Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Ni_xRh_{1-x} Bimetallic Alloy Nanofibers as pH-Universal Electrocatalyst for Hydrogen Evolution Reaction: The Synthetic Strategy and Fascinating Electroactivity

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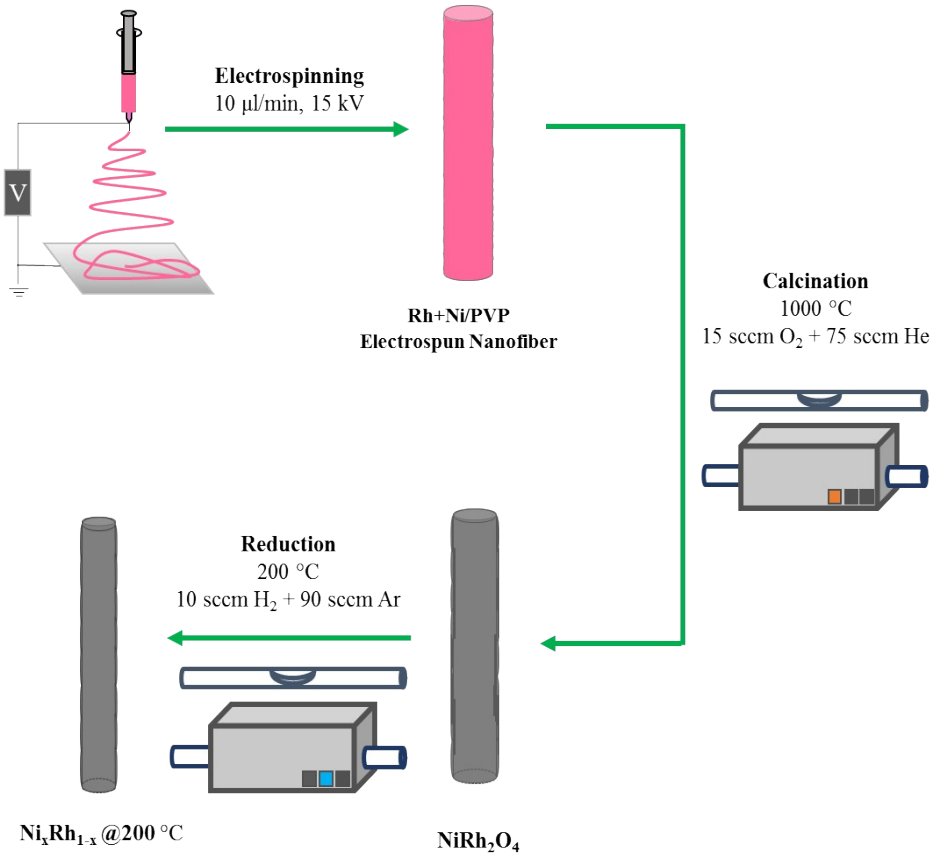

Scheme S1. Schematic illustration for the synthesis of Ni_xRh_{1-x} @200 °C.

