEG field emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Shimadzu AXIS ultra DLD.

X-ray diffraction (XRD) measurements were performed with a PW-1700 diffractometer using a Cu K α ($\lambda = 1.5405$ Å) radiation source (Philips Co.). Raman spectra (Raman) were obtained on a LABRAM HR EVO Raman spectrometer with 532 nm wavelength incident laser light. Inductively coupled plasma mass spectrometer (ICP-MS) was used to analyze all elemental contents of catalysts on a Thermo Elemental IRIS Intrepid. X-ray absorption spectroscopy (XAS) was recorded on the BL11B beam line at the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics, China.

2.2 Electrochemical measurements

Electrochemical performance measurements were carried out by CHI760E electrochemical workstation (CH Instruments, China) in an alkaline solution of 1 mol L^{-1} KOH (Ar-saturated) using a conventional three electrode test system.

The ink was prepared by a mixture of 5 mg catalyst power, 950 µL ethanol and 50 µL Nafion solution, then ultrasonically dispersing more than 30 minutes. Next, a quantity of ink was dropped on the glassy carbon electrode (3 mm in diameter) as the working electrode (to ensure the catalyst loading of 400 µg cm⁻² on the electrode). The saturated calomel electrode and the carbon rod are used as the reference and counter electrode, respectively. The electrochemical impedance spectroscopy (EIS) measurements were executed over a frequency range from 0.1 to 100 kHz with an amplitude of 10 mV. The electrochemical active surface areas (ECSA) of catalysts were acquired from simple cyclic voltammetry (CV) curves recorded in the potential range with no faradic current at different scan rates from 25 to 200 mV s⁻¹. The cyclic voltammetry was performed in the 0.05 V to -0.05 V (vs. RHE) range for the stability test of Ru₃Ni-N-C. In this work, electrochemical results were compared the reversible hydrogen electrode (RHE) according to the equation ($E_{RHE} = E_{SCE} + 0.059$ pH + 0.241 V).

2.3 DFT calculations details

Our calculations are carried out within the framework of the density functional theory with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package.¹ The generalzied gradient approximation proposed by Perdew, Burke, and Ernzerhof is selected for the exchange-correlation potential.² The long range van der Waals interaction are treated using the DFT-D3 approach.³ A plane-wave cutoff energy of 550 eV is applied, and the energy convergence criterion for the iterative solution of the Kohn-Sham equations is set to10⁻⁵ eV. A vacuum layer of 15 Å is added perpendicular to the sheet to avoid artificial interaction between periodic images. The Brillouin zone integration is performed using a 3x3x1 k-mesh. All structures are fully relaxed until the residual forces on the atoms have declined to less

than 0.03 eV/Å.

According to previous studies, the hydrogen adsorption free energy (ΔG_{H^*}) can be widely accepted as a good descriptor to evaluate the HER catalytic activity on a given catalyst, which is defined as follows: $\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S_H$. In this equation, ΔE_{H^*} is the hydrogen adsorption energy, which is determined by $\Delta E_{H^*} = E_{H^*} - E_{H2/2} - E_{Cat}$, where E_{H^*} , $E_{H2/2}$, and E_{Cat} represent the total energies of the adsorbed H^{*} species, free H₂ molecule, and catalyst, respectively, ΔE_{H^*} and ΔS_H are the differences in zeropoint energy and the entropy between the adsorbed state and gas phase, respectively, and T is the temperature.



Fig. S1 (a) SEM image, (b) TEM image, (c)HRTEM image and lattice pattern images by the inverse fast Fourier transform of Ru₃Ni-N-C.



Fig. S2 (a) SEM image, (b) TEM image, (c) HRTEM image and lattice pattern images by the inverse fast Fourier transform of Ru-N-C.



Fig. S3 SEM images of (a) Ru/C, (b) RuNi₂-N-C, (c) RuNi-N-C and (d)Ru₅Ni-N-C.



Fig. S4 TEM images of (a) Ru/C, (b) RuNi₂-N-C, (c) RuNi-N-C and (d)Ru₅Ni-N-C.



