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Supporting information

for

Hierarchical nanoporous intermetallic compounds with self-grown transition-metal hydroxides as bifunctional catalysts for alkaline hydrogen evolution reaction

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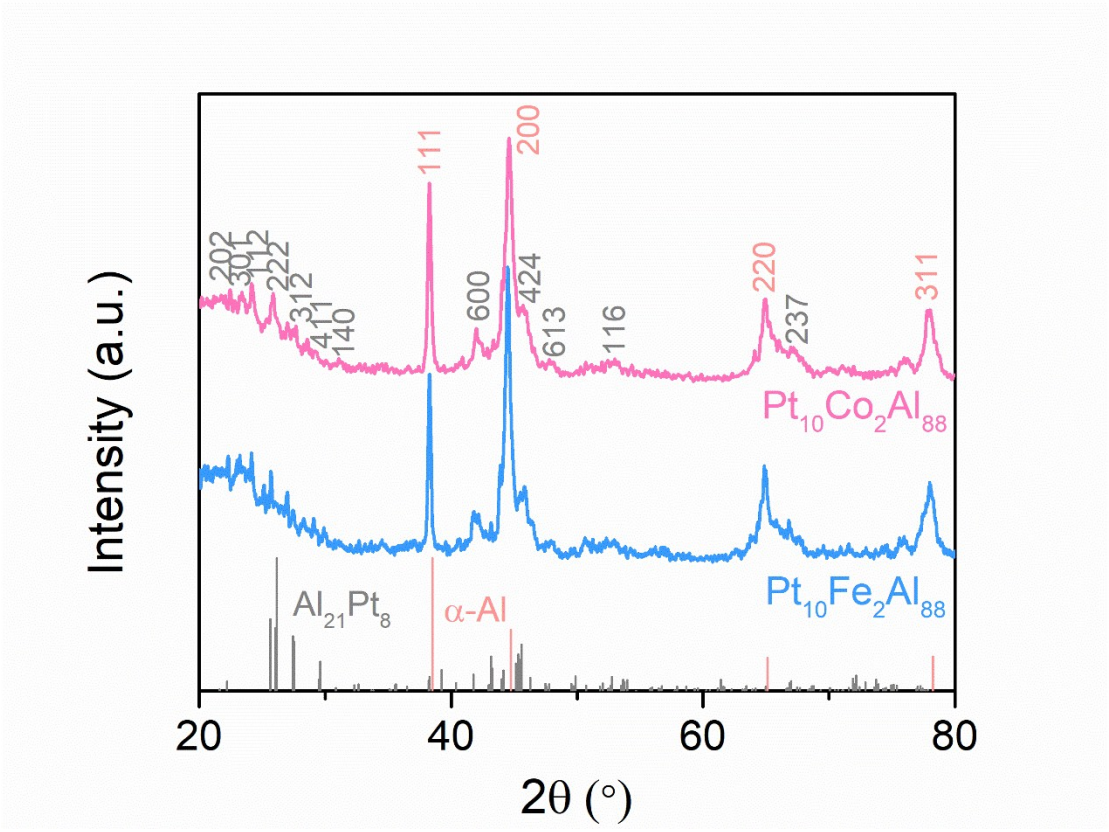

Figure S1. XRD patterns of precursor alloys of $Pt_{10}Co_2Al_{88}$ and $Pt_{10}Fe_2Al_{88}$ Size distribution of small nanopores and large channels in NP $(Pt_{1-x}Co_x)_3Al/Pt_{1-x}Co_x$.

