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

Electronic Supplementary Information:

Eutectic-directed self-templating synthesis of PtNi nanoporous nanowires with superior electrocatalytic performance towards oxygen reduction reaction: experiment and DFT calculation

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Electrochemically active surface area (*ECSA*) calculation

The ECSA of a catalyst containing Pt can be estimated from the following equation:

$$ECSA_{Pt}(m^2g^{-1})=Q_H/(210\times m_{Pt}) \qquad (1)$$

where Q_H is the total charge for hydrogen adsorption or desorption, m_{Pt} is the amount of Pt loaded on the electrode and 210μC cm^{-2} is the charge required for hydrogen adsorption of a monolayer on a polycrystalline Pt surface.

The calculation of transferred electron number (*n*) based upon K-L equation

The transferred electron number (n) can be calculated using the Koutecky-Levich equation which is expressed as follows:

$$1/I = 1/ I_k + 1/ I_d \qquad (2)$$

$$I_d = 0.62nFAD^{2/3}\upsilon^{-1/6}\,\varpi^{1/2}c_{O2} \qquad (3)$$

$$I_k = nFkC_0 \qquad (4)$$

where I is the measured current, I_k is the kinetic current, and I_d is the diffusion limited current, F is Faraday's constant (96485 C mol^{-1}), A is the geometric area of the glassy carbon electrode (0.196 cm^2), D is the diffusion coefficient of molecular oxygen in 0.1 M $HClO_4$ (1.9×10^{-5} cm^2 s^{-1}), υ is the kinematical viscosity (8.93×10^{-3} cm^2 s^{-1}), c_{O2} is the concentration of dissolved molecular oxygen (1.18×10^{-6}mol cm^{-3}), and ϖ is the angular frequency of rotation ($\varpi=2\pi f/60$, f is the RDE rotation rate in r.p.m.), k is the electron transfer rate constant.

The transferred electron number and hydrogen peroxide yield (X_{H2O2}) yield calculation based upon the RRDE data.

The hydrogen peroxide yield (X_{H2O2}) during the ORR can be determined by the following equation:

$$X_{H2O2} = \frac{2I_R/N}{I_D + I_R/N} \qquad (5)$$

$$n = \frac{4I_D}{I_D + I_R/N} \qquad (6)$$

in which I_R is the ring current, I_D is the disk current and N is the current collection efficiency of the Pt ring. N was determined to be 0.37 from the reduction of $K_3Fe[CN]_6$.

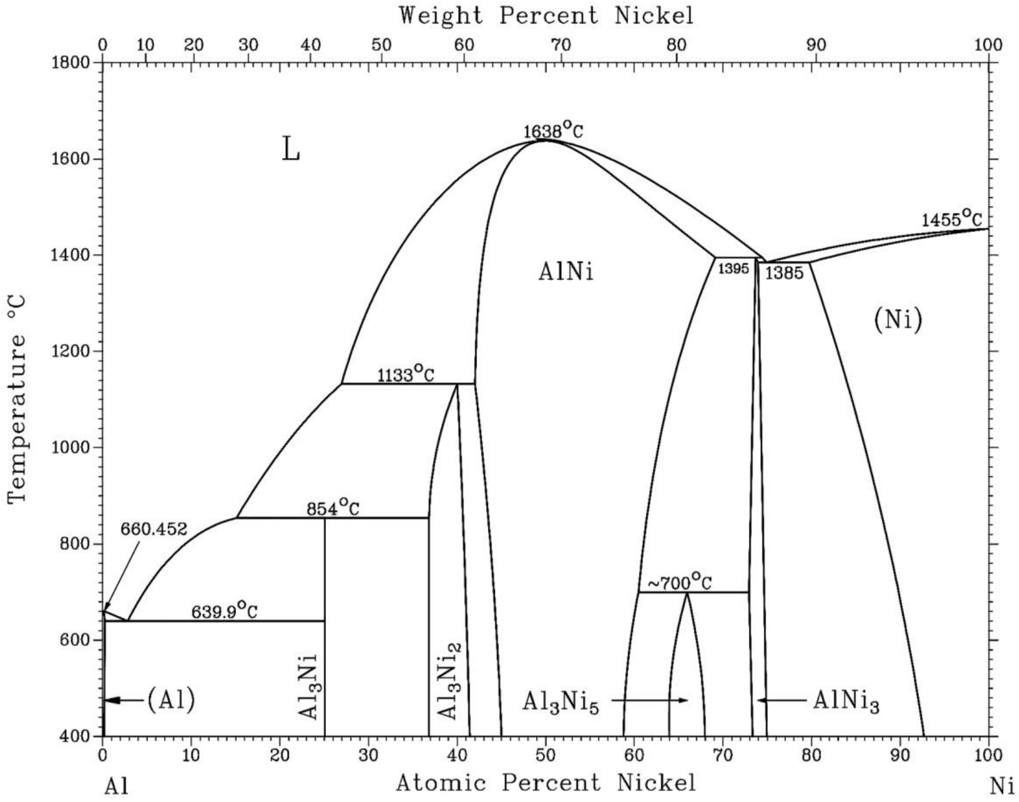


Figure S1. Al-Ni binary alloy phase diagram.[1]

