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The OH^--Driven Synthesis of Pt-Ni Nanocatalysts with Atomic Segregation for Alkaline Hydrogen Evolution Reaction

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Supporting Information

Section S1

Nernst Equation:

1. Pt-Ni Alloy

$$Ni^{2+} + 2e^{-} \Leftrightarrow Ni \quad (1)$$

$$E = E^{\theta} - \frac{RT}{nF} Ln \frac{[Ni]}{[Ni^{2+}]} \quad (2)$$

$$E^{\theta}(Ni^{2+}/Ni) = -0.257\ V$$

$$E_{Ni} = -0.263\ V$$

2. Pt-Ni Hetero

$$Ni(OH)_2 \Leftrightarrow Ni^{2+} + 2OH^{-} \quad (3)$$

$$K_{sp} = [Ni^{2+}] \cdot [OH^{-}]^2 = 5.47 \times 10^{-16}$$

$$Ni^{2+} + 2e^{-} \Leftrightarrow Ni \quad (4)$$

$$E = E^{\theta} - \frac{RT}{nF} Ln \frac{[Ni]}{[Ni^{2+}]} \quad (5)$$

$$E^{\theta}(Ni^{2+}/Ni) = -0.257\ V$$

$$E_{Ni} = -0.587\ V$$

Section S2

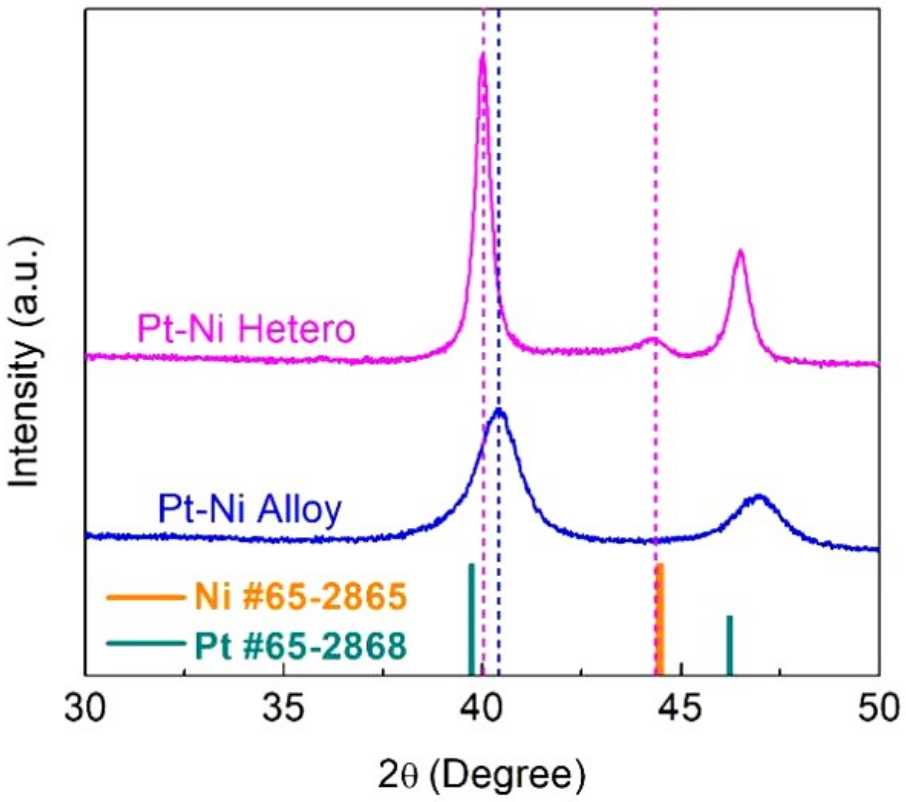

Figure S1 Magnification of the XRD patterns of Pt-Ni alloy and Pt-Ni hetero catalysts.

