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

Electronic Supplementary Material

Interfacial proton enrichment enhances proton-coupled electrocatalytic reactions

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Fig. S1 Digital photographs of $K_2PdCl_4/K_2Ni(CN)_4$ cyanogel.

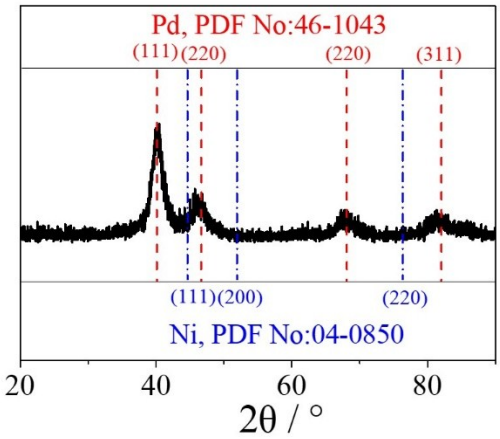

Fig. S2 XRD pattern of PdNi bimetallic nanoparticles by using mixture of K_2PdCl_4 and $NiCl_2$ as precursors.

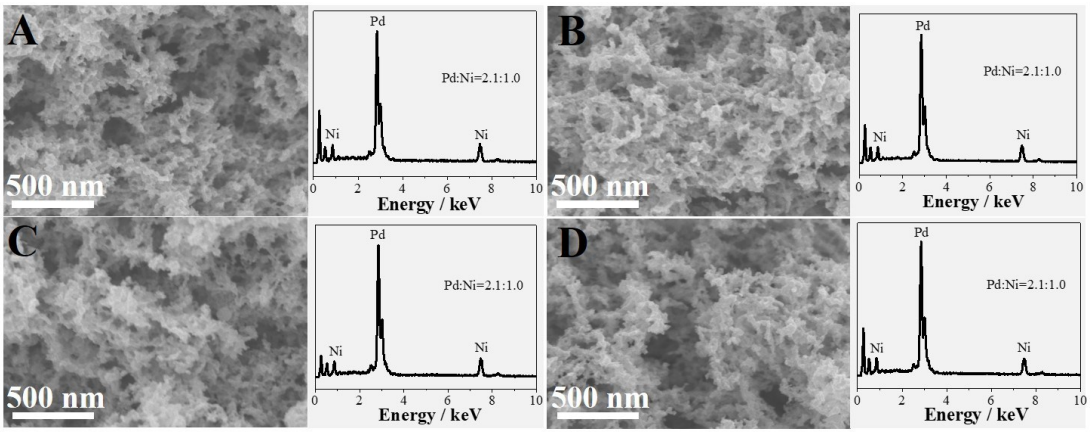

Fig. S3 SEM images and EDX spectra of (A) PdNi-ANSs, (B) PdNi-ANSs@PEI1800, (C) PdNi-ANSs@PEI10000, and (D) PdNi-ANSs@PEI70000.

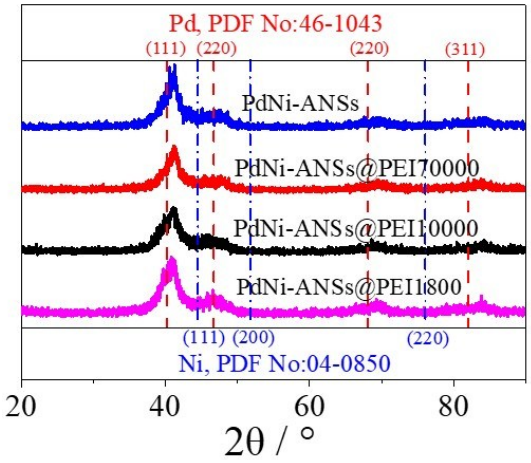

Fig. S4 XRD patterns of PdNi-ANSs without PEI, PdNi-ANSs@PEI1800, PdNi-ANSs@PEI10000, and PdNi-ANSs@PEI70000.

