Supplementary Information for

Boosting the Interfacial Hydrogen Migration for Efficient Alkaline Hydrogen Evolution on Pt-Based Nanowires

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Experimental Section

Chemicals and materials

Platinum (II) acetylacetonate (Pt(acac)₂, 97%), nickel (II) acetylacetonate (Ni(acac)₂, 97%), oleyamine (OAm, >90%), cetyltrimethylammonium bromide (CTAB, >99%), and Nafion (5wt.%) were purchase from Sigma-Aldrich. Tungsten hexacarbonyl (W(CO)₆, 97%) was purchased from Alfa Aesar. 1-Octadecene (C₁₈H₃₆, >95%) was purchased from Shanghai Macklin Biochemical Co. Ltd. Glucose (C₆H₁₂O₆, 97%), Sodium Hypophosphite Monohydrate (NaH₂PO₄·H2O, >95%), ethanol (C₂H₅OH, analytical regent, >99.7%), and isopropanol (C3H8O, analytical reagent, >99.7%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The ultrapure water (18.2 MΩ/cm) used in all experiments was prepared by an ultra-pure purification system (Master-515Q, HHitech). All the chemicals were used without further purification.

Characterizations

Transmission electron microscopy (TEM) was carried out on a JEOL 2100 plus operating at 120KV with the samples deposited on carbon-coated copper TEM grids. HAADF-STEM images, EDS line file were taken on a JEOL ARM-200F microscope with spherical aberration corrector operating at 200 KV. The crystal structure and morphology were characterized by X-ray diffraction (XRD, Rigaku Miniflex-600) equipped with a Cu K α radiation ((provide the instrument) λ =0.15406 nm, 40 kV). The chemical states of Ni, Pt and P were identified by X-ray photoelectron spectroscopy (XPS) using an Escalab 250Xi equipped with an A1 Ka (1486.6 eV) excitation source. All the spectra collected were corrected using a Shirley background. Elemental analysis of PtNiP ultrathin NWs was quantitatively determined by ICP-AES with a SPECTRO BLUE SOP.

Synthesis of PtNi NWs and PtNiP-x NWs catalysts

In a typical synthesis of ultrathin nanowires, $Pt(acac)_2$ (10.0 mg), CTAB (36.0 mg), Glucose (80.0 mg), W(CO)₆ (5 mg), 4 mL OAm and 1 mL 1-Octadecene were mixed in a 30 ml reaction flask, named as solution A after adequate sonication. $Pt(acac)_2$ (5.0 mg), Ni(acac)₂ (11.3 mg) and 3 mL OAm were added in a 30 ml reaction flask, named as solution B after adequate sonication. The resulting homogeneous solution A was then placed in an oil bath at 160 °C to maintain a vigorous stir. After heating for 30 min, the solution A was naturally cooled to 80 °C, followed by the addition of solution B. The mixed solution was kept at 180 °C for 5 h. After finishing the reaction, the products were collected by centrifugation at 13,000 rpm and washed with a hexane/ethanol mixture (v/v=2/1) for two times, then dried under vacuum, obtaining PtNi NWs finally. P-doped nanowires was synthesized by loading PtNi NWs onto carbon supports (Vulcan XC-72) and then placed in a tube furnace with NaH₂PO₄·H₂O as phosphorus source. The loaded samples were heated up to 250 °C by 2 °C/min and maintained at 250 °C for 2 h with N₂ gas flowing at 25 sccm to achieve the PtNiP-x NWs, where x stood for the atomic ratio of P to Pt (P/Pt) in nanowires determined by ICP-AES.

Preparation of working electrode

To prepare the catalyst ink, 2 mg of the prepared PtNiP NWs-x (20 wt%) was mixed with 0.5 mL isopropanol, 0.495 mL ethanol and 0.005 mL Nafion (5 wt%), and sonicated for 1 h to form the homogenously ink. To avoid the influence of temperature on catalytic performance, PtNi NWs after same heat treatment in the absence phosphorus source was used as control samples. For the commercial Pt/C catalysts (20 wt% loading on Vulcan XC-72 carbon support, Johnson Mstthey), the ink solution (2 mg/ml) was prepared via a similar way. In the next step, the as-prepared catalyst inks were dropped onto the glassy carbon rotating disk electrode (GC-RDE, with geometric area of 0.196 cm²), with Pt loading amount of 3.6 µg for PtNi and PtNiP NWs catalysts, and 4 µg for commercial Pt/C, respectively (based on ICP-AES). The working electrodes were obtained after dry at room temperature for 2 h.