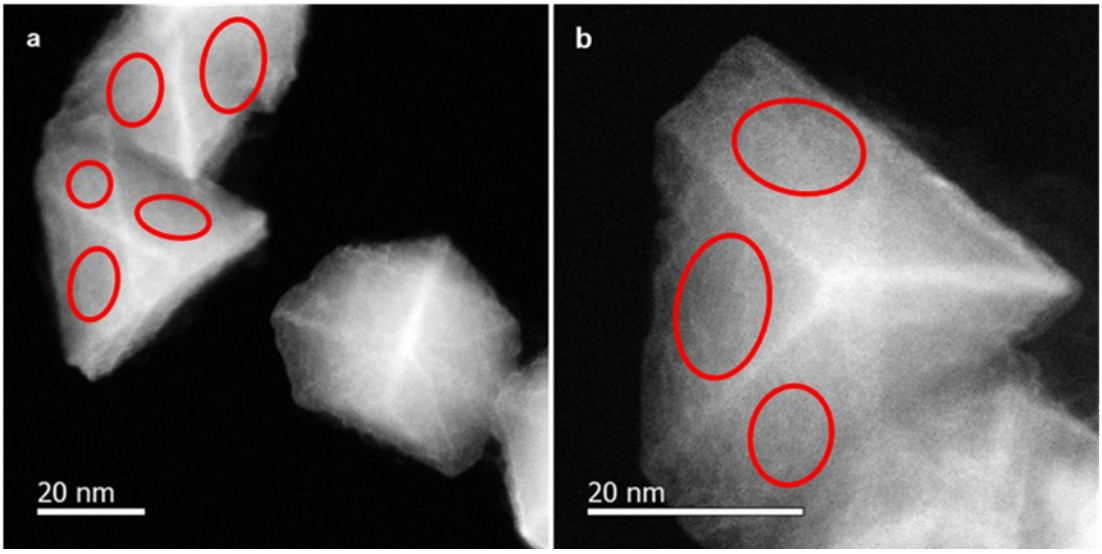

Figure S2 Aberration-Corrected-HAADF-STEM images of the Pt-Ni heterostructure.

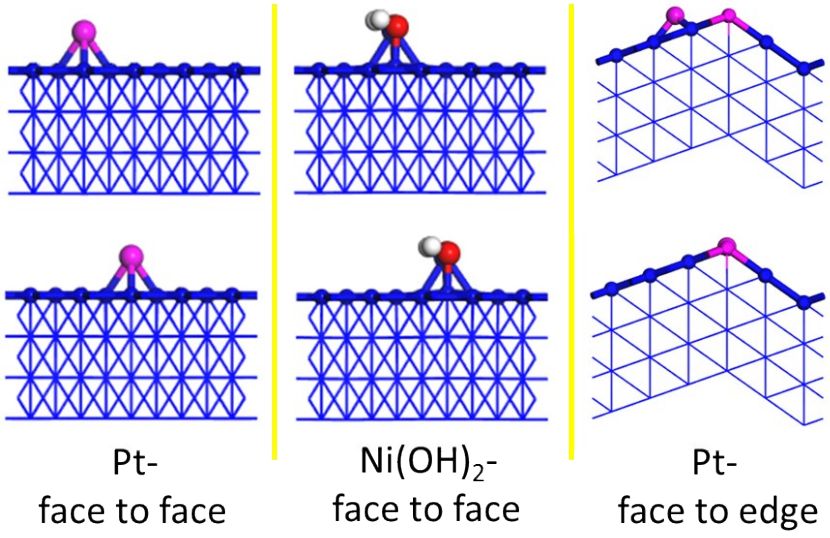

Figure S3 The side view images of the models.