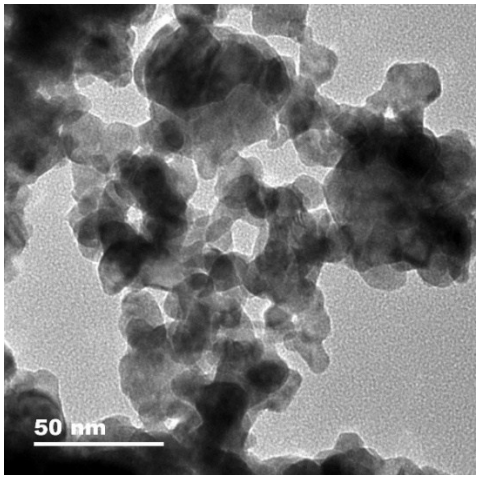

Fig. S5 TEM image of commercial Pd black.

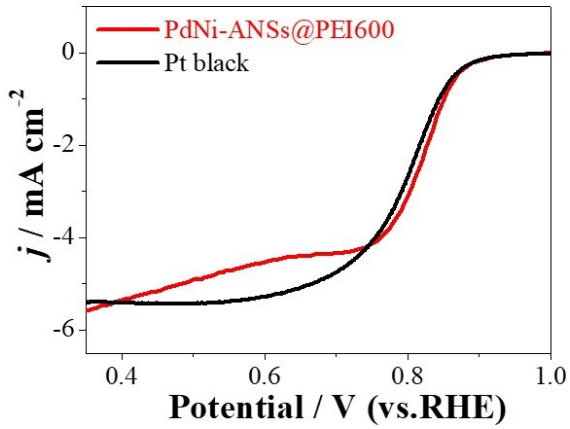

Fig. S6 ORR polarization curves of PdNi-ANSs@PEI600 and commercial Pt black in O_2-saturated 0.5 M H_2SO_4 solution at a sweep rate of 10 mV s^{-1} and a rotation rate of 1600 rpm.

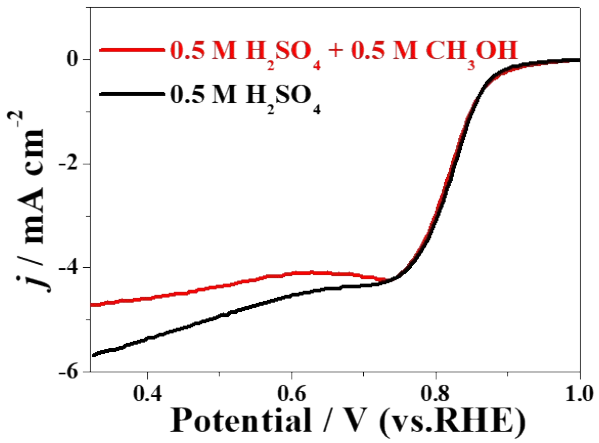

Fig. S7 ORR polarization curves of PdNi-ANSs@PEI600 in O_2-saturated 0.5 M H_2SO_4 and 0.5 M H_2SO_4 + 0.5 M CH_3OH solution at a sweep rate of 10 mV s^{-1} and a rotation rate of 1600 rpm.

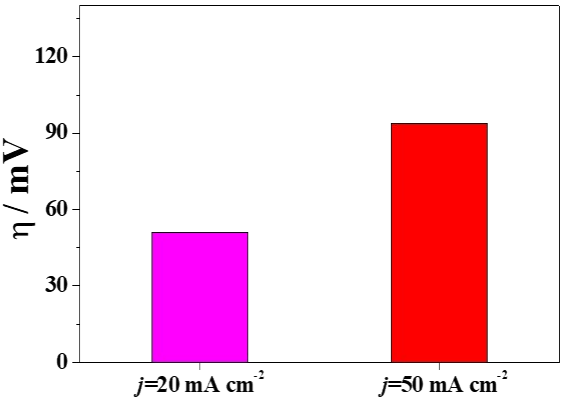

Fig. S8 Overpotentials at j=20 and 50 mA cm^{-2} for the HER on PdNi-ANSs@PEI600.