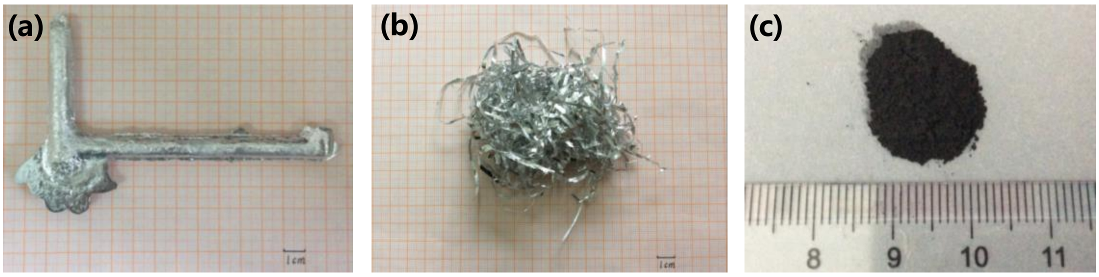


Figure S2. Photographs of (a) $Al_{97.8}Ni_2Pt_{0.2}$ alloy ingot, (b) $Al_{97.8}Ni_2Pt_{0.2}$ alloy ribbons, and (c) PtNi NPNWs catalyst after dealloying.

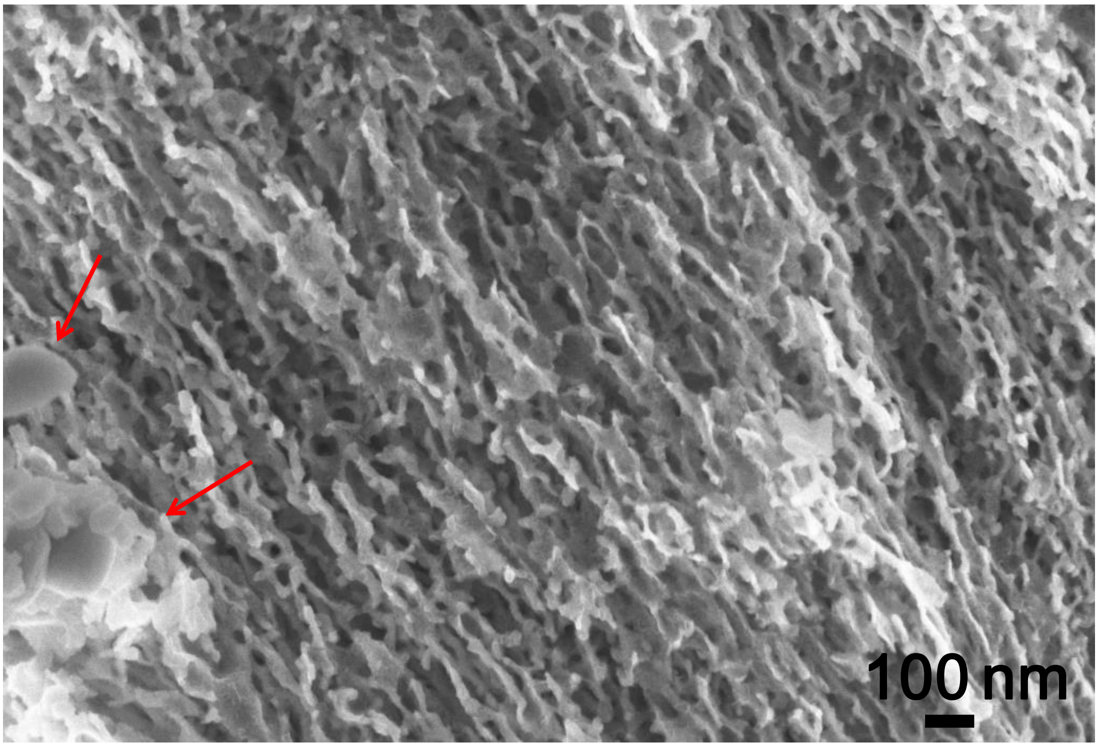


Figure S3. SEM image of the as-dealloyed $Al_{95}Ni_5$ sample after dealloying in 1M NaOH solution. The sub-micron particles are highlighted by red arrows.