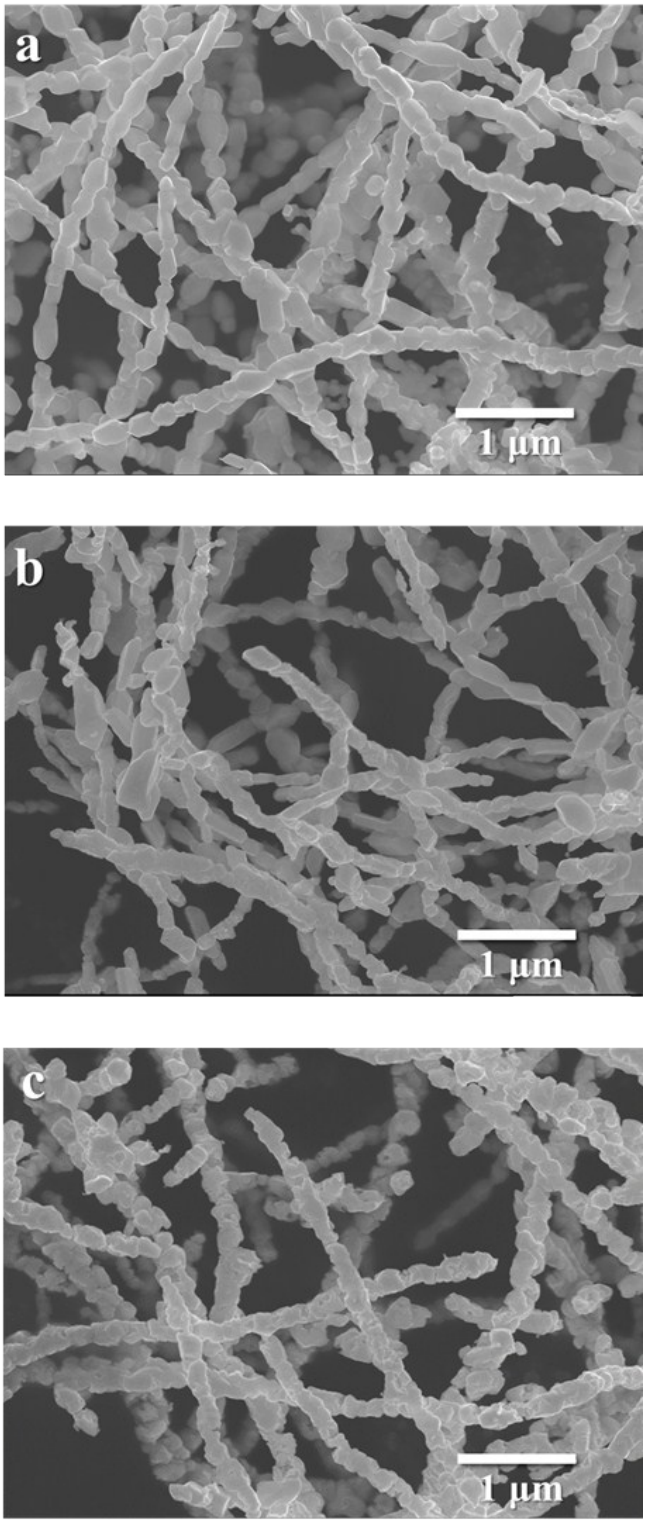

Figure S1. SEM images of Ni_xRh_{1-x} @T °C after being thermally annealed for 2 h under flowing H_2 and Ar at diverse annealing temperatures of (a) 100 °C, (b) 200 °C and (c) 300 °C.

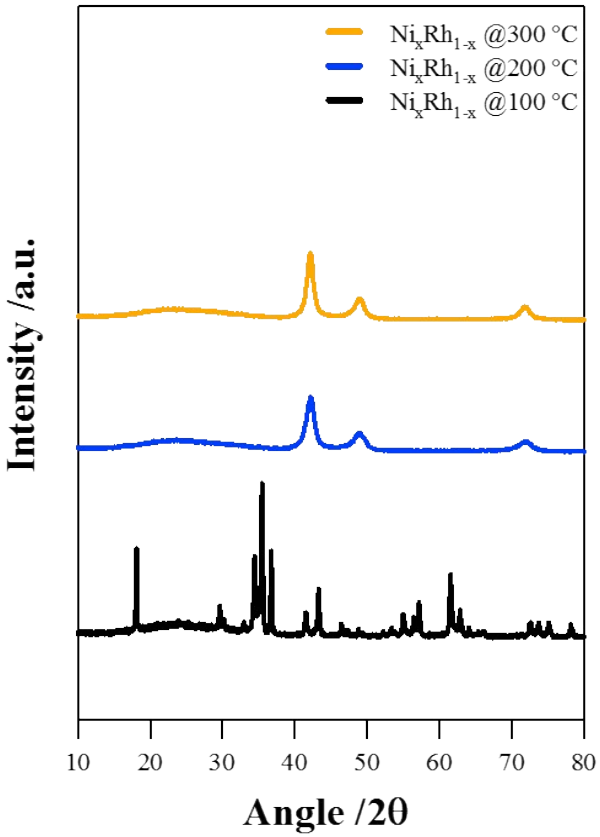

Figure S2. XRD patterns of Ni_xRh_{1-x} @T °C after being thermally annealed for 2 h under flowing H_2 and Ar at diverse annealing temperatures.