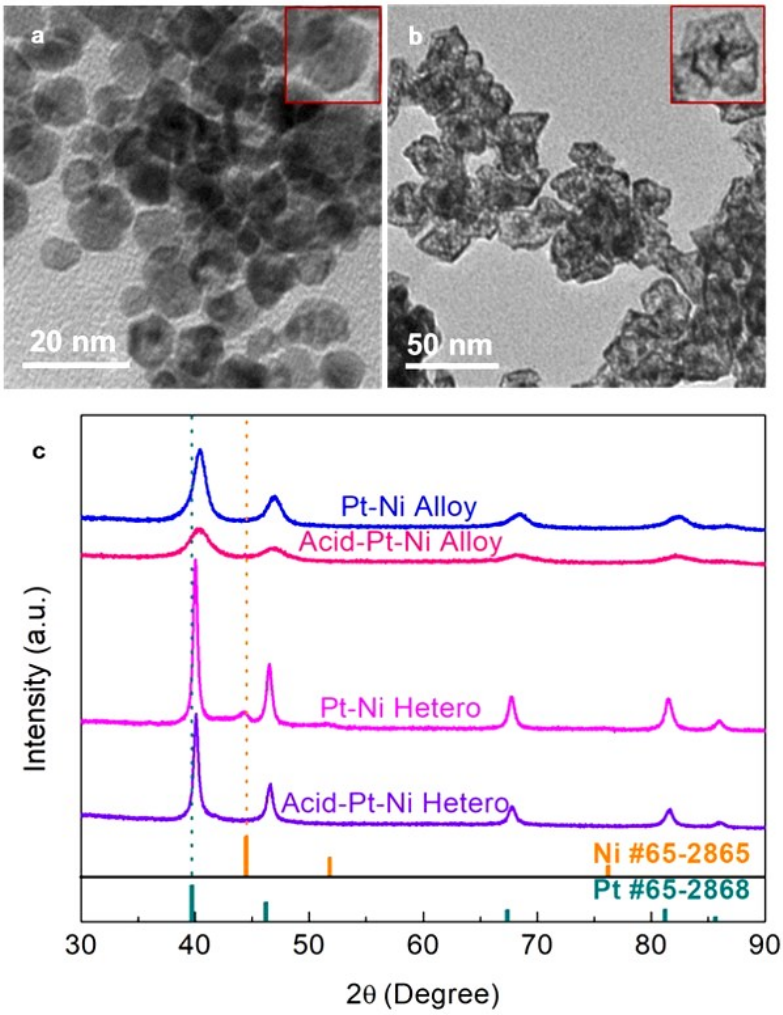

Figure S4 TEM patterns of (a) acid-Pt-Ni alloy and (b) acid-Pt-Ni hetero. (c) XRD patterns of Pt-Ni alloy, Pt-Ni hetero, acid-Pt-Ni alloy and acid-Pt-Ni hetero catalysts, respectively.

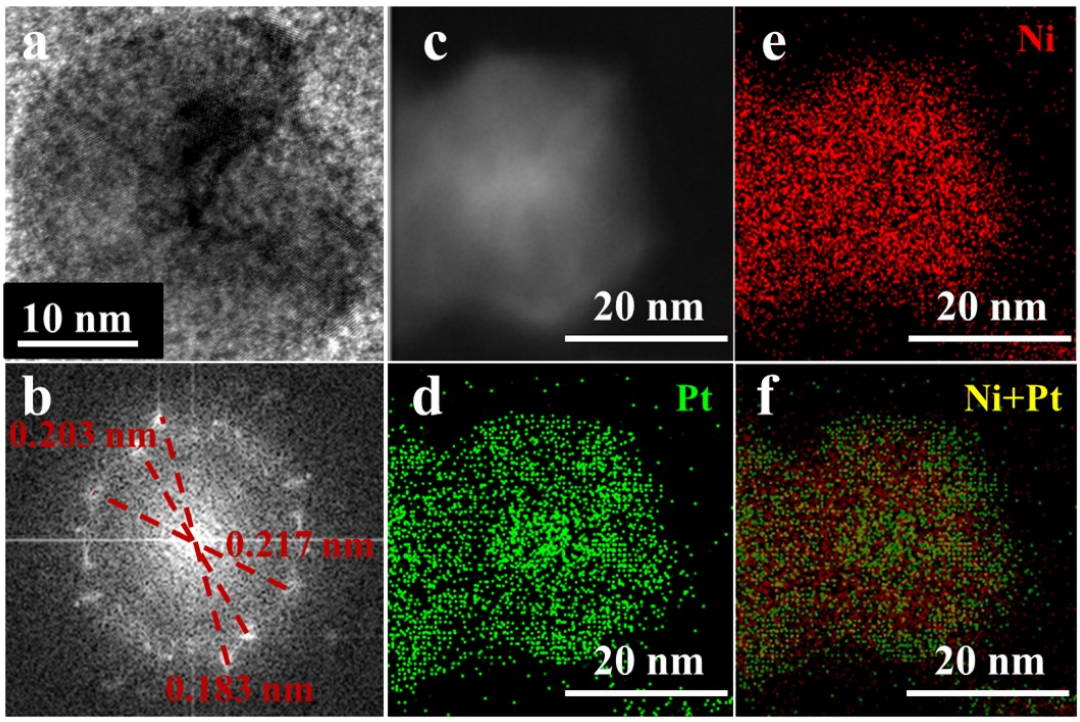

Figure S5. The structure of Ni segregated Pt-Ni after HER. (a) HRTEM image, (b) the corresponding FFT image, (c) HADDF-STEM image of the single crystal, (d) EDS-mapping of Pt species, (e) EDS-mapping of Ni species and (f) EDS-mapping of Ni and Pt species. The lattice fringes of Pt-Ni hetero are 0.183 nm, 0.217 nm and 0.203 nm, which are respectively consistent with the {200} and {111} plane of Pt-Ni, and {111} plane of Ni.