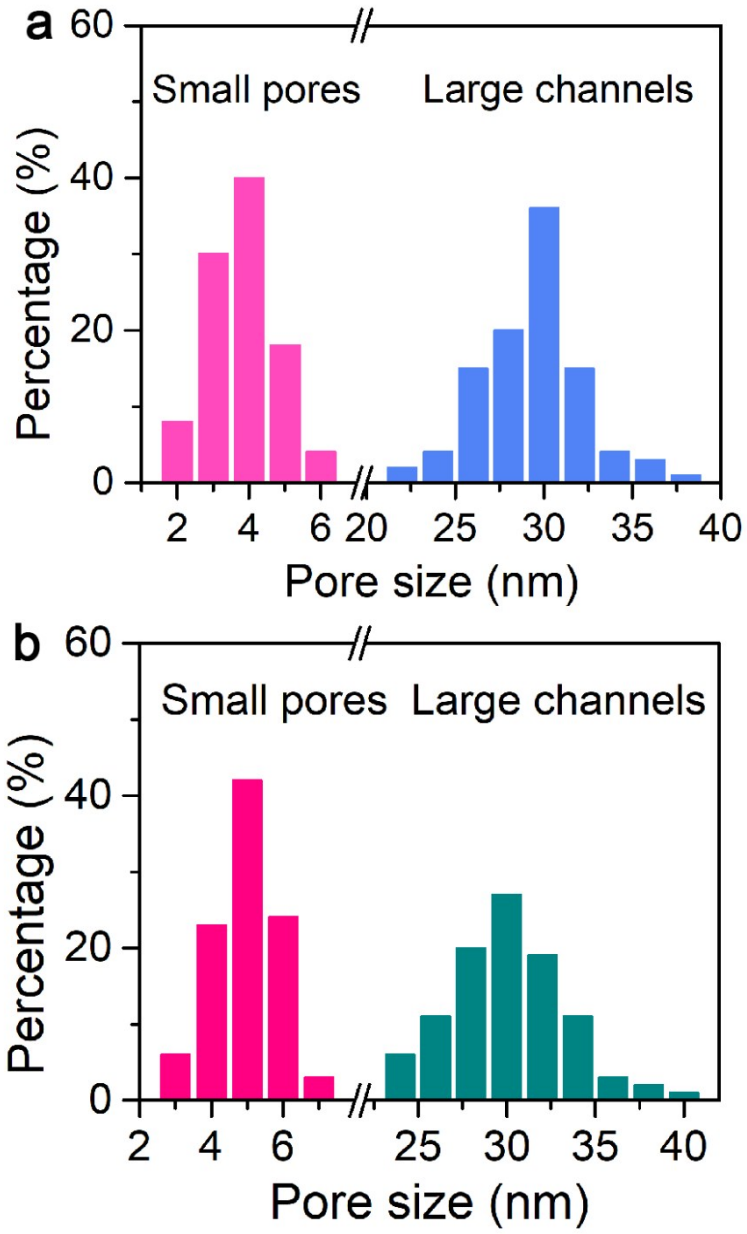

Figure S2. **a**, Size distributions of small nanopores and large channels in NP $(Pt_{1-x}Co_x)_3Al/Pt_{1-x}Co_x$. **b**, Size distributions of small nanopores and large channels in NP $(Pt_{1-x}Fe_x)_3Al/Pt_{1-x}Fe_x$.