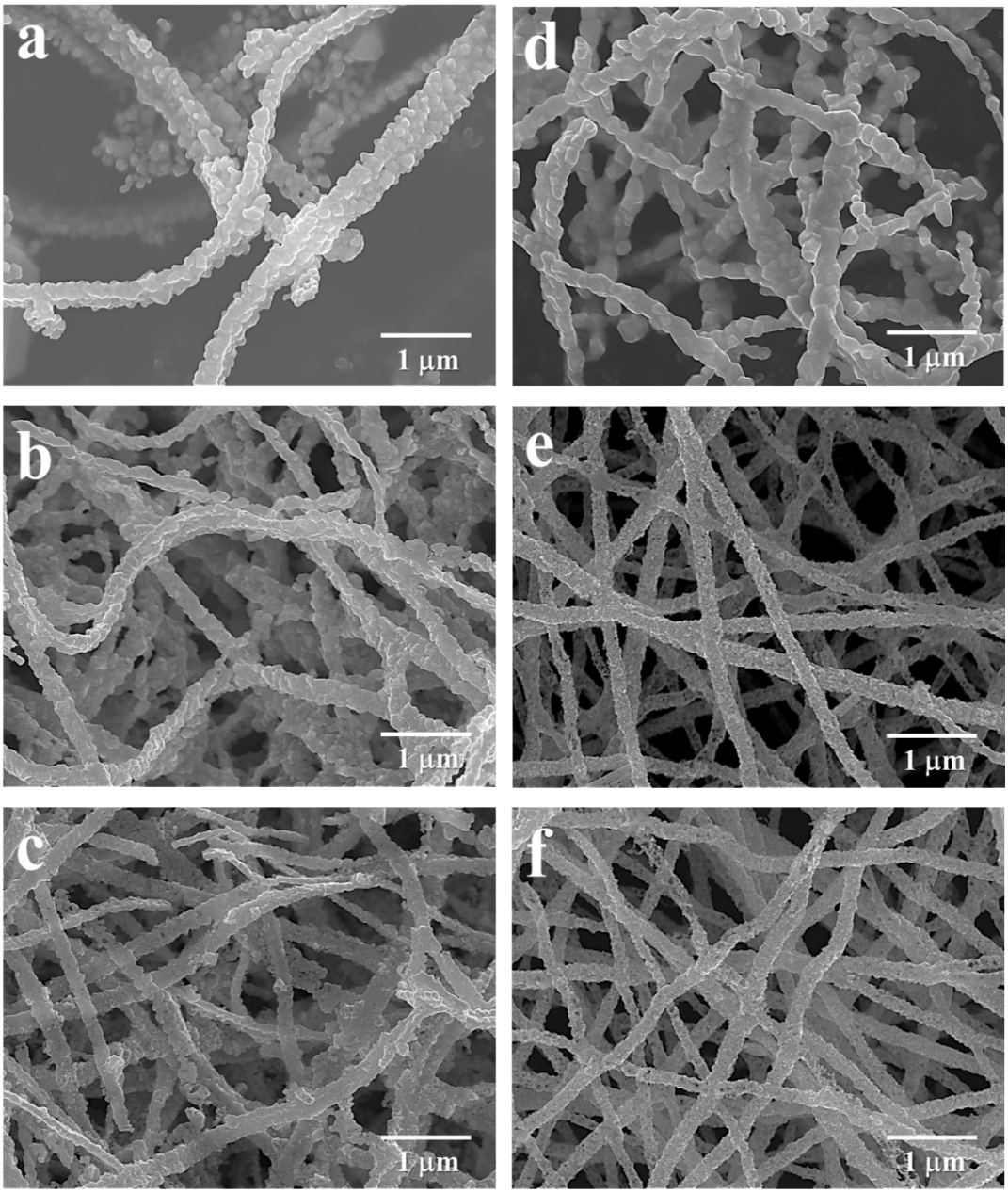

Figure S3. SEM images of $NiRh_2O_4$/NiO nanofibers (a) before, (b) after the reduction at 200 °C and (c) at 300 °C. SEM images of Rh_2O_3/NiO nanofibers (d) before, (e) after the reduction at 200 °C and (f) at 300 °C.