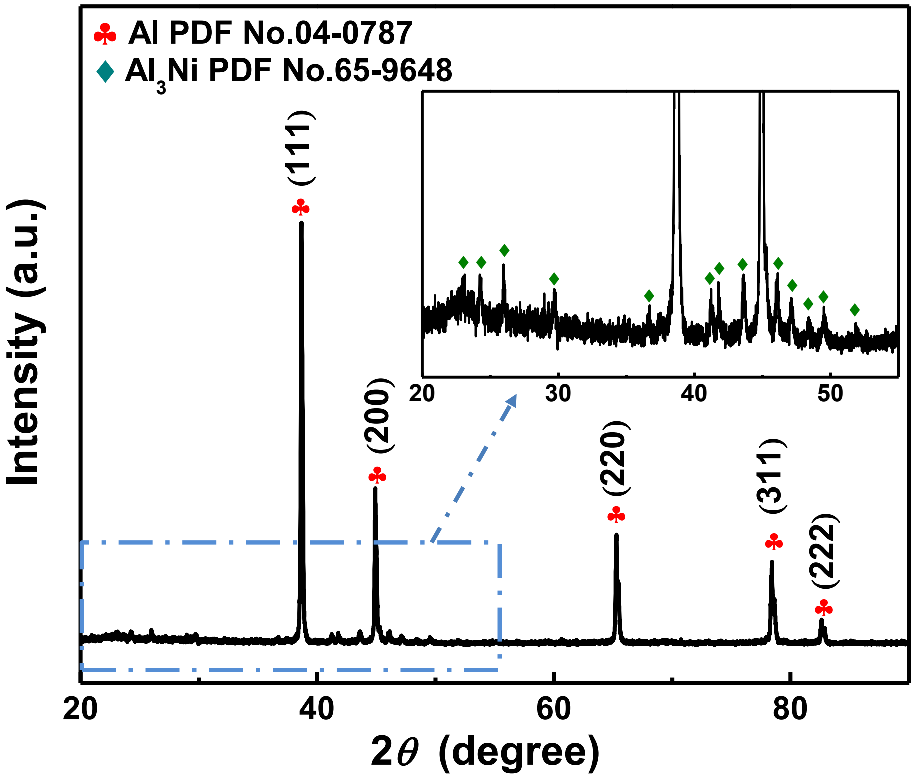
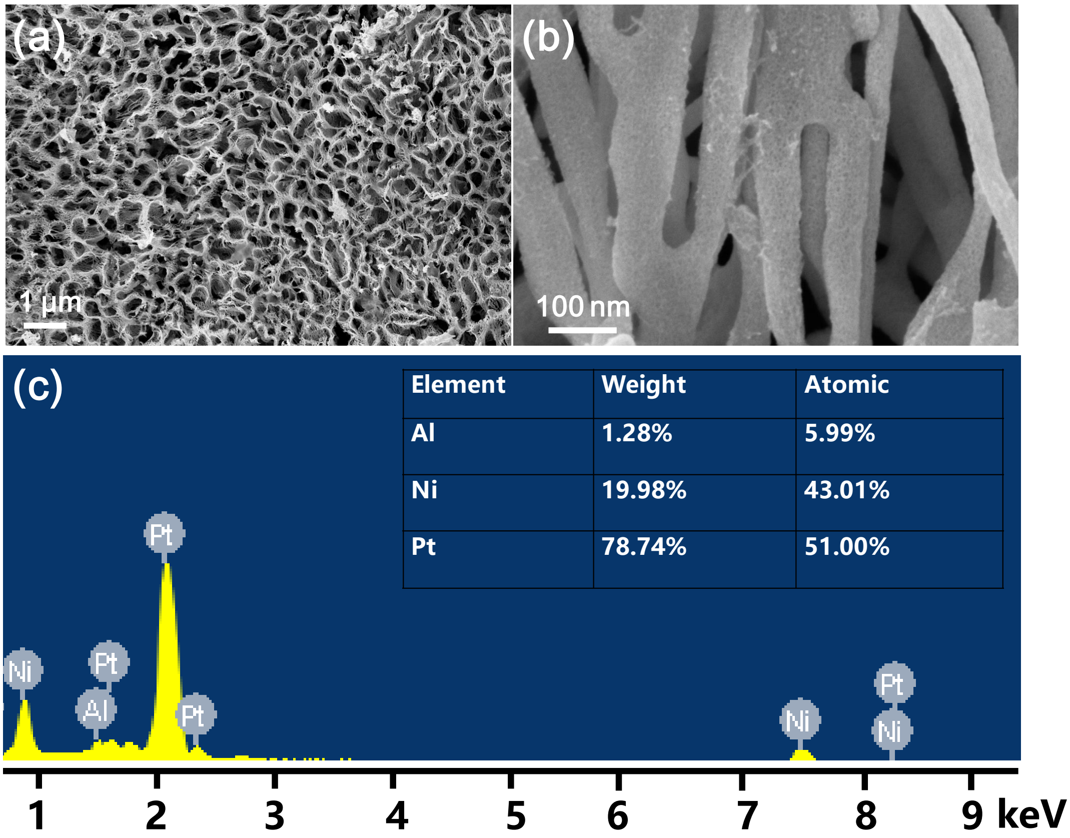


Figure S4. XRD pattern of the $Al_{97.8}Ni_2Pt_{0.2}$ alloy ribbons. The inset shows magnified XRD pattern with the 2θ angle ranging from 20° to 55°.