Electrochemical measurements.

All the electrochemical tests and HER measurements were conducted in a three-electrode system using a DH7001A electrochemical workstation (Donghua Testing Technology Co., Ltd.),

at room temperature. A Hg/HgO (1.0 M KOH) electrode was used as the reference electrode and a graphite rod was used as the counter electrode. All potentials were converted to the reversible hydrogen electrode reference. Linear sweep voltammetry (LSV) was performed in a N2-saturated 1 M KOH electrolyte with a sweep rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was evaluated with 5 mV amplitude in a frequency range from 0.1 to 100 000 Hz at varying voltages. Voltage drop of the polarization curve was manually compensated by using solution resistance determined from EIS at open circuit voltage. The electrochemical active surface area (ECSA) was calculated by integrating the hydrogen adsorption/desorption charge area between 0.05 and 0.38 V vs RHE from the cyclic voltammetry (CV) in a N₂-saturated 0.1 M HClO₄ electrolyte. The accelerated durability test was conducted by sweeping 10 000 cycles of CV in the range between -0.1 and 0.1 V vs RHE. For CO stripping measurements, CO gas (99.99%) was purged into 1 M KOH electrolyte for 30 min to obtain a CO-saturated solution. Adsorption of CO from the CO-saturated solution was carried out for 30 min at the applied potential of 0.1 V vs RHE, then the CO-adsorbed working electrode was transferred into a N₂saturated 1 M KOH electrolyte. In the following CV experiments, the sweep potential was beginning from 0.05 to 1.45 V vs RHE at a sweep rate of 50 mV s⁻¹.

DFT calculations

Spin-polarized DFT calculations were carried out by using Vienna Ab-initio Simulation Package (VASP).^[1-2] Projected augmented wave (PAW) method^[3] was used to describe the interaction between the valence electron and the ion-core. Perdew-Burke-Ernzerhof (PBE) functional with the generalized gradient approximation (GGA)^[4] was adopted to treat the electronic exchange-correlation energy. The kinetic energy cutoff was taken as 450 eV. The energy and force convergence criteria were 10⁻⁵ eV and 0.02 eV/Å, respectively. The DFT-D3 method^[5] was used to describe the dispersion effects.

The Pt (111) surface was modeled by a $p(2 \times 2)$ supercell containing four atomic layers, and the PtNi surface was obtained by replacing several Pt atoms on Pt₃Ni (111) surface with Ni. A vacuum spacing of about 15 Å was chosen to avoid the interaction between the supercell and its images along the z direction. The PtNiP surface was modeled by the PtNi surface with an adsorbed P atom in its most stable configuration (between bridge site and *hcp* hollow site). For all the optimization, the bottom two atomic layers were fixed to mimic the bulk and the remaining ions were allowed to relax with the fixed supercell size. The $(3 \times 3 \times 1)$ Monkhorst-Pack^[6] meshes were used to sample the first Brillouin zone. In addition, the projected density of states (PDOS) and d-band center were treated by the VASPKIT code.^[7]

For the minimum energy path of a chemical process, the climbing image nudged elastic band (CI-NEB) method^[8] was employed to locate the transition state (TS) between initial state (IS) and final state (TS). Five images along the reaction path were used and the spring constant was set to be -5.0 eV/Å^2 . The IS, TS, and FS were confirmed by the frequency analysis through the default frequency calculation algorithm provided by VASP.

The hydrogen adsorbed free energy ($\Delta G_{\rm H}$) was calculated following the computational hydrogen electrode model developed by Nørskov et al.^[9]: $\Delta G_{\rm H} = \Delta E_{\rm H} + \Delta E_{\rm ZPE} - T\Delta S$. In this equation, $\Delta E_{\rm H}$ is the binding energy of the H atom with respect to the free H₂ molecule. $\Delta E_{\rm ZPE}$ and ΔS are the zero-point energy and entropy differences between the adsorbed H atom and the and the gas phase, respectively, and T is the surface temperature. Due to $\Delta E_{\rm ZPE} - T\Delta S = 0.24$ eV at T = 300 K is a reasonable, well-established approximation^[10-12], the $\Delta G_{\rm H}$ can be rewritten as: $\Delta G_{\rm H} = \Delta E_{\rm H} + 0.24$ eV.

Supplementary Data



Fig. S1 Low-magnification TEM image of PtNiP-0.03 NWs.



Fig. S2 Low-magnification TEM image of PtNiP-0.81 NWs.



Fig. S3 XRD patterns of original PtNi NWs and P-doped counterparts.