Table S1. Thermodynamic data used in the free energy of formation calculations.

	ZPE (eV)	TS (eV)
H_2O	0.56	0.67
H_2	0.27	0.41
Pt	0	0
Ni	0	0
Alloy	0	0
H^*	0.17	0.08
OH^*	0.30	0.08
$(HO\text{-}H)^*$	0.55	0.21

Table S2. Summary of the atomic ratios for Pt-Ni alloy and Pt-Ni hetero from XPS results.

Sample	Pt/Ni	Pt^{2+}/Pt	Ni^{2+}/Ni
Pt-Ni alloy	0.58/0.42	0.77/0.23	0.56/0.44
Pt-Ni hetero	0.41/0.59	0.77/0.23	0.81/0.19

Table S3. The alkaline HER activities of this work and some representative Pt-based materials recently reported.

Catalyst	Electrolyte	η (mV vs. RHE)	ECSA (m^2/g_{Pt})	Ref.
PtNi frames/$Ni(OH)_2$	0.1M KOH	~90 (10 mA cm^{-2})	None	Science, 2014[1]
Pt NWs/SL-$Ni(OH)_2$	0.1M KOH	57.8 (4 mA cm^{-2})	22.8	Nat. Commun., 2015[2]
Pt/C/20wt% SL $Ni(OH)_2$	0.1M LiOH	121 (5 mA cm^{-2})	None	ACS catal., 2015[3]
$Co(OH)_2$@PdNi HNSs/NF	1M NaOH	90 (10 mA cm^{-2})	None	Adv. Mater., 2015[4]
Pt-Ni/C	0.1M KOH	~70 (10 mA cm^{-2})	23	J. Mater. Chem. A, 2016[5]
PtCuNi/CNF@CF	1M KOH	150 (5 mA cm^{-2})	35.8	ACS Appl. Mater. Interfaces, 2016[6]
PtNi Nanohexapod	0.1 M KOH	29 (5 mA cm^{-2})	23	Nanoscale, 2016[7]
Pt_3Ni_3 NWs/C-air	0.1M KOH	~70 (5mA cm^{-2})	None	Angew. Chem. Int. Ed., 2016[8]
Ni_3N/Pt	1 M KOH	50 (10 mA cm^{-2})	None	Adv. Energy Mater., 2017[9]
Hcp-excavated Pt-Ni nano-multipods	0.1M KOH	65 (10 mA cm^{-2})	None	Nat. Commun., 2017[10]
Er-WS_2-Pt	1 M KOH	~50 (10 mA cm^{-2})	None	Adv. Mater., 2017[11]
3D PdNN	1 M KOH	110 (10 mA cm^{-2})	85.6	ACS Appl. Mater. Interfaces, 2017[12]
NiEt-OAm_6	1M NaOH	180 (10 mA cm^{-2})	None	Electrochim. Acta, 2017[13]
PtNi/CNFs	1 M KOH	82 (10 mA cm^{-2})	None	J. Mater. Sci., 2017[14]
PtCoNi FNs	0.5 M KOH	54 (10 mA cm^{-2})	~28	Int. J. Hydrogen Energy, 2017[15]
PtNi NCs	0.5 M KOH	160 (10 mA cm^{-2})	~32	Int. J. Hydrogen Energy, 2017[15]
Pt-$Co(OH)_2$/CC	1 M KOH	32 (10 mA cm^{-2})	None	ACS catal., 2017[16]
Pd-Pt-S	1 M	71 (10 mA cm^{-2})	None	ACS Appl.

	KOH			Mater. Interfaces, 2017[17]
Pt/Fe-NF	0.05 M KOH	~65 (10 mA cm^{-2})	None	Int. J. Hydrogen Energy, 2017[18]
$Au_{33}Pt_{67}$ NPs	0.1 M KOH	88 (10 mA cm^{-2})	None	Electrochim. Acta, 2018[19]
20 % Pt-C	0.1 M KOH	61 (10mA cm^{-2})	12.9	This work
Pt-Ni alloy	0.1 M KOH	82 (10mA cm^{-2})	10.5	This work
Pt-Ni hetero	0.1M KOH	48 (10mA cm^{-2})	3.9	This work

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