Element	Weight	Atomic
Al	1.28%	5.99%
Ni	19.98%	43.01%
Pt	78.74%	51.00%

Figure S5. (a-b) SEM images and (c) EDX spectrum of the PtNi NPNWs obtained by the two-step dealloying method. The corresponding compositions are listed in Figure S5c.

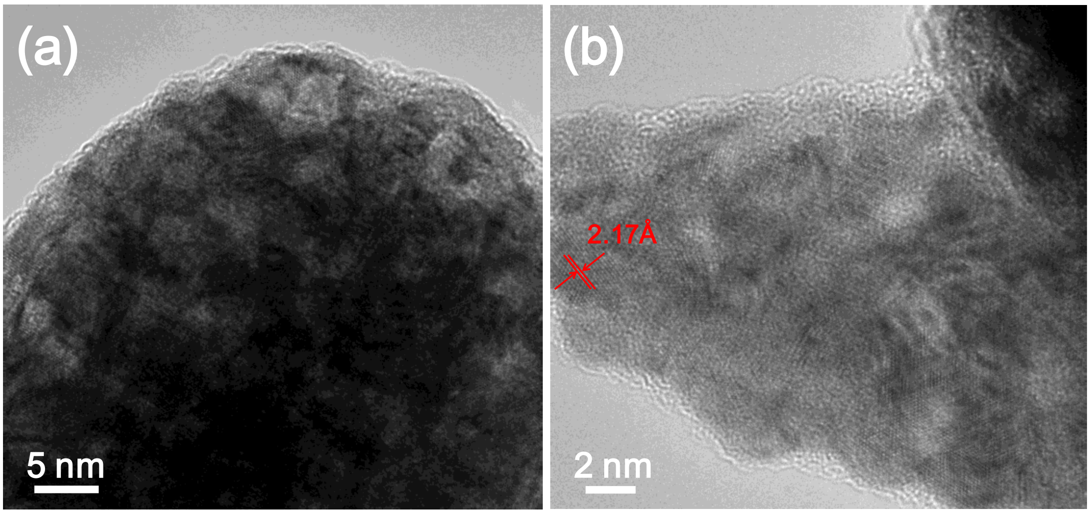


Figure S6. HRTEM images showing the microstructure of the PtNi NPNWs.

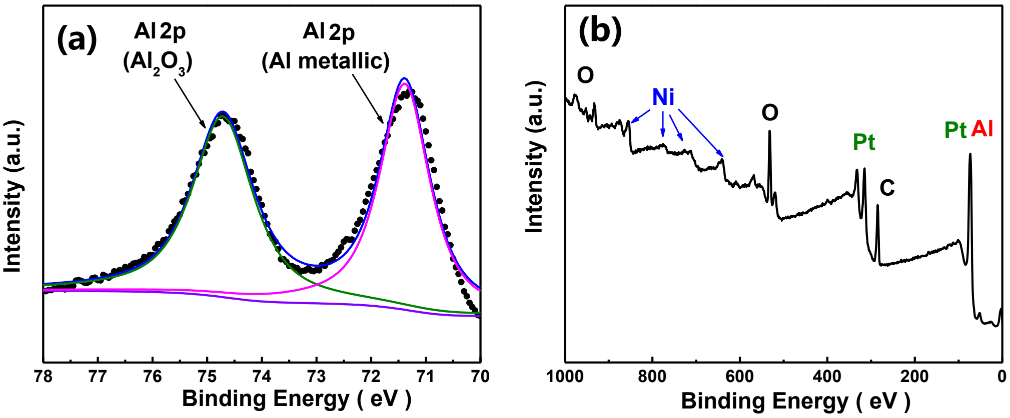
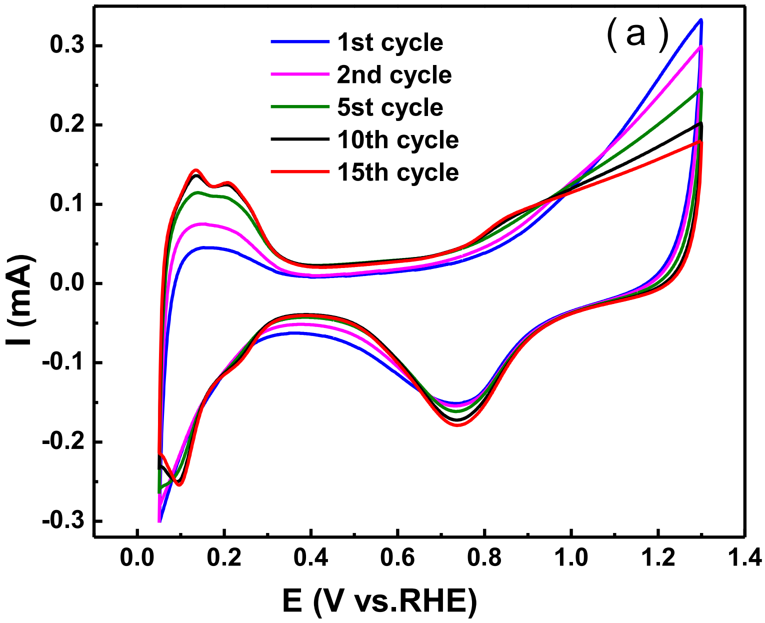