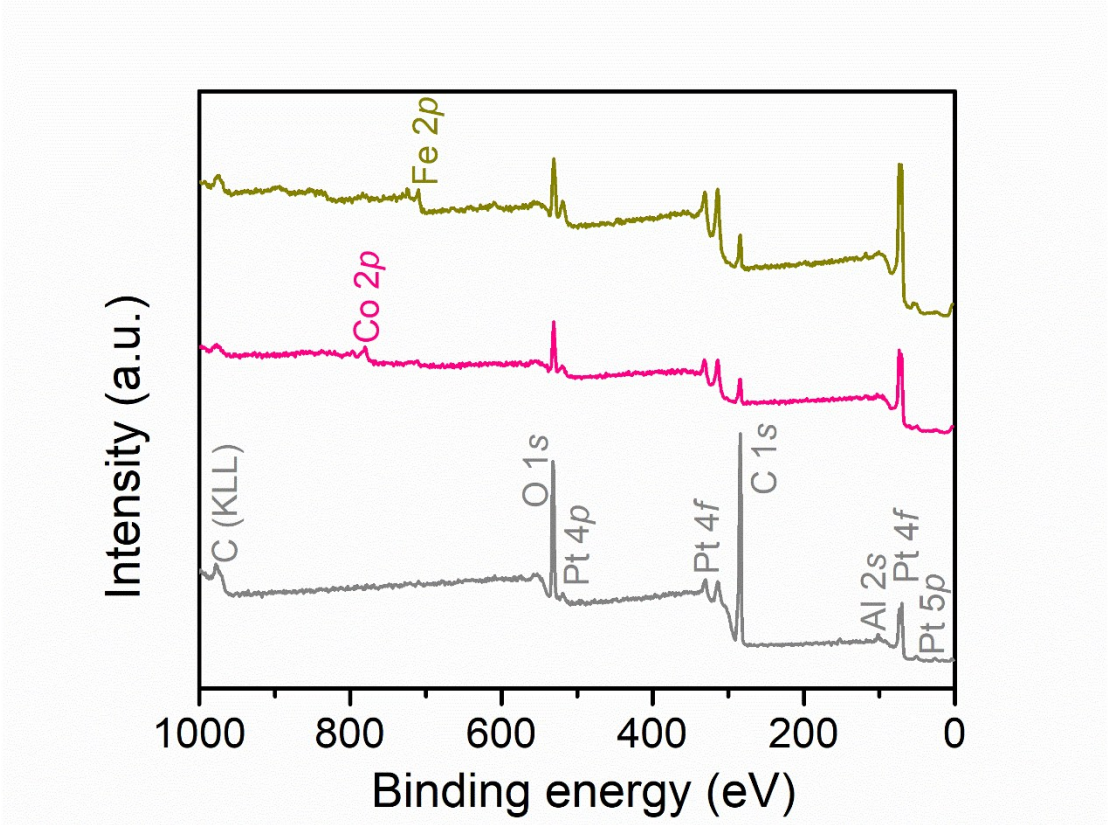

Figure S3. XPS survey for as-dealloyed NP Pt_3Al/Pt, $(Pt_{1-x}Co_x)_3Al/Pt_{1-x}Co_x$, and $(Pt_{1-x}Fe_x)_3Al/Pt_{1-x}Fe_x$.

