Supporting information

Ni-Pd core-shell nanoparticles with Pt-like oxygen reduction electrocatalytic performance in both acidic and alkaline electrolytes

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Table S1. Composition of the PdNi nanoparticles and carbon content in the catalysts

Samples	Pd:Ni in precursor (molar ratio)	Pd:Ni by ICP-AES (molar ratio)	Carbon content by EA (wt.%)
Pd/C	4:0	/	82.5
Ni@Pd3/C	3:1	3.8:1	84.3
Ni@Pd2/C	2:1	2.5:1	81.6
Ni@Pd/C	1:1	1.3:1	82.0
Ni3@Pd/C	1:3	1:3.3	81.2
Pd3@Ni/C	3:1	4.1:1	83.7
Ni/C	0:4	/	82.6

Table S2. Comparison of the electron transfer numbers and H_2O_2% of the catalysts at 0.6 V (vs. RHE)

Catalysts	0.1 M $HClO_4$ solution		0.1 M KOH solution	
	Electron transfer number	H_2O_2%	Electron transfer number	H_2O_2%
Pt/C	3.98	0.5%	3.99	0.4%
Ni@Pd3	3.90	5.0%	3.98	1%
Ni@Pd2	3.90	5.2%	3.98	0.8%
Ni@Pd	3.88	6.1%	3.97	1.4%
Ni3@Pd	3.79	10.6%	3.87	6.3%
Pd	3.97	1.2%	3.97	1.4%
Pd3@Ni	3.91	4.4%	3.94	3.0%

Table S3. ORR performance comparison between the as-prepared Ni@Pd3 NPs and other NiPd-based catalysts reported recently

Catalyst	Onset potential (V versus RHE)	Half-wave potential (V versus RHE)	Mass activity ($mA\ mg^{-1}$)	Electron transfer number	Electrolyte	Ref.
Nanoporos PdNi alloys	~0.95	~0.83	~35 at 0.85 V	/	0.1 M $HClO_4$	39
Nanoporos PdNi alloys	~0.98	~0.88	~150 at 0.90 V	/	0.1 M $HClO_4$	40
$Pd_{80}Ni_{20}$/C	~0.85	~0.65	~55 at 0.75 V ~25 at 0.80 V	4	0.5 M H_2SO_4	41
$Pd_{0.90}Ni_{0.10}$ nanowires	~0.97	~0.85	/	/	0.1 M $HClO_4$	42
PdNi/CB (1:2)	~0.98	~0.8	73 at 0.85 V	~3.7	0.1 M KOH	43
Pd–Ni/C	~0.97	~0.88	/	3.4	0.1 M KOH	44
Ni@Pd3 NPs	~0.99	~0.87	~105 at 0.85 V ~25 at 0.90 V	3.91	0.1 M $HClO_4$	This work
Ni@Pd3 NPs	~0.98	~0.86	~95 at 0.85 V ~38 at 0.90 V	3.98	0.1 M KOH	This work