Figure S7 (a) XPS spectrum of Al 2p for the PtNi NPNWs catalyst. (b) XPS broad scan spectrum of the PtNi NPNWs catalyst.



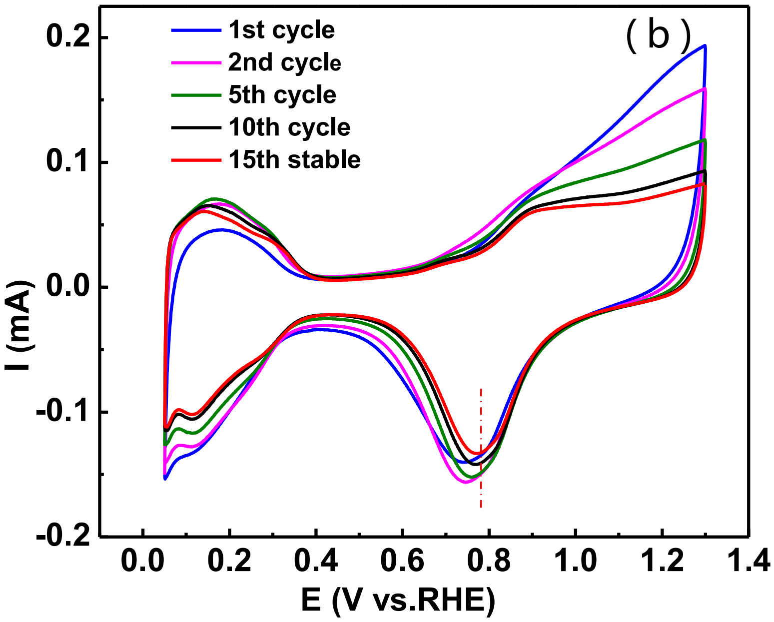


Figure S8. The evolution of CV curves for (a) PtC and (b) the PtNi NPNWs catalyst in the N_2-purged 0.1 M $HClO_4$ solution. (Scan rate: 50 mV s^{-1})

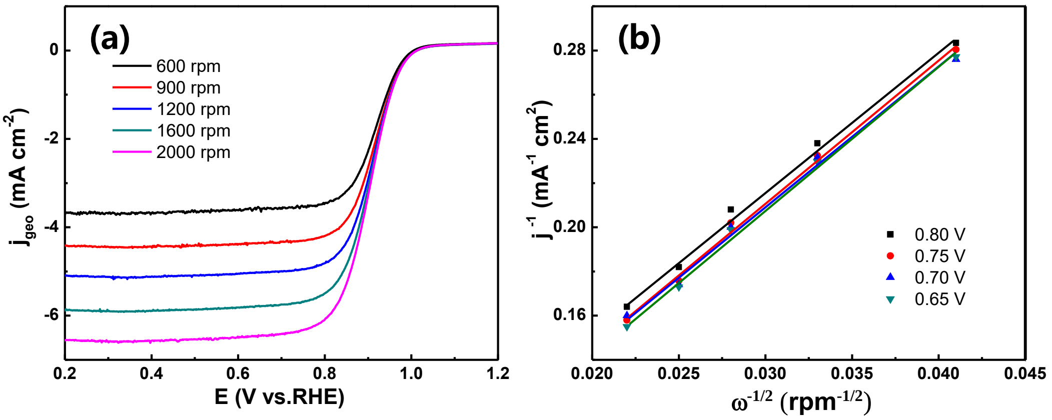


Figure S9. (a) The ORR polarization curves for the PtNi NPNWs at different rotation speeds in the O_2-saturated $HClO_4$ solution at 10 mV s^{-1}. (b) The Koutecky-Levich plots from ORR data for PtNi NPNWs at different potentials.