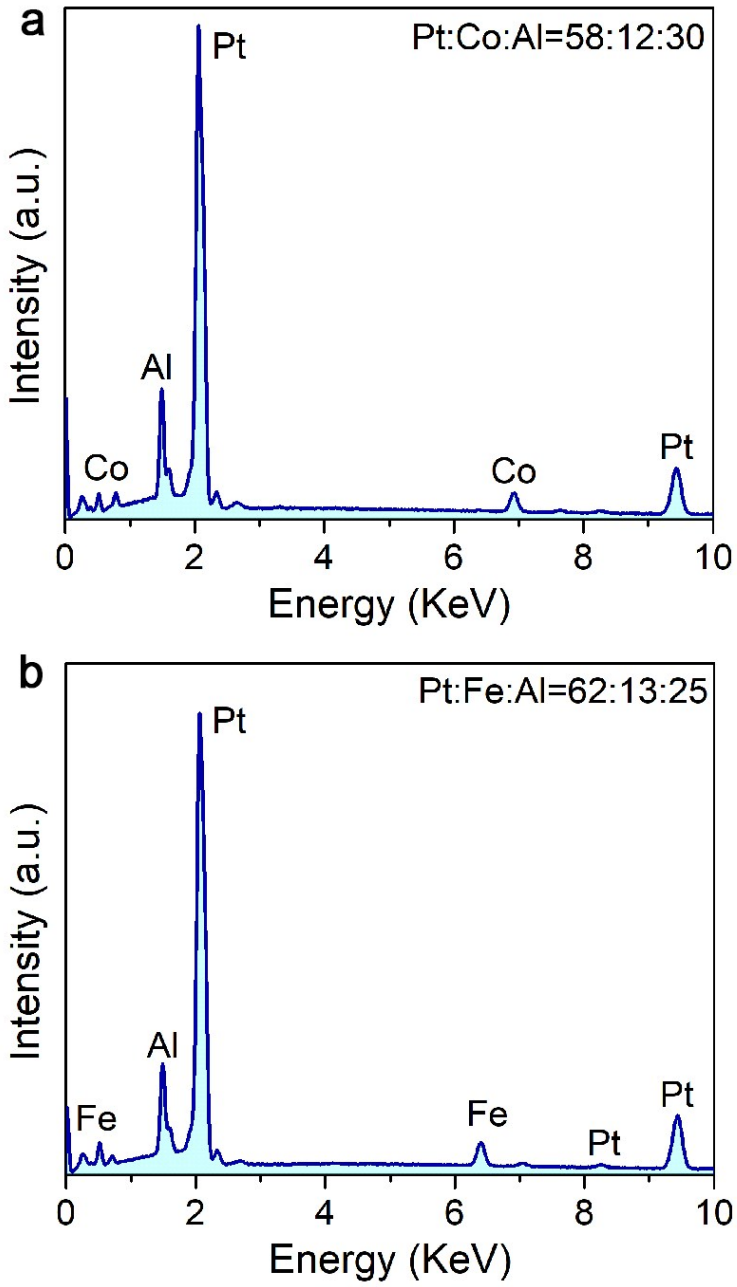

Figure S4. a, EDS spectrum of NP $(Pt_{1-x}Co_x)_3Al/Pt_{1-x}Co_x$. **b**, EDS spectrum of NP $(Pt_{1-x}Fe_x)_3Al/Pt_{1-x}Fe_x$.

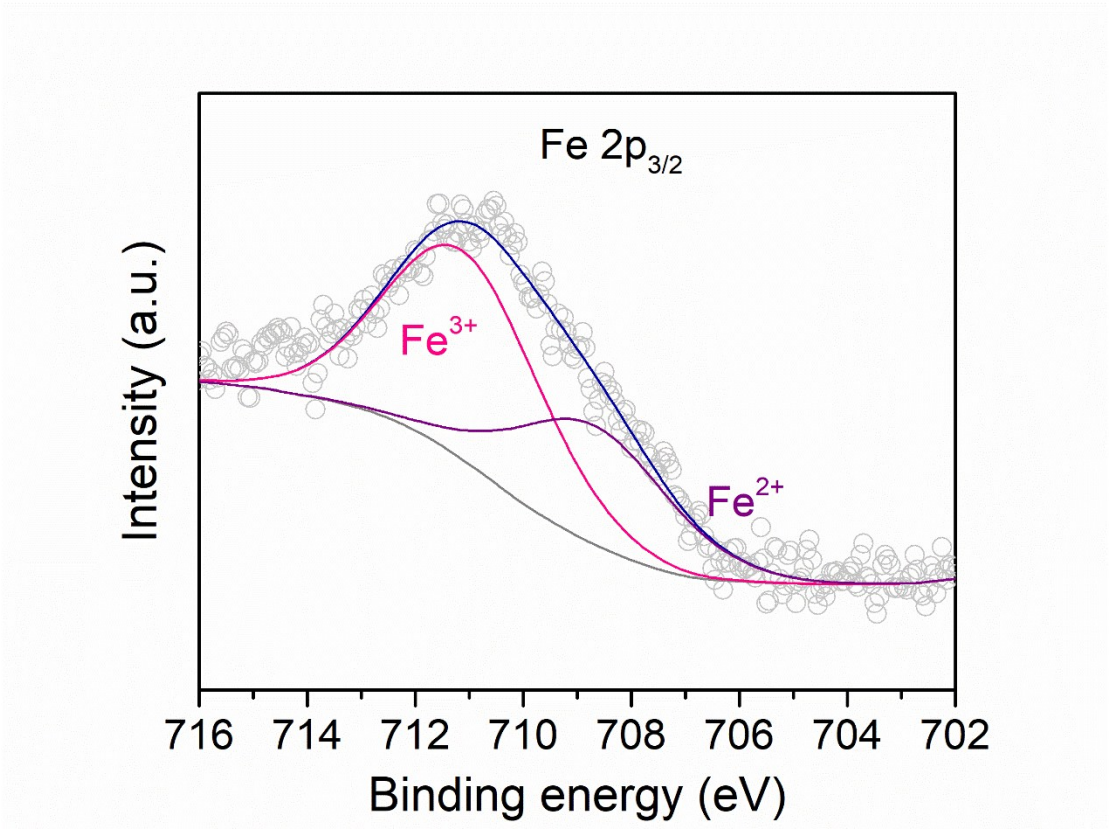

Figure S5. High-resolution XPS spectrum of Fe 2p in the as-dealloyed NP $(Pt_{1-x}Fe_x)_3Al/Pt_{1-x}Fe_x$.