Fig. S5 The particle size analyses of Ru₃Ni-N-C, Ru₅Ni-N-C, RuNi-N-C, RuNi₂-N-C and Ru-N-C.



Fig. S6 X-ray diffraction patterns of Ru/C, Ru-N-C, RuNi₂-N-C, RuNi-N-C, Ru₃Ni-N-C and Ru₅Ni-N-C.



Fig. S7 (a) The TEM image of Ru₃Ni-N-C. (b) ε_{xy} , (c) ε_{xx} and (d) ε_{yy} strain component determined via geometric phase analysis (GPA) of Ru₃Ni-N-C.



Fig. S8 (a) The TEM image of Ru-N-C. (b) ε_{xy} , (c) ε_{xx} and (d) ε_{yy} strain component determined via geometric phase analysis (GPA) of Ru-N-C.



Fig. S9 The intensity difference between Ru and Ni atoms in Fig. 1(e).



Fig. S10 The EELS line-scan profile of Ru₃Ni-N-C.



Fig. S11 The HAADF-STEM image of Ru-N-C.



Fig. S12 (a) Ru 3p XPS spectra of Ru₃Ni-N-C and Ru-N-C. (b) Ni 2p XPS spectra of Ru₃Ni-N-C and Ni-N-C.



Fig. S13 Polarization curves of Ru₅Ni-N-C, Ru₃Ni-N-C, RuNi-N-C and RuNi₂-N-C.



Fig. S14 Polarization curves of (a) Ru₃Ni-N-C, (b) Ru-N-C, (c) Pt/C and (d) Ru/C.



Fig. S15 The error bars with the overpotential of Ru₃Ni-N-C, Ru-N-C, Pt/C and Ru/C.



Fig. S16 Mass activities of Pt/C and Ru₃Ni-N-C normalized to the mass of Pt or Ru at various overpotentials.



Fig. S17 The mass activities of Ru₃Ni-N-C, Ru₅Ni-N-C, RuNi-N-C and RuNi₂-N-C.



Fig. S18 CV curves of (a) Ru/C, (b) Ru-N-C, (c) RuNi₂-N-C, (d) RuNi-N-C, (e) Ru₅Ni-N-C and (f) Ru₃Ni-N-C with different scan rates from 25 to 200 mV s⁻¹ in 1M KOH at room temperature.



Fig. S19 CV curves of Ru/C, Ru-N-C, Ru₅Ni-N-C, Ru₃Ni-N-C, RuNi-N-C and RuNi₂-N-C with the scan rate 200 mV s⁻¹ in 1M KOH at room temperature.



Fig. S20 The capacitive current at 0.125 V as a function of the scan rates from 25 to 200 mV s^{-1} of the corresponding electrocatalysts.



Fig. S21 Nyquist plots of Ru/C, Pt/C, Ru-N-C and Ru₃Ni-N-C at the overpotential of 10 mA cm⁻².



Fig. S22 The TEM images of Ru₃Ni-N-C before and after the stability test.



Fig. S23 HRTEM images and lattice pattern images by the inverse fast Fourier transform of Ru_3Ni -N-C (a) before and (b) after the stability test. The HAADF-STEM and EELS element mapping images of Ru_3Ni -N-C (c) before and (d) after the stability test.



Fig. S24 (a) Ru 3p and (b) Ni 2p XPS spectra of Ru₃Ni-N-C before and after the stability test.



Fig. S25 Comparison of performance with other AEMWEs.



Fig. S26 The in-situ Raman spectra of (a) Ru₃Ni-N-C, (b) Ru-N-C and (c) Ru/C under various potentials in 1 M KOH solution.



Fig. S27 Gaussian fits of three interfacial water types of Ru_3Ni -N-C at 0 mV to -100 mV vs. RHE.



Fig. S28 Gaussian fits of three interfacial water types of Ru-N-C at 0 mV to -100 mV vs. RHE.



Fig. S29 Gaussian fits of three interfacial water types of Ru/C at 0 mV to -100 mV vs. RHE.