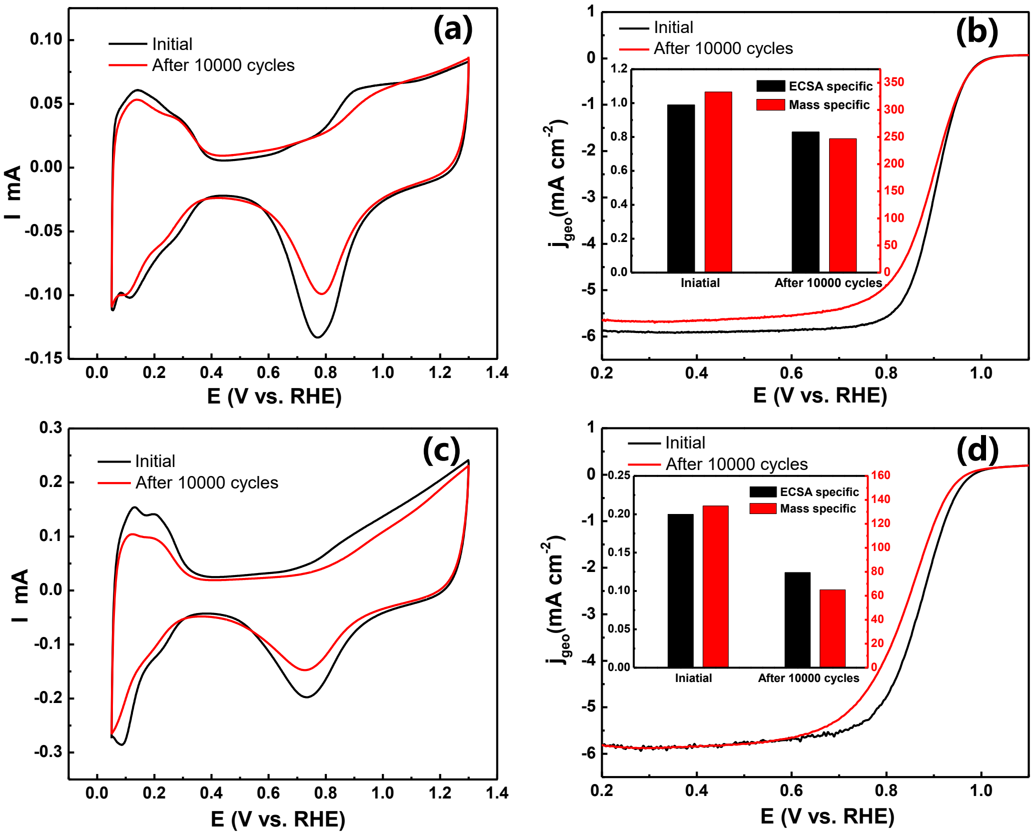


Figure S10. CVs of (a) PtNi NPNWs and (c) PtC catalysts in the N_2-saturated 0.1 M $HClO_4$ solution before and after 10000 potential cycles. ORR polarization curves for (b) PtNi NPNWs and (d) PtC catalysts before and after 10000 potential cycles in the O_2-saturated 0.1 M $HClO_4$ solution at 1600 rpm and 10 mV s^{-1}. The insets in (b , d) show histograms of the ECSA- and mass-normalized specific kinetic current densities for the PtNi NPNWs and PtC catalysts at 0.90 (V vs. RHE) before and after 10000 potential cycles, respectively.