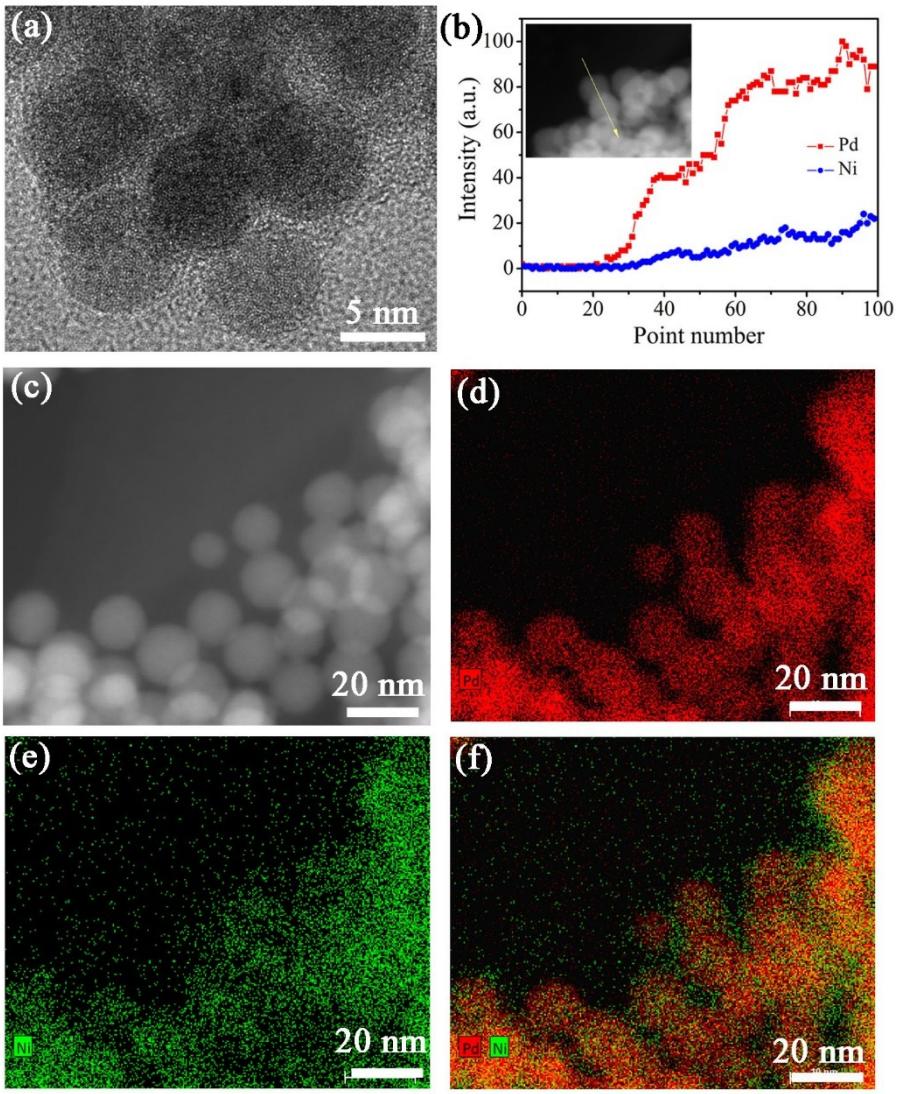

Fig. S1. (a) HRTEM image; (b) STEM-EDX line scan; and (c-f) HAADF-STEM image with the corresponding high resolution elemental mapping of the Pd3@Ni NPs. Green denotes Ni and red highlights the Pd distribution within NPs.

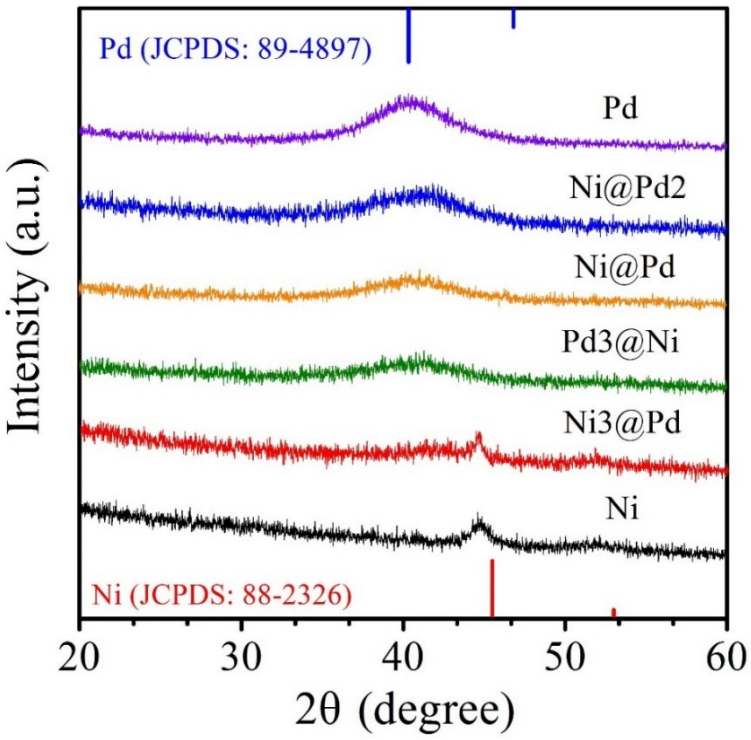

Fig. S2. XRD of the products with different molar ratios of precursors (Pd:Ni), including pure Pd, Pd:Ni=2:1 in OAM; Pd:Ni=1:1 in OAM; Pd:Ni=1:3 in OAM; Pd:Ni=3:1 in OAM+ODE; and (f) pure Ni.