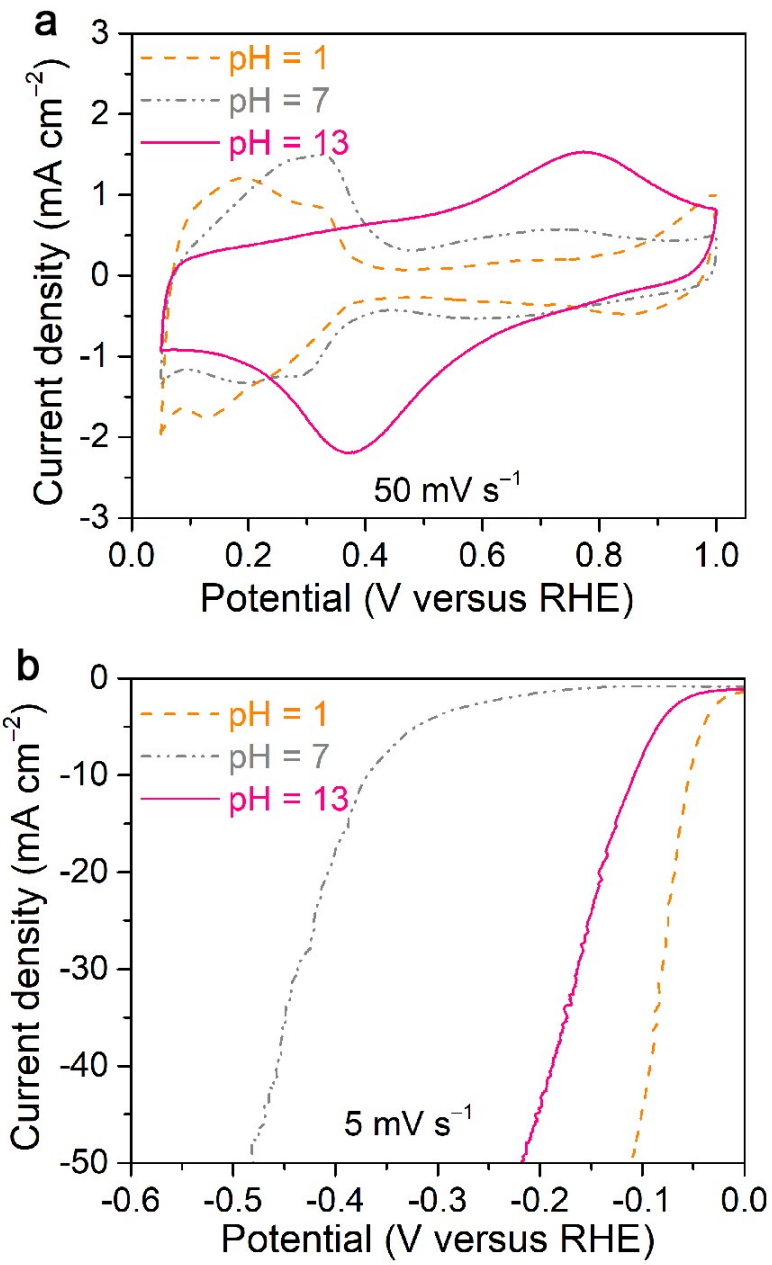

Figure S6. (a) CV curves and (b) HER polarization curves of NP $(Pt_{1-x}Fe_x)_3Al/Pt_{1-x}Fe_x$ catalyst in 0.1 M H_2SO_4 (pH = 1), 0.1 M PBS buffer solution (pH = 7) and 0.1 M KOH (pH =13). Scan rate: 50 mV s^{-1} (a) and 5 mV s^{-1} (b).