Fig. S30 The Stark slopes of 4-HB-H₂O, 2-HB-H₂O and K⁺-H₂O in (a) Ru-N-C and (b) Ru/C.



Fig. S31 The Bode phase plots of (a) Ru₃Ni-N-C and (b) Ru-N-C.



Fig. S32 Nyquist plots of (a) Ru₃Ni-N-C and (b) Ru-N-C at various potentials.



Fig. S33 Kinetic barrier of water dissociation on Ni_{SA} site, Ru site and Ni site in Ru₃Ni-N-C. IS, TS and FS represent the initial, transition and final state, respectively.



Fig. S34 The optimized adsorption structure at (a) IS, (b) TS and (c) FS on Ni site in Ru₃Ni-N-C. IS, TS and FS represent the initial, transition and final state, respectively.



Fig. S35 Optimized adsorption structure of H^* on (a) Ru site in Ru-N-C, (b) Ru site in Ru₃Ni-N-C, (c) Ni site in Ru₃Ni-N-C, (d) Ni₂ site in Ru₃Ni-N-C and (e) Ni_{SA} site in Ru₃Ni-N-C.

Sample	Path	Ν	R/Å	$\sigma^2/\text{\AA}^2$	∆E/eV	R-factor
Du N C	Ru-O	2.5	2.00	0.004	1 2	0.01
Ku-IN-C	Ru-Ru	2.6	2.69	0.004	-1.3	0.01
Ru ₃ Ni-N-	Ru-O	2.5	1.98	0.005	5.0	0.01
С	Ru-Ni	3.6	2.67	0.005	-3.0	0.01

Table S1 EXAFS fit parameters at Ru K-edge EXAFS for Ru-N-C and Ru₃Ni-N-C.

 S_0^2 was fixed as 1.0. N is the coordination number. R is the distance between absorber and backscatter atoms. σ^2 is the Debye-Waller factor. R-factor is residual factor.

Table S2 EXAFS fit parameters at Ni K-edge for Ni-N-C and Ru₃Ni-N-C.

Sample	Path	Ν	R/Å	$\sigma^2/\text{\AA}^2$	$\Delta E/eV$	R-factor
N: N C	Ni-N	2.4	1.85	0.006	11.0	0.01
INI-IN-C	Ni-Ni	Ii-Ni 2.3 2.58 0.	0.007	-11.0	0.01	
Ru ₃ Ni-N-	Ni-N	2.5	1.86	0.005	10.0	0.02
С	Ni-Ru	1.3	2.61	0.007	-10.9	0.02

 S_0^2 was fixed as 1.0. N is the coordination number. R is the distance between absorber and backscatter atoms. σ^2 is the Debye-Waller factor. R-factor is residual factor.

Table S3 The contents of Ru and N1 measured by IC.

Sample	Ru(wt%)	Ni(wt%)	Ni:Ru molar ratio
RuC	4.680	0	-
Ru-N-C	6.898	0	-
RuNi ₂ -N-C	6.865	10.970	2.752:1
RuNi-N-C	6.802	6.007	1.521:1
Ru ₃ Ni-N-C	7.873	2.102	1:2.175
Ru ₅ Ni-N-C	7.252	1.315	1:3.202

Sample	C(wt%)	N(wt%)	O(wt%)
RuC	74.42	-	23.97
Ru-N-C	83.45	1.35	13.21
RuNi ₂ -N-C	79.15	1.51	16.63
RuNi-N-C	82.4	3.02	10.68
Ru ₃ Ni-N-C	77.7	1.76	14.44
Ru ₅ Ni-N-C	79.69	1.21	16.61

 Table S4 The element contents estimated from XPS measurements.

Table S5 The fitting results of the Nyquist plot of Ru₃Ni-N-C.

	Value	Error	Error%
R _s	7.42 Ω	0.0355	0.478
R _{ct}	32.5 Ω	0.392	1.21
CPE-T	0.0116	0.000202	1.74
CPE-P	0.685	0.00561	0.818

Table S6 The fitting results of the Nyquist plot of Ru-N-C.