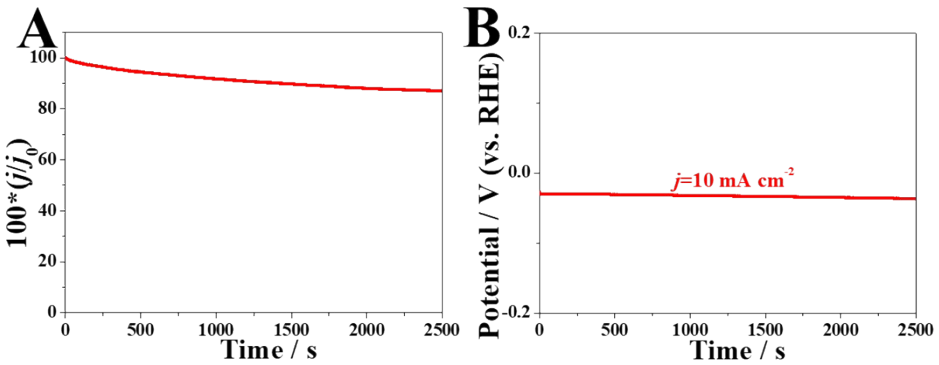

Fig. S9 (A) Chronoamperometry and (B) chronopotentiometry curves of PdNi-ANSs@PEI600 in O_2-saturated (E=0.7 V) and N_2-saturated 0.5 M H_2SO_4 (j=10 mA cm^{-2}), respectively.

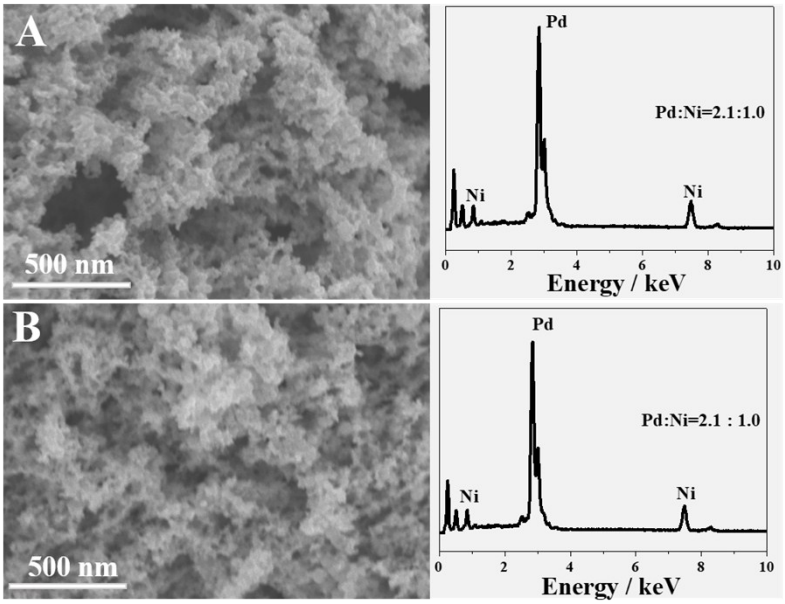

Fig. S10 SEM images and EDX spectra of PdNi-ANSs@PEI600 after the stability test for (A) ORR and (B) HER.

Table S1. HER activity of some newly reported Pd-based electrocatalysts and PdNi-ANSs@PEI600.

Catalysts	E_{onset} (mV vs. RHE)	η_{10} (mV)	Electrolyte	Ref.	Year
PdNi-ANSs@PEI600	10	25	0.5 M H_2SO_4	This work	2018
Li-$Pd_3P_2S_8$	-52	91	0.5 M H_2SO_4	1	2018
Pd-TiO_2 nanotube	-	38	1 M $HClO_4$	2	2018
Pt@Pd/rGO	-39	56	0.5 M H_2SO_4	3	2017
PdMnCo/N-Doped C	-23	39	0.5 M H_2SO_4	4	2017
PtPd/N-rich graphene	-14	58	0.5 M H_2SO_4	5	2017
$PdBi_2$	-11	78	0.5 M $HClO_4$	6	2017
CuPtPd	-1	28	0.5 M H_2SO_4	7	2017
Pd/g-CN_x	-12	55	0.5 M H_2SO_4	8	2016

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