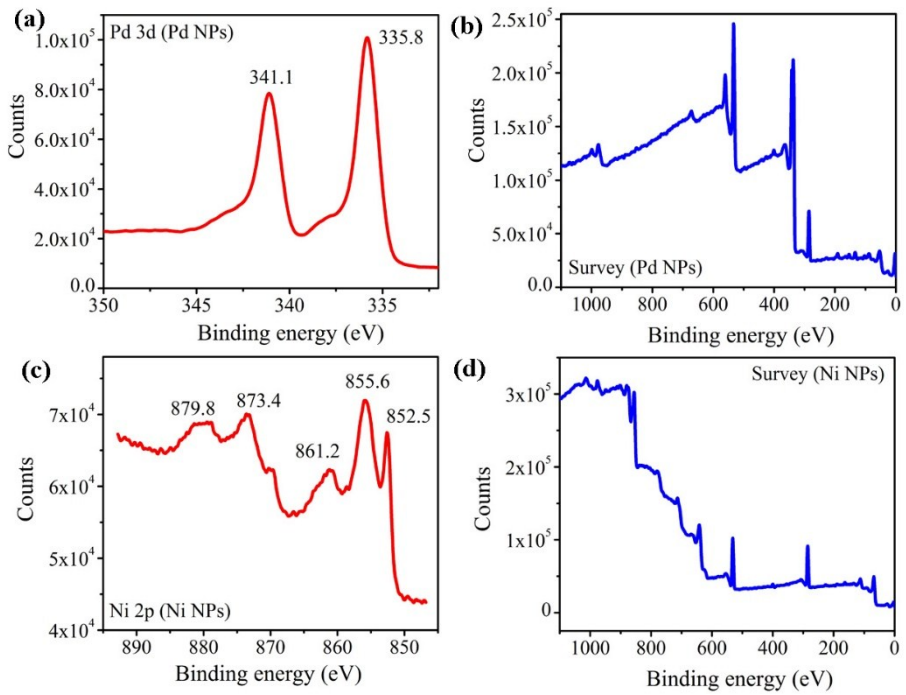

Fig. S3. (a-b) Pd 3d and survey signal of the Pd NPs in the XPS spectra; and (c-d) Ni 2p and survey signal of the Ni NPs in the XPS spectra.

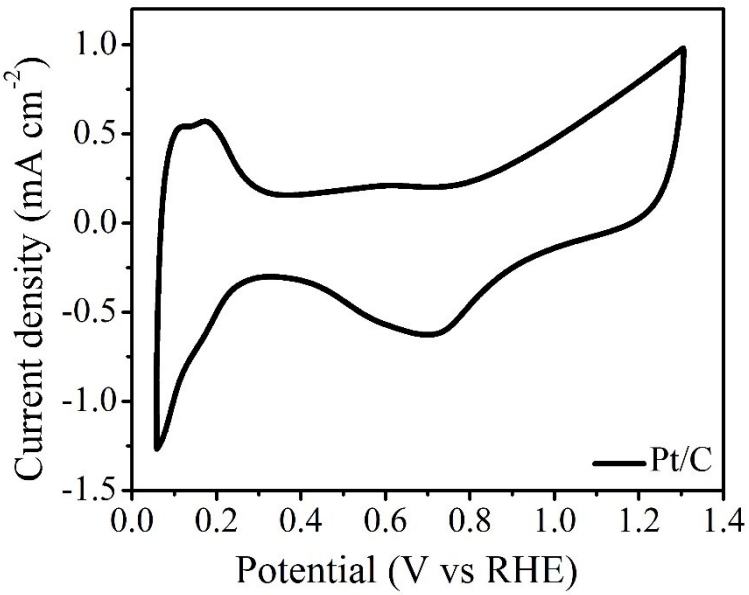

Fig. S4. CV curves of the commercial Pt/C (wt.20%) tested in a N_2-saturated 0.1 M $HClO_4$ solution at a sweep rate of 20 mV s^{-1}.