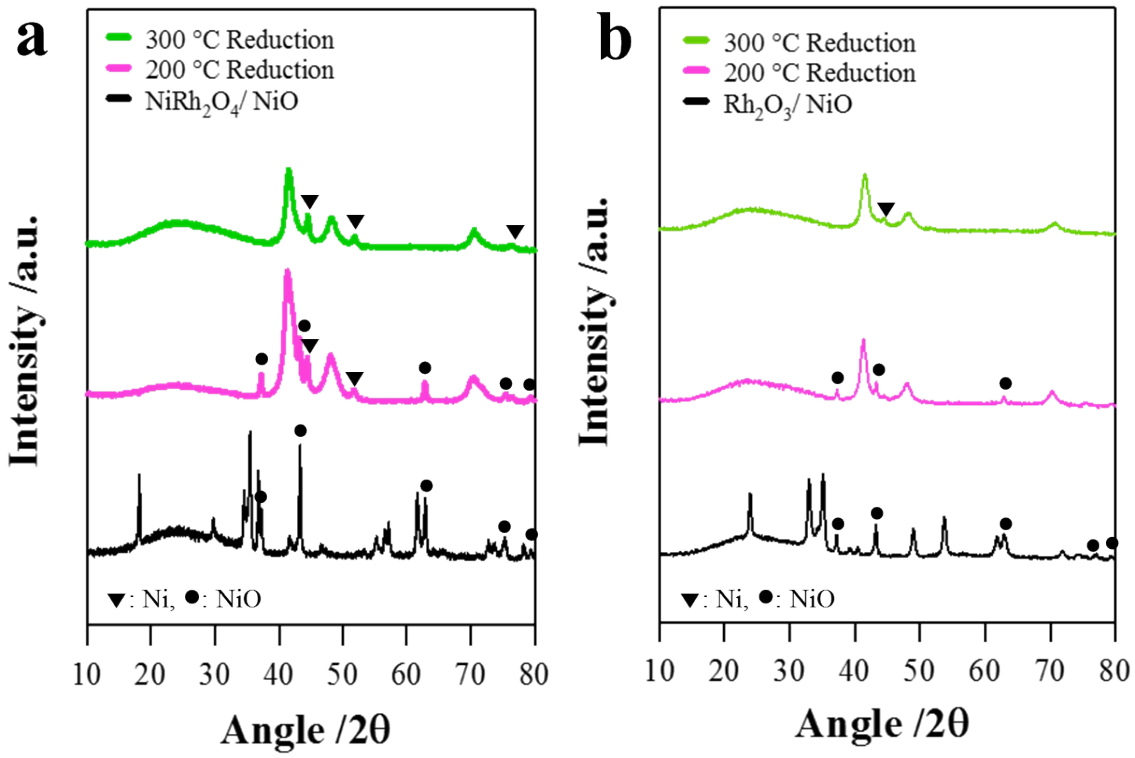

Figure S4. XRD patterns of (a) $NiRh_2O_4$/NiO and (b) Rh_2O_3/NiO nanofibers before (black line) and after (pink and green lines) the thermal hydrogen reduction.