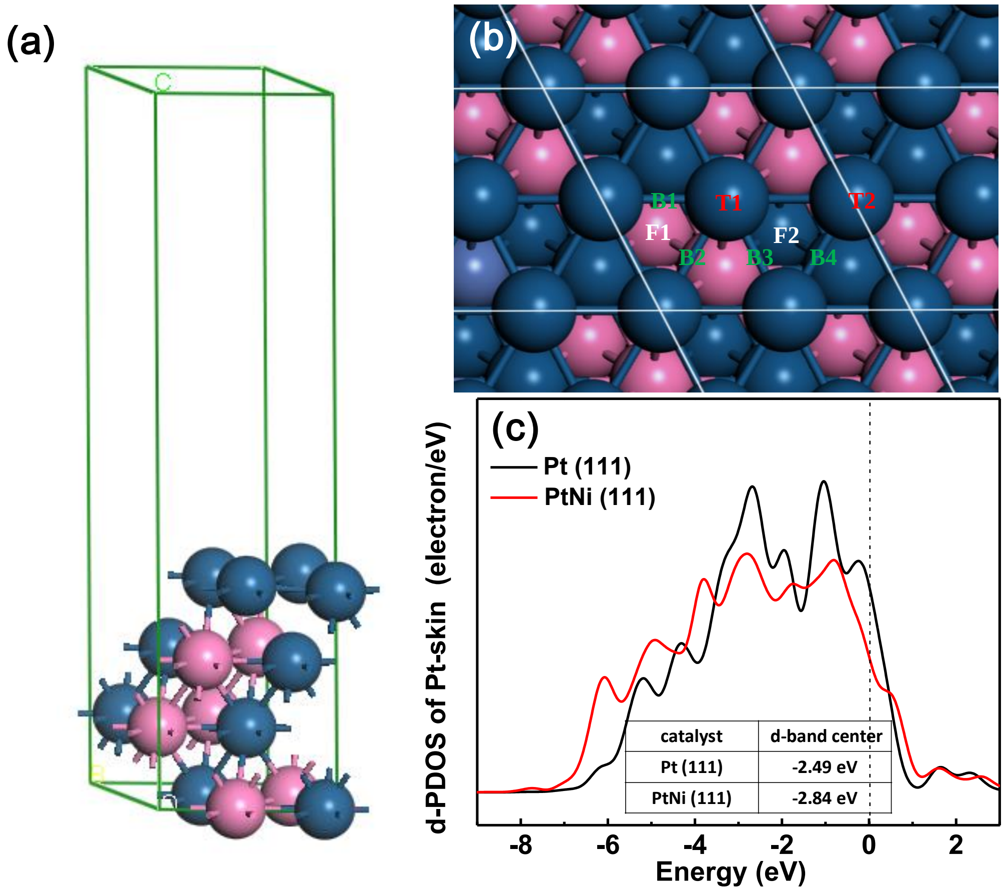


Figure S11. (a) Atomic structure and (b) various surface sites of the Pt surface-segregated PtNi(111) surface model. In the figure, blue balls represent Pt atoms, and pink balls represent Ni atoms. (T1, T2: top sites; F1, F2: f.c.c. sites; B1-B4: bridge sites) (c)The d-PDOS plots of Pt skin on Pt (111) and PtNi(111) surface.

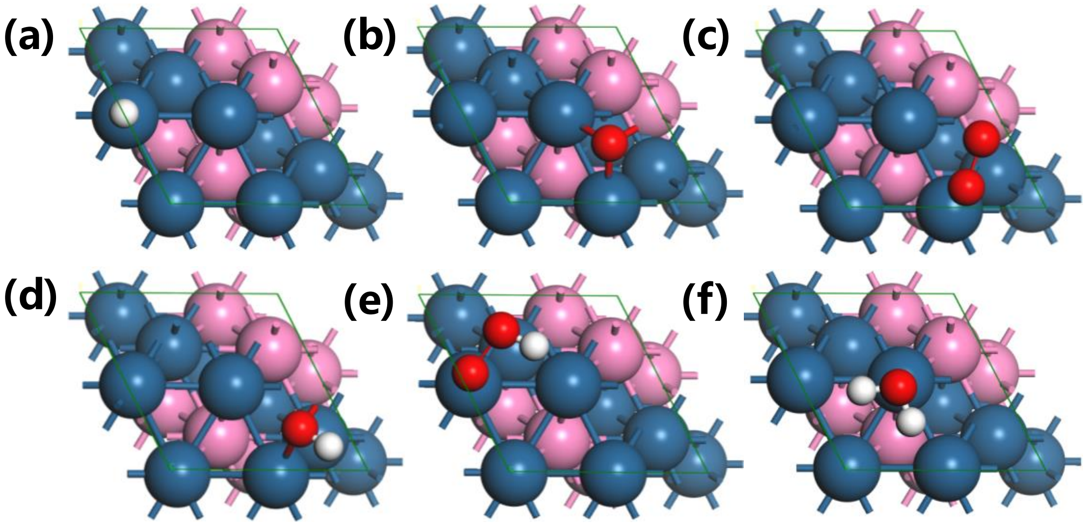


Figure S12. Atomic structures of the most stable adsorption geometries for various ORR chemical species adsorbed on the PtNi (111) surface. In the figure, blue balls represent Pt atoms, pink balls represent Ni atoms, red balls represent O atoms, and white balls represent H atoms. (a) *H adsorbed at top site T2, (b) *O adsorbed at f.c.c site F2, (c) *O_2 adsorbed at bridge site B4, (d) *OH adsorbed at bridge site B4, (e) *OOH adsorbed at top site T2, (f) *H_2O adsorbed at top site T1.