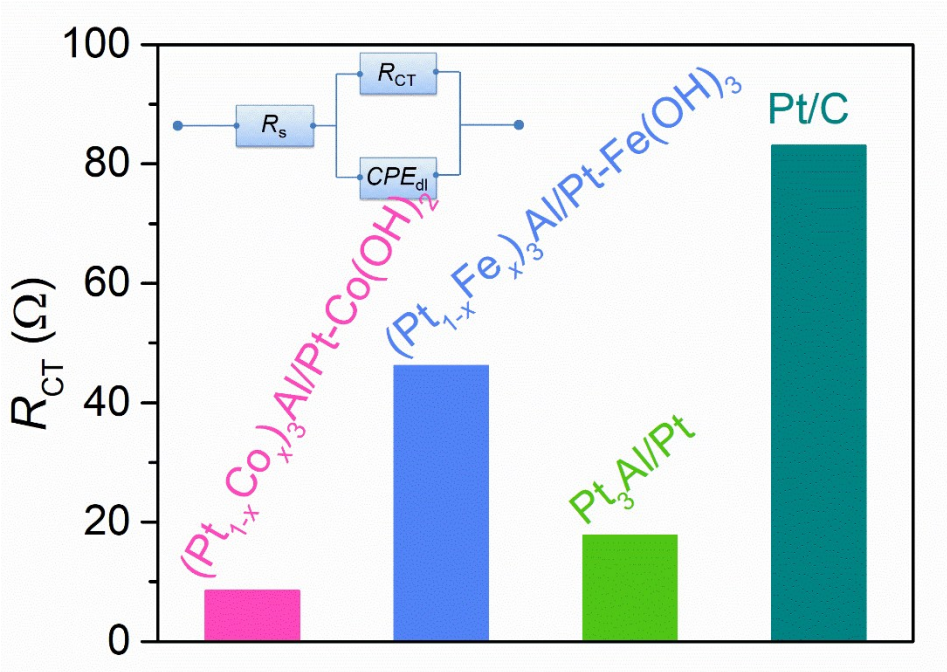

Figure S7. Charge-transfer resistance (R_{CT}) of NP $(Pt_{1-x}Co_x)_3Al/Pt\text{-}Co(OH)_2$ with the values of $(Pt_{1-x}Fe_x)_3Al/Pt\text{-}Fe(OH)_3$, Pt_3Al/Pt and Pt/C in 0.1 M KOH.