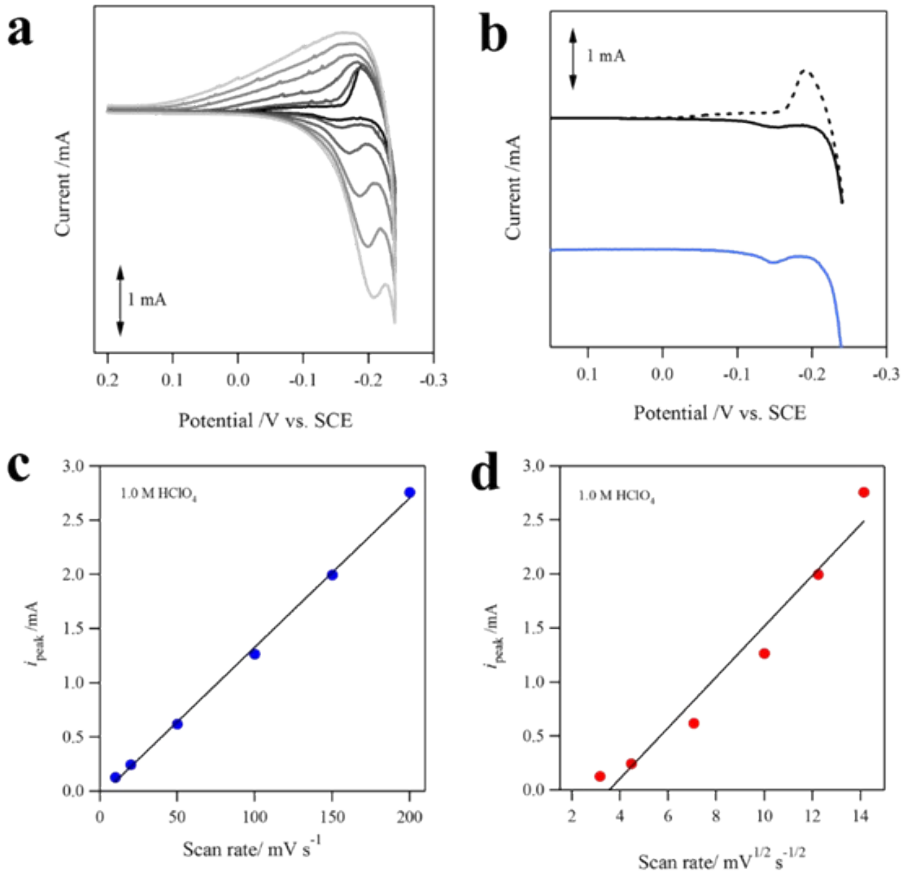

Figure S5. (a) Cyclic voltammograms (CV) of Ni_xRh_{1-x} @200 °C in 1.0 M $HClO_4$ at various scan rates of 10. 20. 50. 100. 150 and 200 mV s^{-1}. (b) CV and LSV curves of Ni_xRh_{1-x} @200 °C in 1.0 M $HClO_4$ at 10 mV s^{-1}. Plots of the cathodic peak current (i_{pc} around -0.15 V) vs. (c) scan rate and (d) scan rate $^{1/2}$, respectively.

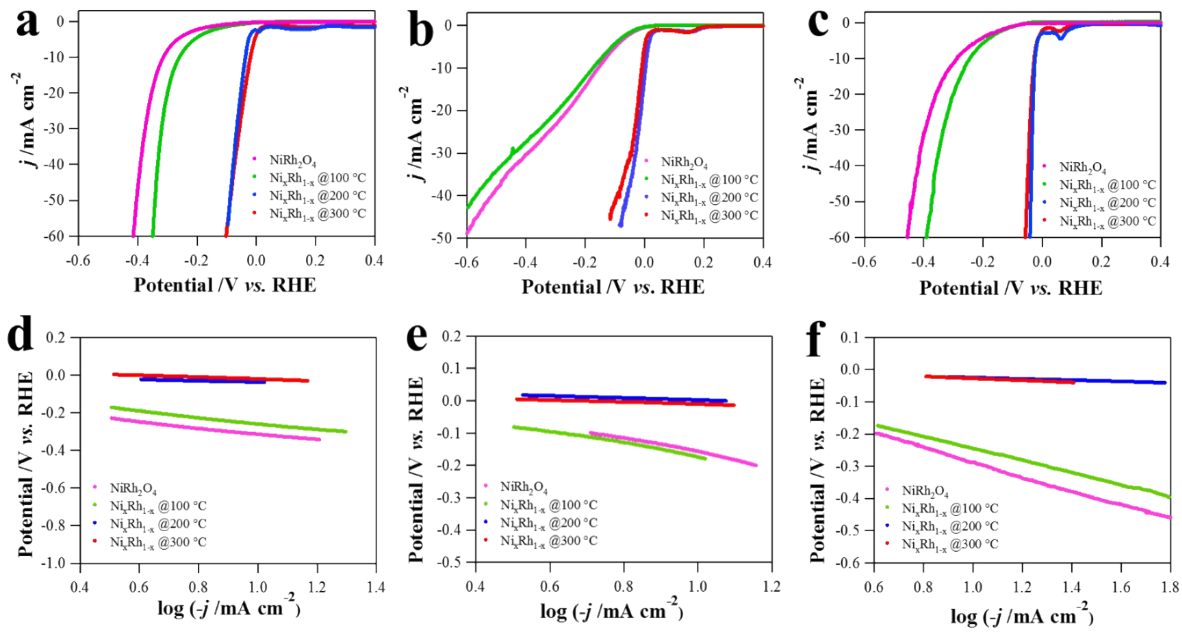

Figure S6. Polarization curves with *i*R compensation obtained using GC electrodes modified with $NiRh_2O_4$, Ni_xRh_{1-x} @100 °C, Ni_xRh_{1-x} @200 °C and Ni_xRh_{1-x} @300 °C in N_2-saturated aqueous solution of (a) 1.0 M NaOH, (b) 1.0 M PBS (pH 7.4) and (c) 1.0 M $HClO_4$. Scan rate of 10 mV s^{-1} and a rotating speed of 1600 rpm. The corresponding (d,e,f) Tafel plots for the HER obtained the RDE voltammograms shown in (a,b,c) respectively.