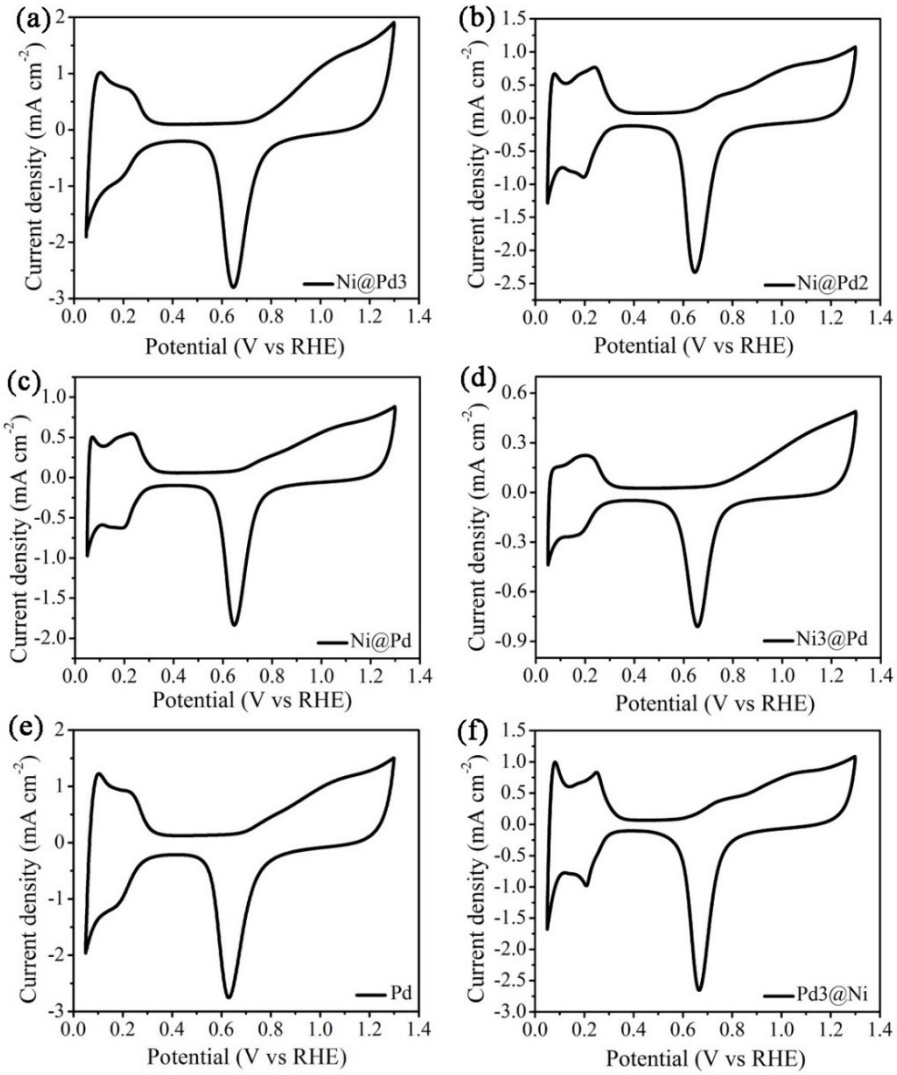

Fig. S5. CV curves of the as-prepared catalysts in a N_2-saturated 0.1 M KOH solution at a sweep rate of 20 mV s^{-1}.

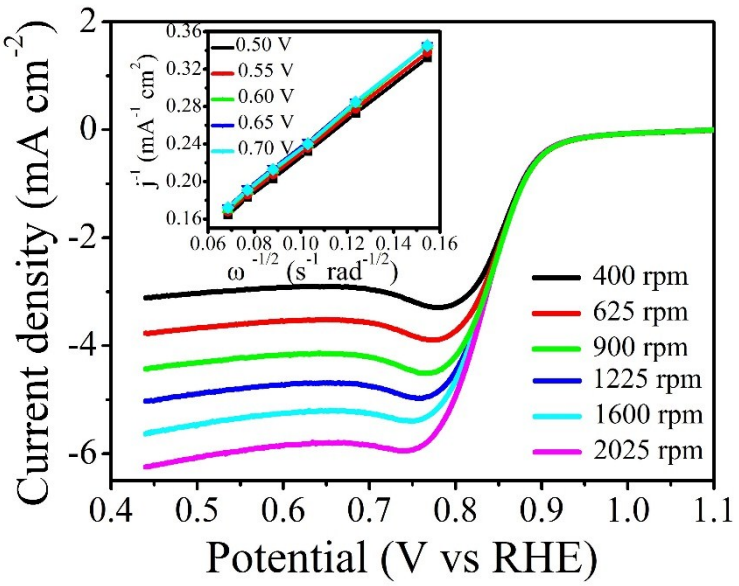

Fig. S6. Polarization curves of Ni@Pd3/C NPs at various rotating speeds in 0.1 M $HClO_4$ solution and the corresponding Koutecky-Levich plots at various potentials (Inset image).

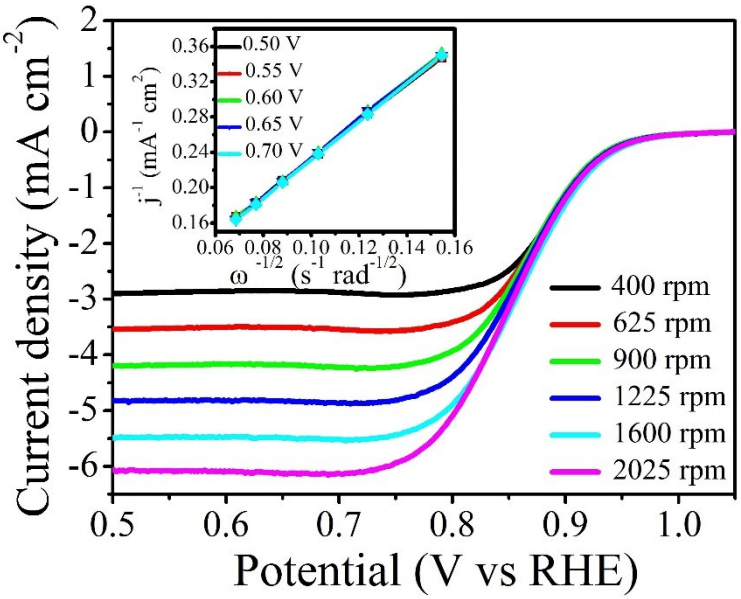

Fig. S7. Polarization curves of Ni@Pd3/C NPs at various rotating speeds in 0.1 M KOH solution and the corresponding Koutecky-Levich plots at various potentials (Inset image).