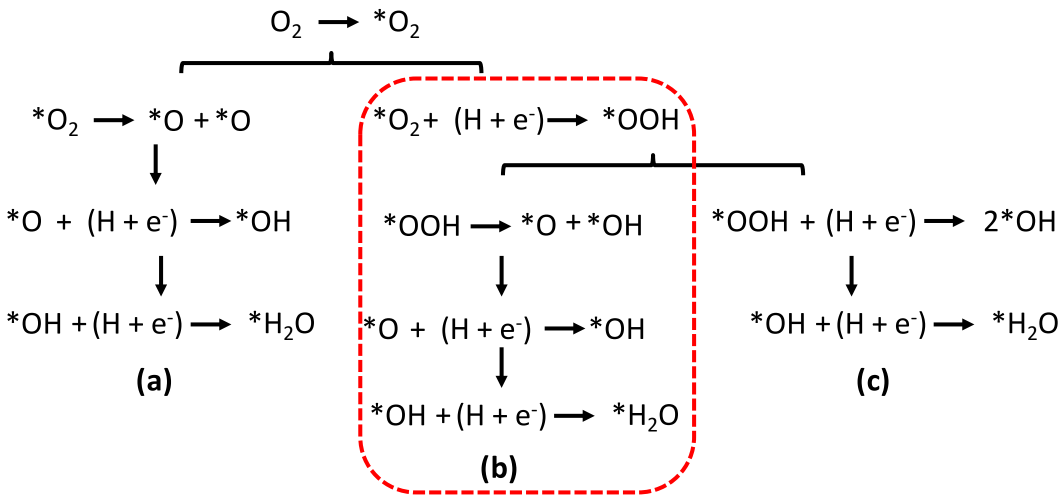


Figure S13. Three possible ORR mechanisms: (a) O_2 dissociation ORR mechanism, (b) OOH dissociation ORR mechanism, and (c) H-OOH dissociation ORR mechanism. In the figure, the asterisk (*) denotes the chemical species bound on the PtNi (111) surface.

Table S1. Comparison of ORR parameters for the PtNi NPNWs and commercial PtC in the oxygen-saturated 0.1 M $HClO_4$ solution.

	ORR			
Sample	E_{half} (V vs. RHE)	$j_{\mathrm{ECSA,0.90V}}$(mA cm^{-2})	$j_{\mathrm{mass,0.90V}}$ (mA mg$^{-1}{}_{\mathrm{Pt}}$)	ECSA (m^{2} g^{-1})
PtC	0.864	0.20	135	66
PtNi NPNWs	0.898	0.99	333	33.6

Table S2. Comparison of ORR parameters for the PtNi NPNWs and commercial PtC catalysts before and after 10000 cycles in the oxygen-saturated 0.1 M $HClO_4$ solution.

		ORR			
	Cycling number	E_{half} (V vs. RHE)	$j_{ECSA,0.90V}$ (mA cm^{-2})	$j_{mass,0.90V}$ (mA mg^{-1}_{Pt})	ECSA (m^2 g^{-1})
PtC	initial	0.864	0.2	135	66
	10000	0.833	0.14	65	47
PtNi NPNWs	initial	0.898	0.99	333	33.6
	10000	0.886	0.83	247	29.8

Table S3. Adsorption energies (ΔE_{ads}) (in units of eV) of various ORR chemical species on the PtNi (111) Surface. (T1, T2: top sites; F1, F2: f.c.c. sites; B1-B4: bridge sites) The asterisk (*) denotes the chemical species bound on the Pt (111) or PtNi(111) surface.

chemical species	T1	T2	F1	F2	B1	B2	B3	B4
*H	3.52	3.68	3.54	3.67	-	-	-	-
*O	-	-	5.49	5.75	-	-	-	-
*O_2	-	-	-	-	1.63	1.54	1.72	1.80
*OH	2.76	2.89	-	-	2.89	2.56	2.80	2.90
*OOH	1.09	1.18	-	-	-	-	-	-
*H_2O	0.50	0.50	-	-	-	-	-	-

Table S4. Adsorption energies (ΔE_{ads}) (in units of eV) of various ORR intermediate species on the Pt (111) and PtNi (111)**.** The asterisk (*) denotes the chemical species bound on the Pt (111) or PtNi(111) surface.

	*H	*O	*O_2	*OH	*OOH	*H_2O
Pt(111)	4.08	6.33	2.08	3.12	1.32	0.52
PtNi(111)	3.68	5.75	1.80	2.90	1.18	0.50

Table S5. Calculated heats of reaction (E_r) and activation energies (E_a) (in units of eV) for various elementary steps of ORR on the Pt (111) and PtNi(111) surface. The asterisk (*) denotes the chemical species bound on the Pt (111) or PtNi(111) surface.

Reaction steps	Pt(111)		PtNi(111)	
	E_a	E_r	E_a	E_r
$*O_2 \rightarrow *O + *O$	0.93	-0.94	1.46	-0.34
$*O_2 + *H \rightarrow *OOH$	0.28	-0.26	0.25	-0.52
$*OOH \rightarrow *O + *OH$	0.29	-0.99	0.52	-0.70
$*OOH + *H \rightarrow 2*OH$	0.46	-1.84	0.64	-2.15
$*O + *H \rightarrow *OH$	0.79	-0.24	0.50	-0.65
$*OH + *H \rightarrow *H_2O$	0.20	-0.70	0.09	-1.18

Reference

1. K. Morsi, *Adv. Mater. Sci. Eng.*, 2001, **A299**, 1-15.