	Value	Error	Error%
R _s	8.01 Ω	0.0245	0.306
R _{ct}	57.6 Ω	0.415	0.721
CPE-T	0.00457	0.0000564	1.24
CPE-P	0.743	0.00335	0.450

Table S7 The fitting results of the Nyquist plot of Pt/C.

	Value	Error	Error%
R _s	11.4 Ω	0.0902	0.792
R _{ct}	43.1 Ω	0.314	0.728
CPE-T	0.00200	0.0000486	2.43
CPE-P	0.648	0.00538	0.831

Table S8 The fitting results of the Nyquist plot of Ru/	C.
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	Value	Error	Error%
R _s	7.56 Ω	0.0518	0.686
R _{ct}	125 Ω	1.35	1.07
CPE-T	0.00125	0.0000268	2.14
CPE-P	0.824	0.00497	0.604

 Table S9 HER performance in alkaline comparison of Ru₃Ni-N-C to other electrochemical catalysts.

Sample	η ₁₀ (mV)	Tafel slope (mV dec ⁻¹)	Reference
Ru ₃ Ni-N-C	8	35	This work
MoC@NPC	47	71	4
MoC	128	82	5
RuP ₂ @NPC	52	69	6
Ru SAs-Ni ₂ P	57	75	7
Ru-NiFeP/NF	56	68	8
RuCoP	23	37	9
Ru@C ₂ N	17	38	10
Ru@CN-0.16	32	53	11
NiRu ₂ @NC	53	38	12
CoRu _{0.25} @N-C	27	74	13
Ru ₂ P/RGO-20	13	40	14
CuRu/CB	85	43	15
Ru@SC-CDs	29	57	16
NiO/Ru@Ni	39	75	17
S-RuP@NPSC	92	90	18

Catalyst (cathode anode)	Current density (A/cm ²)	Reference
Ru ₃ Ni-N-C NiFe-LDH	2.38 at 2.00 V_{cell}	This work
Pt/C NiFe-LDH	1.00 at 2.03 V_{cell}	19
Ru ₁ -Mo ₂ C NiFe-LDH	2.00 at 2.03 V_{cell}	19
Ru/NDC-4 IrO ₂	0.72 at 2.00 V_{cell}	20
$Ru-Ru_2P/V_2CT_x \parallel RuO_2$	2.00 at 2.04 V_{cell}	21
α -Co(OH) ₂ @Ru RuO ₂	0.52 at 2.00 V_{cell}	22
Pt mesh S-FeOOH	1.00 at 1.99 V_{cell}	23
PtRu/C IrO ₂	1.15 at 2.00 V_{cell}	24
Ir@Zr-CoP Ir@Zr-CoP	2.00 at 2.13 V_{cell}	25
Pt/C IrO ₂	1.00 at 2.04 V_{cell}	26
NiMoCo NiMoCo	1.00 at 2.11 V_{cell}	27
MoO ₂ /MoNi ₄ HS-RuCo/NC	1.00 at 2.07 V_{cell}	28
NA-LT-CA NA-LT-CA	0.80 at 1.98 V_{cell}	29
NA-CA NA-CA	0.50 at 2.05 V_{cell}	29

Table S10 Performance comparison of our AEMWEs with other AEMWEs reported in previous literatures.

Potencial(mV)	0	-10	-20	-40	-60	-80	-100
K ⁺ -H ₂ O fraction (Ru ₃ Ni-N-C)	1.09%	1.98%	2.52%	3.30%	3.83%	4.37%	4.99%
K ⁺ -H ₂ O fraction (Ru-N-C)	0.98%	1.44%	1.91%	2.44%	2.96%	3.35%	3.86%
K ⁺ -H ₂ O fraction (Ru/C)	0.82%	1.19%	1.51%	1.97%	2.37%	2.68%	2.99%

Table S11 Fitted K^+ - H_2O fractions in operando Raman for Ru_3Ni -N-C, Ru-N-C and Ru/C.

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