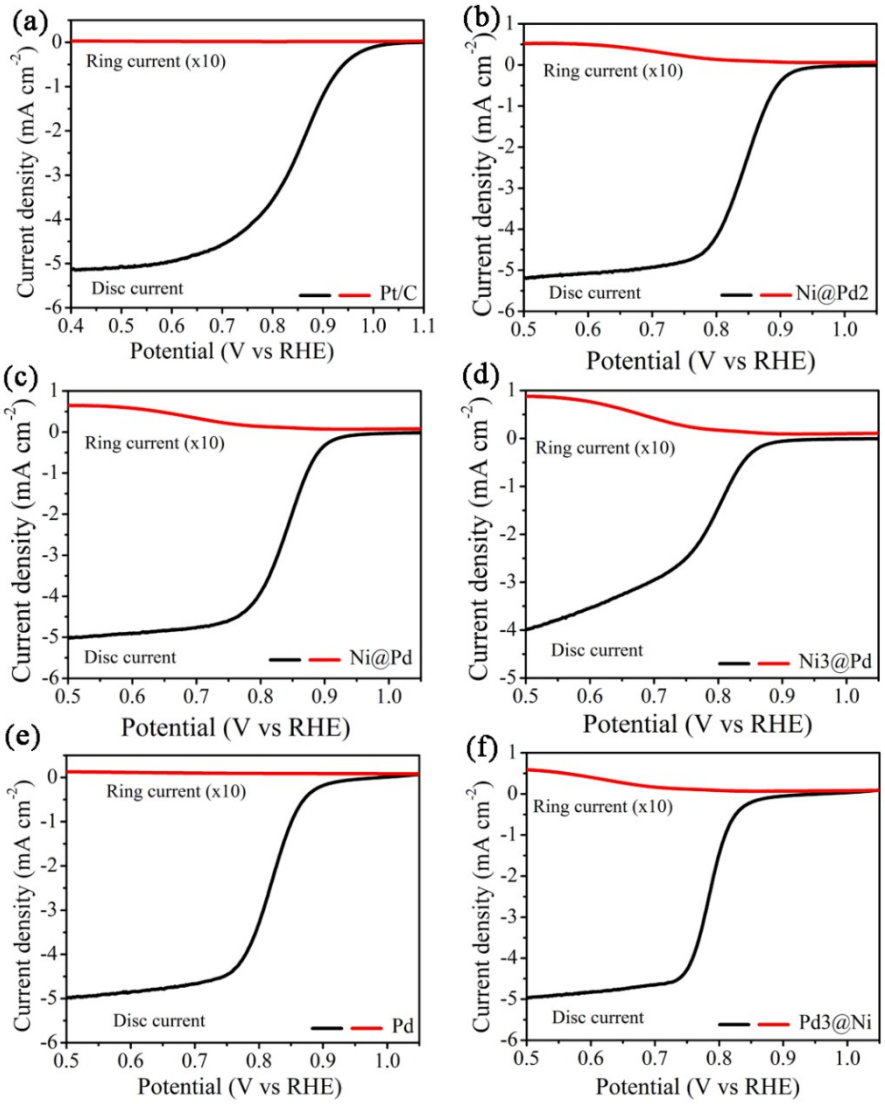

Fig. S8. LSV polarization curves of the catalysts at a rotating speed of 1600 rpm in the RRDE tests to calculate the electron transfer number and H_2O_2% in 0.1 M $HClO_4$ solution: (a) Pt/C (wt.20%), (b) Ni@Pd2, (c) Ni@Pd, (d) Ni3@Pd, (e) Pd, and (f) Pd3@Ni.