Table S1. Comparison of HER activities of the synthesized nanofibers in 1.0 M NaOH, 1.0 M PBS and 1.0 M $HClO_4$ aqueous media.

Catalyst	Solution	Potential at 10 mA cm^{-2} (mV *vs*. RHE)	Tafel Slope (mV dec^{-1})
Ni_xRh_{1-x} @100 °C	1.0 M NaOH	−260	−164.4
	1.0 M PBS	−174	−189.8
	1.0 M $HClO_4$	−245	−186.2
Ni_xRh_{1-x} @200 °C	1.0 M NaOH	−37	−36.7
	1.0 M PBS	−9.4	−31.4
	1.0 M $HClO_4$	−24	−29.6
Ni_xRh_{1-x} @300 °C	1.0 M NaOH	−30	−49.5
	1.0 M PBS	−10.4	−30
	1.0 M $HClO_4$	−25	−31.2
$NiRh_2O_4$	1.0 M NaOH	−316	−161.8
	1.0 M PBS	−156	−224.4
	1.0 M $HClO_4$	−288	−221.7

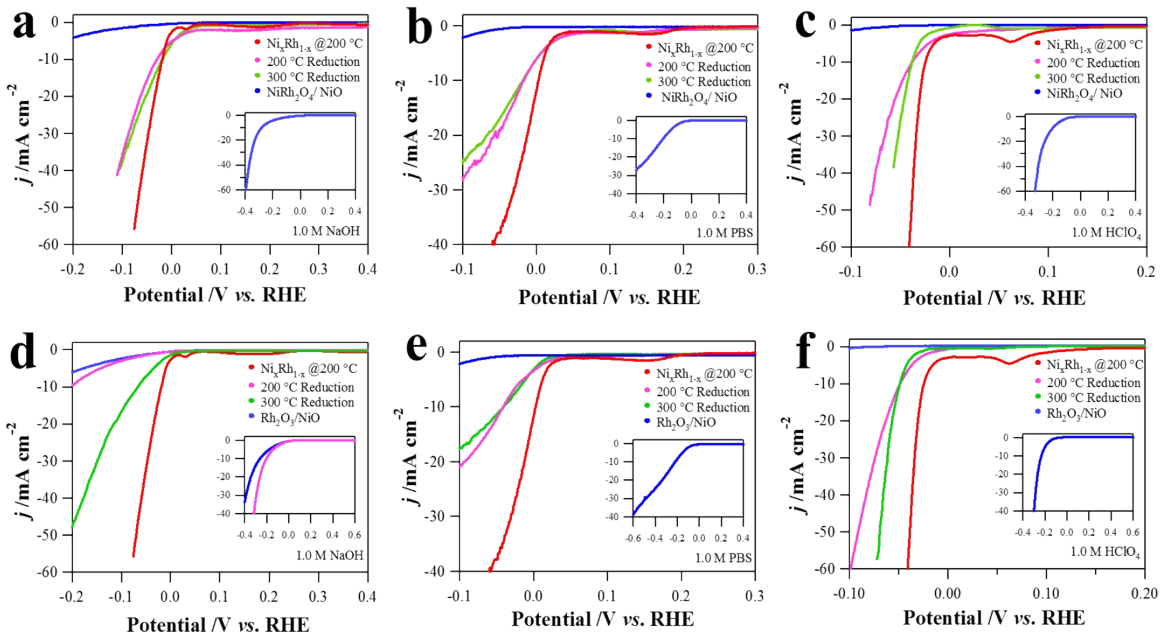

Figure S7. RDE voltammograms of the heterogeneous materials before and after thermal hydrogen reduction and that of Ni_xRh_{1-x} @200 °C obtained in 1.0 M NaOH, 1.0 M PBS (pH 7.4) and 1.0 M $HClO_4$ with a rotation rate of 1600 rpm. Precursor materials for the thermal hydrogen reduction are (a,b,c) $NiRh_2O_4$/NiO and (d,e,f) Rh_2O_3/NiO. Insets show the polarization curves in wider potential ranges for less active materials.