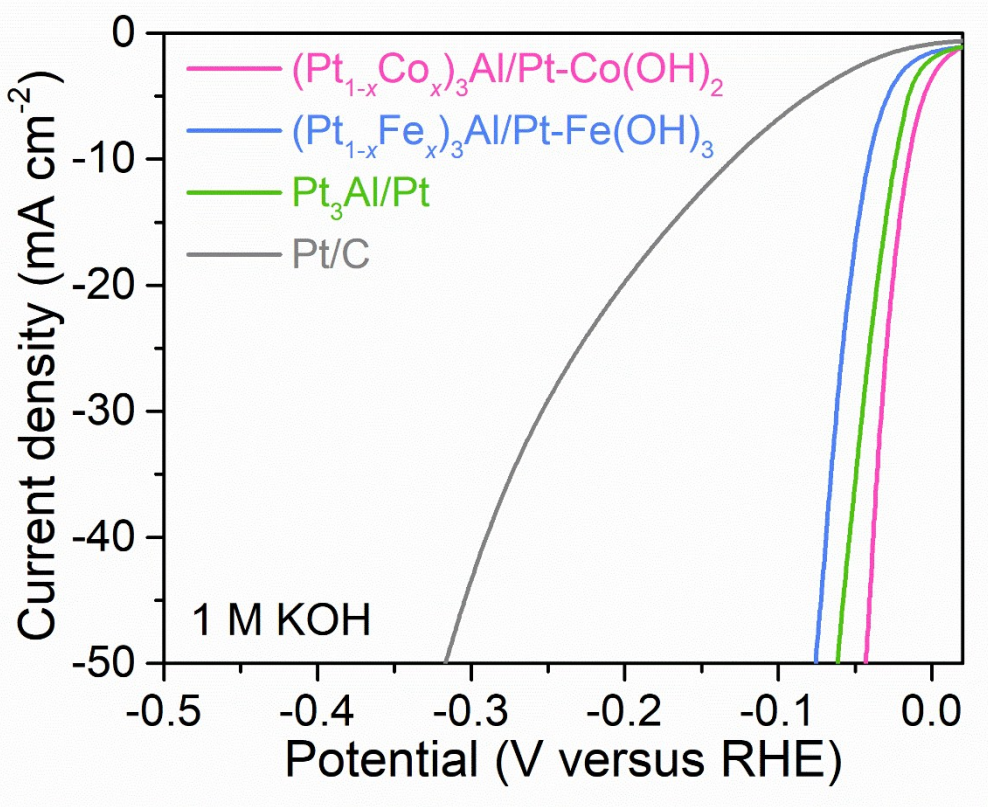

Figure S8. Typical HER polarization curves NP $(Pt_{1-x}Co_x)_3Al/Pt\text{-}Co(OH)_2$, $(Pt_{1-x}Fe_x)_3Al/Pt\text{-}Fe(OH)_3$, Pt_3Al/Pt and commercially available Pt/C catalysts in 1 M KOH solution. Scan rate: 5 mV s^{-1}.

Table S1. Comparisons of overpotential at 10 mA cm^{-2} and Tafel slopes for NP $(Pt_{1-x}Co_x)_3Al$/Pt-$Co(OH)_2$ electrodes with previously reported HER catalysts in 0.1 M/1 M KOH electrolytes.

Electrocatalysts	Overpotential (mV) at 10 mA/cm^2	Tafel slope (mV/decade)	Electrolyte	References
NP $(Pt_{1-x}Co_x)_3Al$/Pt-$Co(OH)_2$	43 15	48 34	0.1 M KOH 1 M KOH	This work
NP $(Pt_{1-x}Fe_x)_3Al$/Pt-$Fe(OH)_2$	108 43	78 36	0.1 M KOH 1 M KOH	This work
NP Pt_3Al/Pt	67 24	55 29	0.1 M KOH 1 M KOH	This work
Pt/C	160 130	138 93	0.1 M KOH 1 M KOH	This work
Pt-Ni alloy	65	74	0.1 M KOH	1
$Co(OH)_2$/Pt(111)	~248	/	0.1 M KOH	2
Pt@2D-$Ni(OH)_2$	~190	72	0.1 M KOH	3
$Ni(OH)_2$/Pt	75	/	0.1 M KOH	4
$Ni(OH)_2$/ Pt-islands/ Pt(111) surface	~138	/	0.1 M KOH	5
$Ni(OH)_2$/Pt/C	~90		0.1 M KOH	5
$Ni(OH)_2$ modified Pt surface	~75	/	0.1 M KOH	6
NiO_x/Pt_3Ni Pt_3Ni_3-NWs	~45	/	0.1 M KOH	7
Pd/$FeO_x(OH)_{2-2x}$	/	162	0.1 M KOH	8
β-$Ni(OH)_2$/Pt	92	42	0.1 M KOH	9
3%Pt/VC	~70	/	0.1 M KOH	10
Pt_3Ni frames/ $Ni(OH)_2$/C	59 (4 mA cm^{-2})	/	0.1 M KOH	11
Ru/C_3N_4/C	79	69	0.1 M KOH	12
Ru-NC-700	47	14	0.1 M KOH	13
Pt NWs/ SL-$Ni(OH)_2$	~48	/	0.1 M KOH	14
Pd-CN_x	180	150	0.5 M KOH	15
Pt-$Co(OH_)2$/CC	32	70	1 M KOH	16
Pt-Ni ASs	27.7	27	1 M KOH	17
PtCo–Co/TiM	28	35	1 M KOH	18
PtO_2– CoOOH/TM	14	39	1 M KOH	19

Pt@PCM	139	73.6	1 M KOH	20
Pt_3Ni_2-NWs-S/C	42	/	1 M KOH	21
RuCo@NC	28	31	1 M KOH	22
Ru_2P/RGO-20	13	56	1 M KOH	23
RuP_2@NPC	52	69	1 M KOH	24
Ni_3N/Pt	50	36.5	1 M KOH	25
IrP_2@NC	28	64	1 M KOH	26

Supplementary references

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