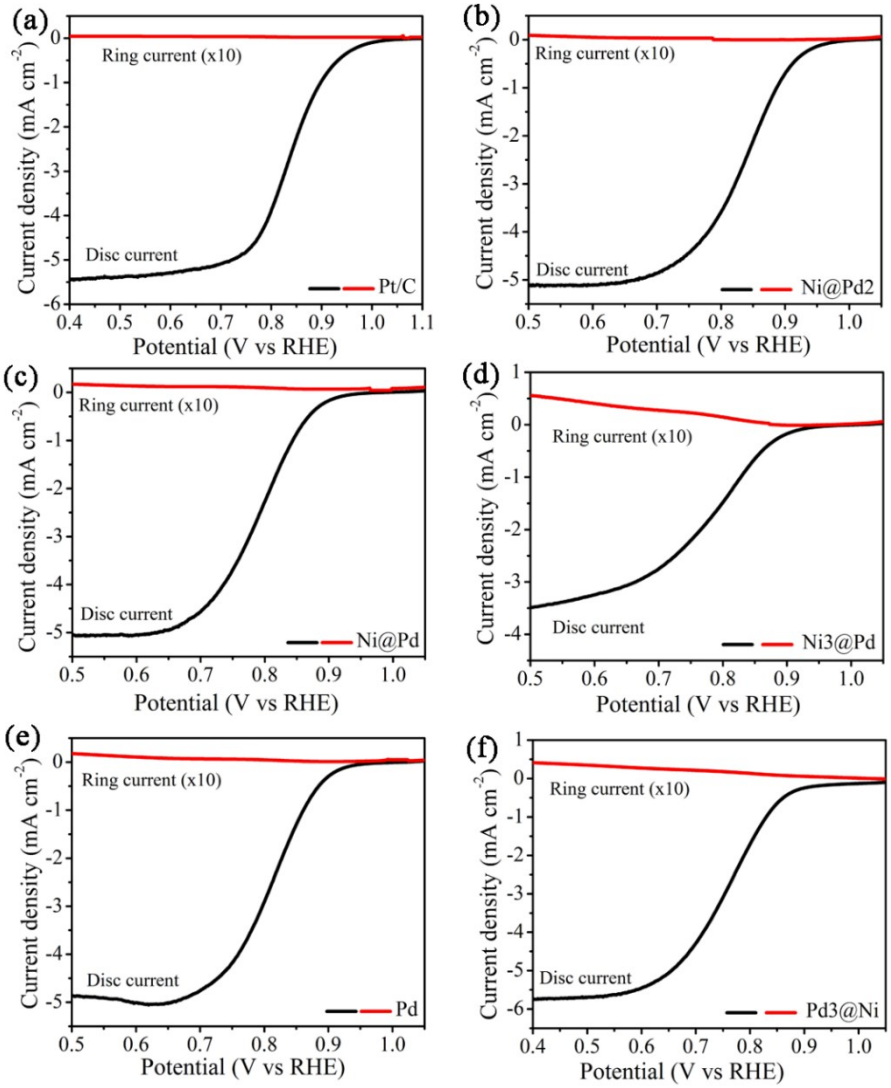

Fig. S9. LSV polarization curves of the catalysts at a rotating speed of 1600 rpm in the RRDE tests to calculate the electron transfer number and H_2O_2% in 0.1 M KOH solution: (a) Pt/C (wt.20%), (b) Ni@Pd2, (c) Ni@Pd, (d) Ni3@Pd, (e) Pd, and (f) Pd3@Ni.

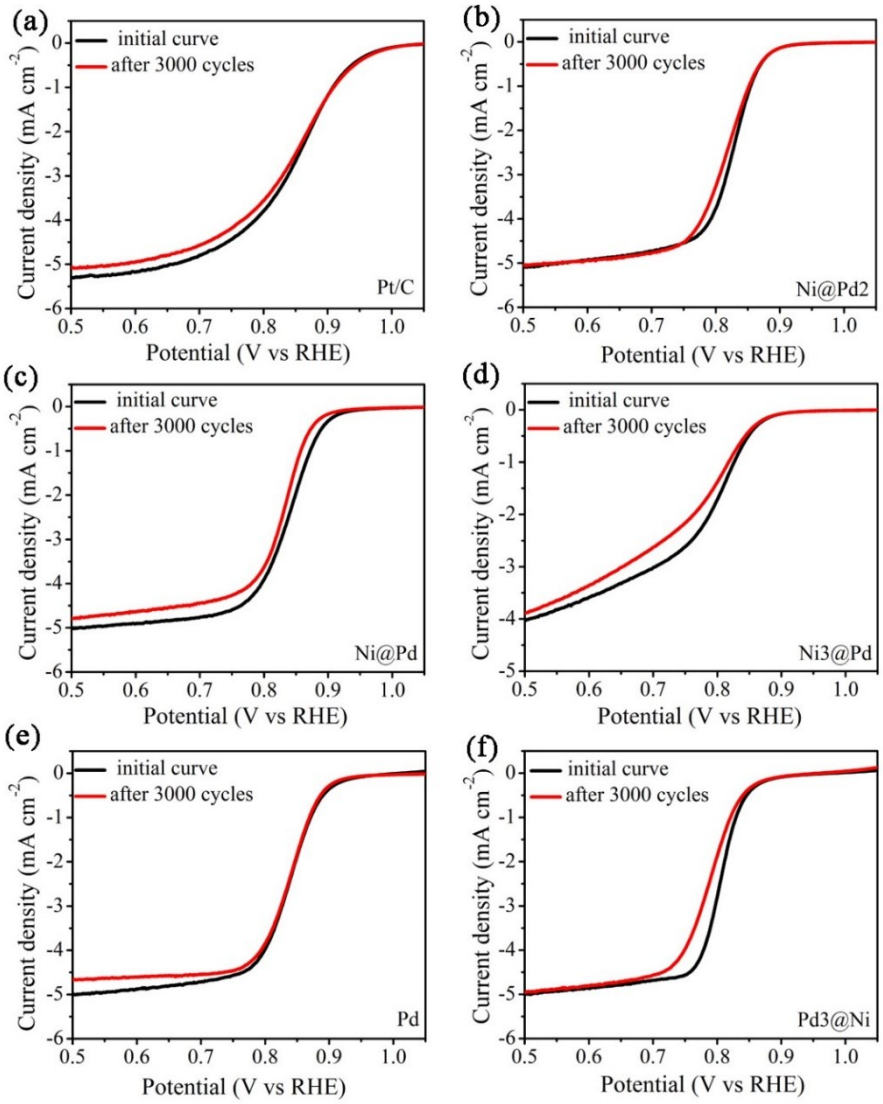

Fig. S10. LSV curves of the catalysts before and after 3000 cycles in 0.1 M $HClO_4$ solution: (a) Pt/C (wt.20%), (b) Ni@Pd2, (c) Ni@Pd, (d) Ni3@Pd, (e) Pd, and (f) Pd3@Ni.