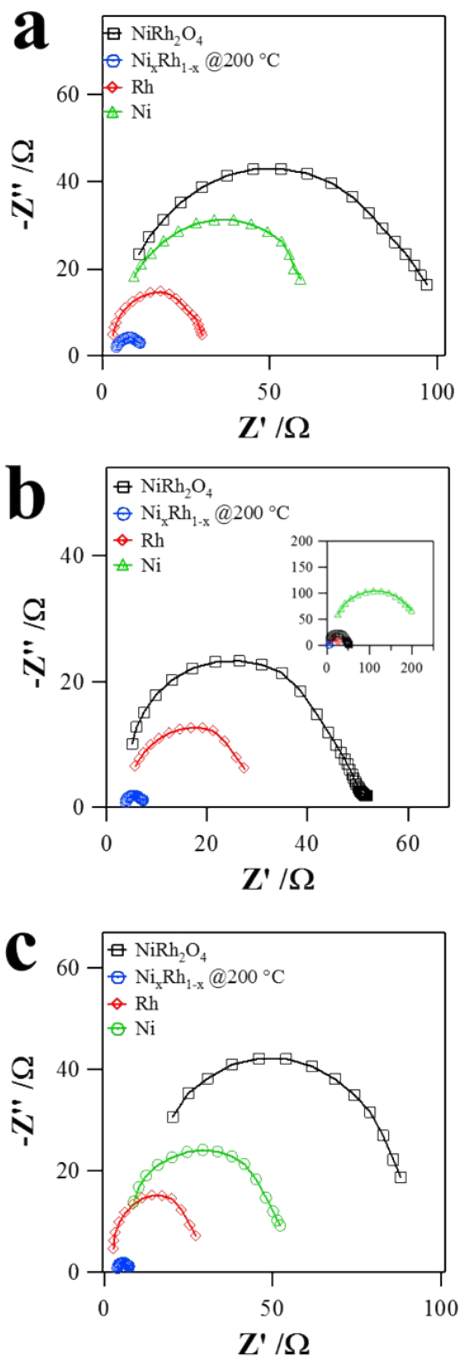

Figure S8. EIS study for the nanofibers of $NiRh_2O_4$, Ni_xRh_{1-x} @200 °C, pure Rh and pure Ni. The Nyquist plots measured in (a) 1.0 M NaOH, (b) 1.0 M PBS (pH 7.4) and (c) 1.0 M $HClO_4$ aqueous solution at overpotential of 0.1 V in the frequency range from 1 Hz to 10 kHz.