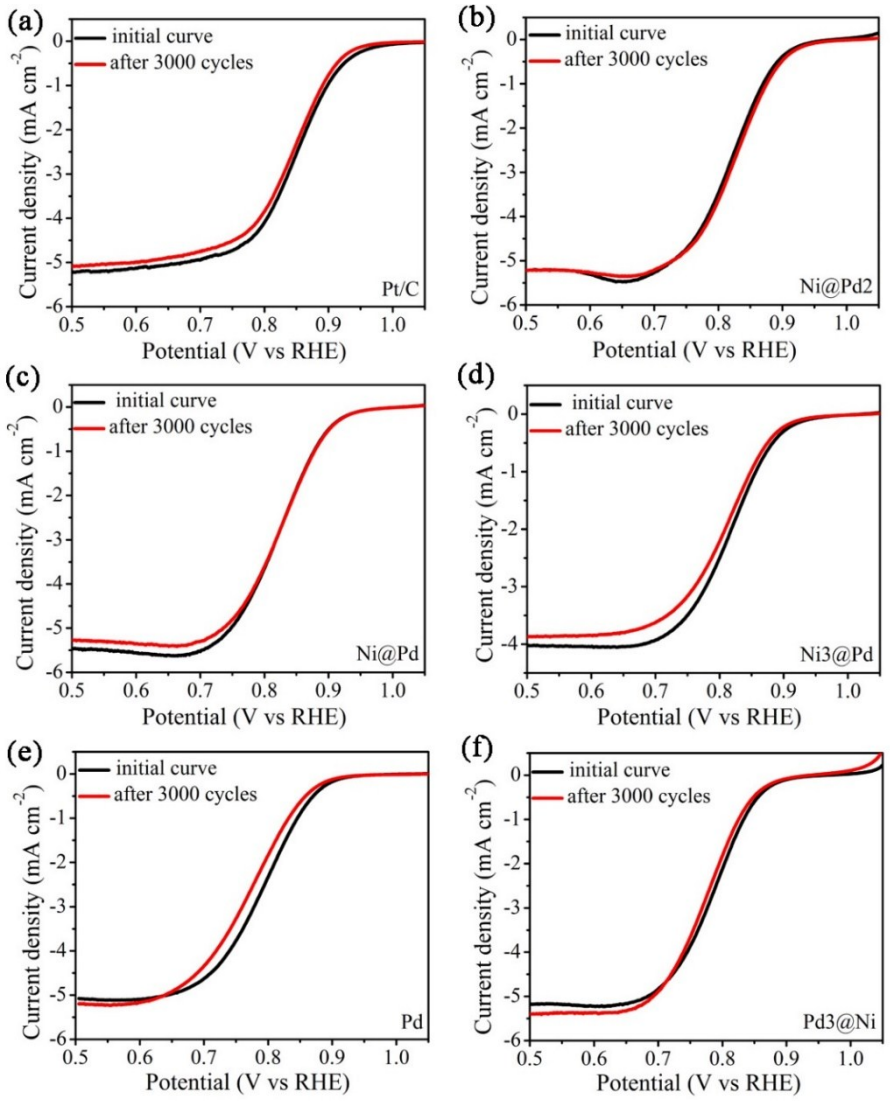

Fig. S11. LSV curves of the catalysts before and after 3000 cycles in 0.1 M KOH solution: (a) Pt/C (wt.20%), (b) Ni@Pd2, (c) Ni@Pd, (d) Ni3@Pd, (e) Pd, and (f) Pd3@Ni.