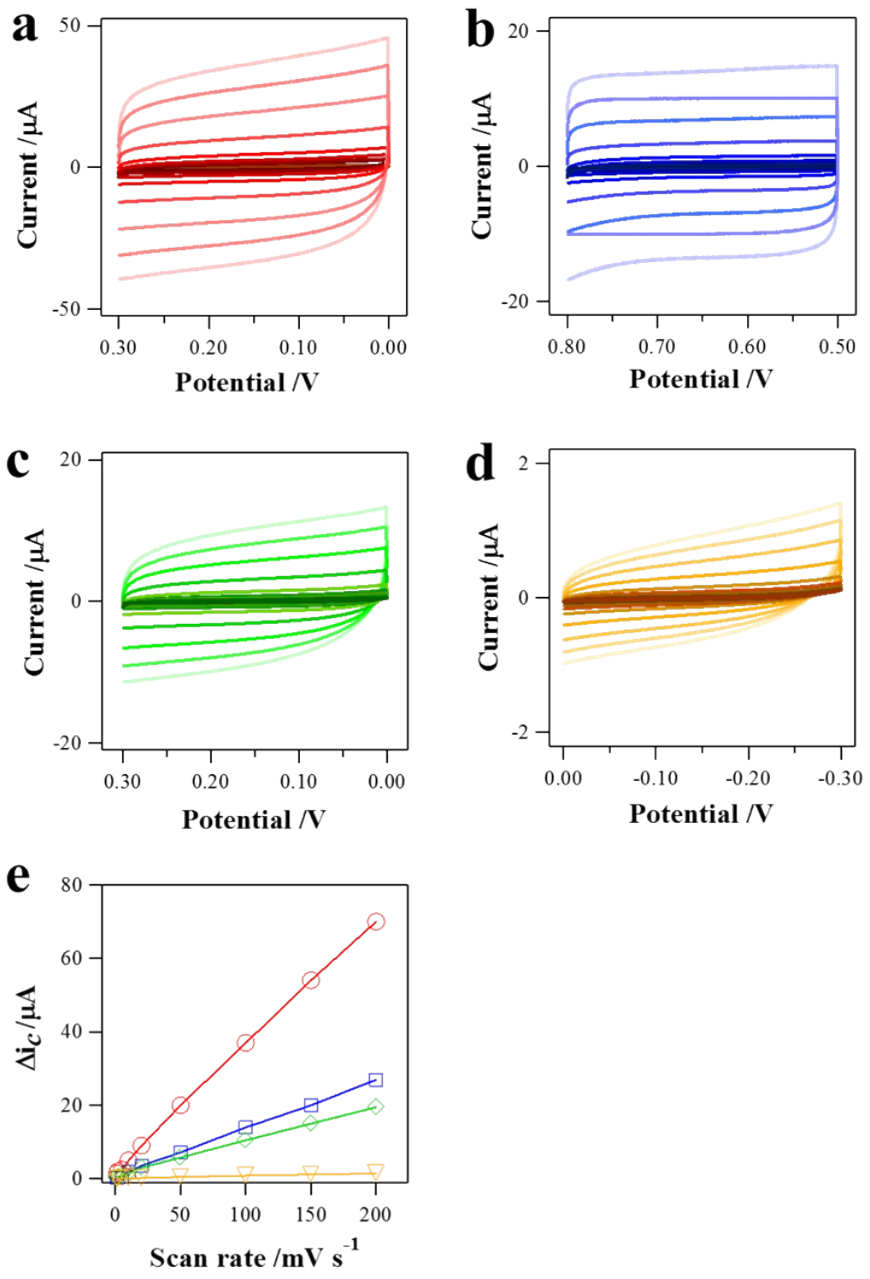

Figure S9. Cyclic voltammograms of (a) Ni_xRh_{1-x} @200 °C, (b) $NiRh_2O_4$, (c) Rh and (d) Ni nanomaterials obtained in 1.0 M KCl solution at various scan rates of 1, 2, 5, 10, 20, 50, 100, 150, and 200 mV s^{-1} with a potential range of 0.3 V. (e) Plots of absolute charging current differences (Δi_c) *vs* scan rate: Ni_xRh_{1-x} @200 °C (○) at 0.15 V, $NiRh_2O_4$ (□) at 0.65 V, pure Rh (◇) at 0.15 V and pure Ni (▽) at −0.15 V. Potential values are versus SCE.

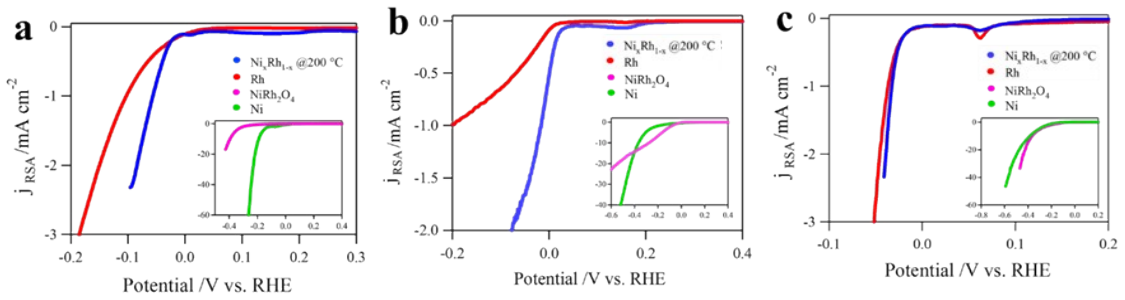

Figure S10. RDE polarization curves normalized by the corresponding electrochemical active surface area (ESA) for Ni_xRh_{1-x} @200 °C, $NiRh_2O_4$, pure Rh and pure Ni in N_2-saturated aqueous solution of (a) 1.0 M NaOH, (b) 1.0 M PBS and (c) 1.0 M $HClO_4$, respectively. For estimating ESAs, the slopes in Figure S9 and typical specific capacitance (C_s) of 35 μF cm^{-2} were used.