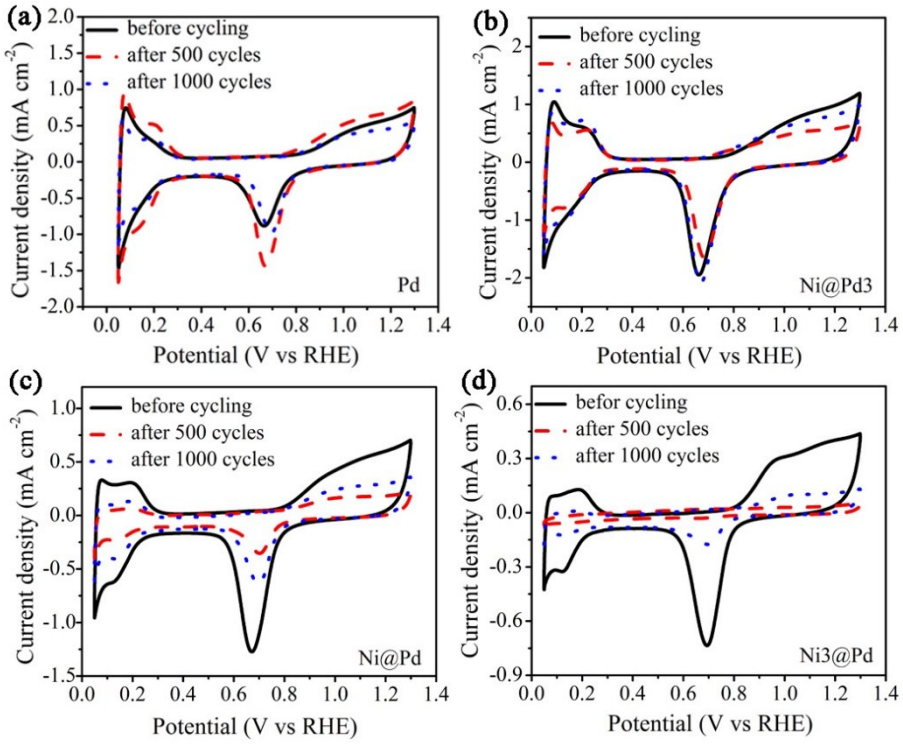

Fig. S12. Initial and post-potential cycling CV curves for Pd, Ni@Pd3, Ni@Pd and Ni3@Pd catalysts in N_2-saturated 0.1 M $HClO_4$ solution at the sweep rate of 20 mV s^{-1} at room temperature.

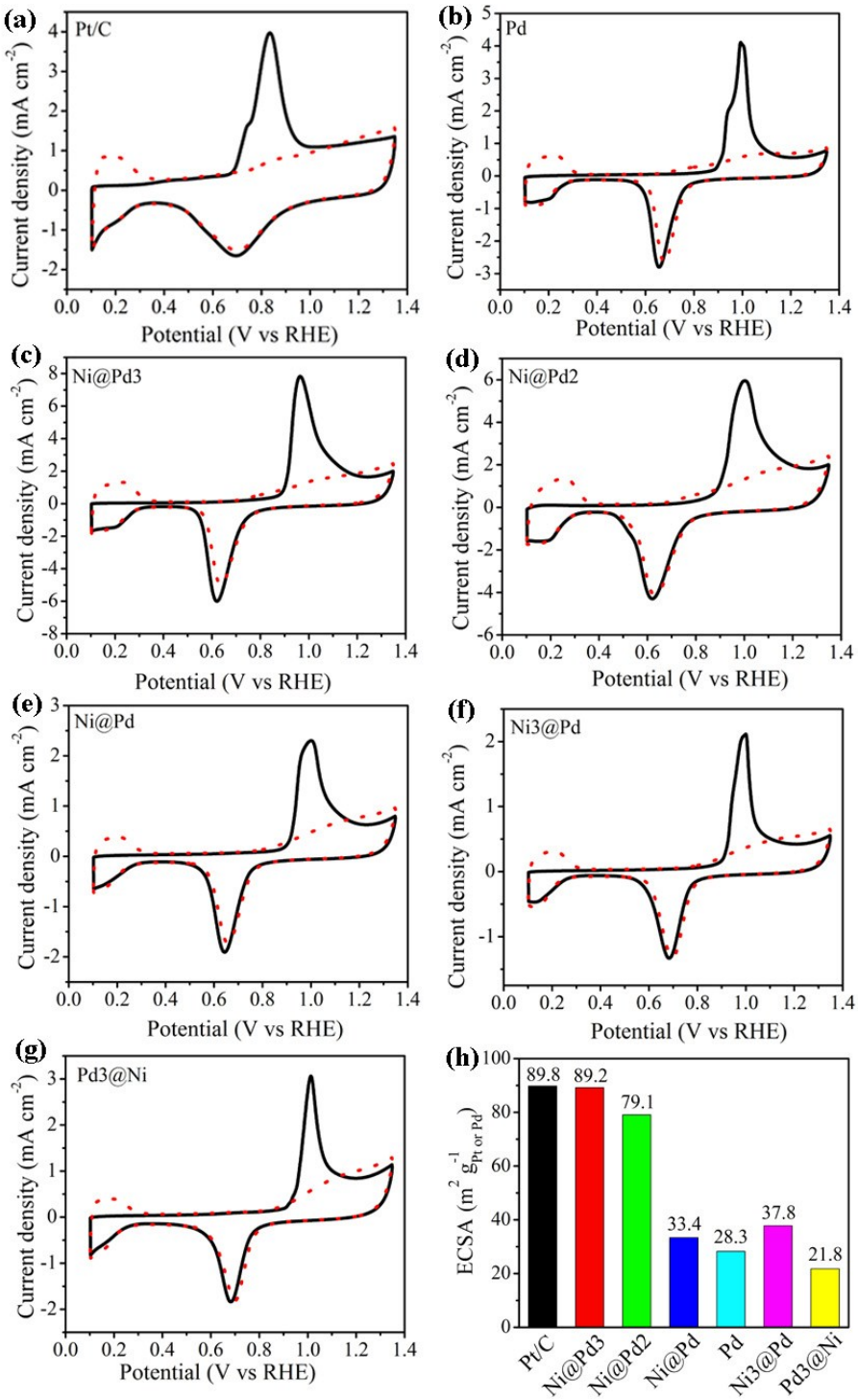

Fig. S13. (a-g) CO-stripping voltammograms of Pt/C and the as-prepared catalysts in 0.1 M $HClO_4$ solutions at a scan rate of 20 mV s^{-1} with the first cycle (black solid line) and the second cycle (red dot line), and (h) ECSA for Pt/C and the as-prepared catalysts.