Fig. S4 HADDF images of PtNiP-0.11 NWs.



Fig. S5 EDS mapping of PtNiP-0.11 NWs in another region.



Fig. S6 Low-magnification TEM image of PtNi NWs after heat treatment under N_2 atmosphere.



Fig. S7 Overpotentials at 10 mA cm⁻² of Pt/C, PtNi NWs and P-doped nanowires in N_2 -saturated 1 M KOH.



Fig. S8 HER Polarization curves of as-prepared PtNi NWs (before heat treatment) and PtNi NWs (after heat treatment under N_2 atmosphere) in 1 M KOH. The overpotential of as-prepared PtNi NWs and PtNi NWs at 10 mA cm⁻² is 32 mV and 24 mV respectively.



Fig. S9 Exchange current density of Pt/C, PtNi NWs and P-doped nanowires in N₂-saturated 1 M KOH.



Fig. S10 Mass activity of Pt/C, PtNi NWs and P-doped counterparts as a function of applied potentials.



Fig. S11 Specific activity of Pt/C, PtNi NWs and P-doped counterparts as a function of applied potentials.



Fig. S12 Low-magnification TEM images of PtNiP-0.11 NWs after durability test via 10000 CV cycles between -0.1 V and 0.1 V vs RHE.



Fig. S13 CV (a) and HER polarization curves (b) of PtNiP-0.11 NWs before or after etching in acid.



Fig. S14 Theoretical calculation models of Pt slab (a and d), PtNi slab (b and e) and PtNiP slab (c and f). (a)-(c) top view, (d)-(f) side view. Dark blue, Pt. Cyan, Ni. Purple, P.



Fig. S15 The optimized water dissociation configurations on Pt. IS, initial state. TS, transition state. FS, final state. Dark blue, Pt. Red, O. Light brown, H. Only the top layer of slab is shown for clear observation.



Fig. S16 The optimized water dissociation configurations on PtNi. IS, initial state. TS, transition state. FS, final state. Dark blue, Pt. Cyan, Ni. Red, O. Light brown, H. Only the top layer of slab is shown for clear observation.



Fig. S17 The optimized water dissociation configurations on PtNiP. IS, initial state. TS, transition state. FS, final state. Dark blue, Pt. Cyan, Ni. Purple, P. Red, O. Light brown, H. Only the top layer of slab is shown for clear observation.



Fig. S18 The optimized hydrogen migration configurations on PtNi. IS, initial state. TS, transition state. FS, final state. Dark blue, Pt. Cyan, Ni. Red, O. Light brown, H. Only the top layer of slab is shown for clear observation.



Fig. S19 The optimized hydrogen migration configurations on PtNiP. IS, initial state. TS, transition state. FS, final state. Dark blue, Pt. Cyan, Ni. Purple, P. Red, O. Light brown, H. Only the top layer of slab is shown for clear observation.



Fig. S20 The optimized hydrogen migration configurations on PtNi in the presence of adsorbed OH⁻. IS, initial state. TS, transition state. FS, final state. Dark blue, Pt. Cyan, Ni. Red, O. Light brown, H. Only the top layer of slab is shown for clear observation.



Fig. S21 The optimized hydrogen migration configurations on PtNiP in the presence of adsorbed OH⁻. IS, initial state. TS, transition state. FS, final state. Dark blue, Pt. Cyan, Ni. Purple, P. Red, O. Light brown, H. Only the top layer of slab is shown for clear observation.



Fig. S22 CO-stripping curves of Pt/C, PtNi NWs and P-doped counterparts in 1 M KOH.



Fig. S23 The charge density difference of H_2O adsorbed on Pt slab, PtNi slab and PtNiP slab. The bottom parts present the corresponding O-H bond lengths of H_2O molecule in each model.



Fig. S24 Calculated energy barriers of hydrogen migration across Pt-Ni interface on PtNi and PtNiP slabs in the presence of OH⁻. IS, initial state. FS, final state.



Fig. S25 Nyquist plots of Pt/C at varying overpotentials. The lower plots are corresponding zoom-in parts.



Fig. S26 Nyquist plots of PtNi NWs at varying overpotentials. The lower plots are corresponding zoom-in parts.



Fig. S27 Nyquist plots of PtNiP-0.11 NWs at varying overpotentials. The lower plots are corresponding zoom-in parts.



Fig. S28 The equivalent circuit for the simulation of Nyquist plots.



Fig S29. The CV curves of Pt/C and PtNi NWs at different scan rate.

Samples	Pt	Ni	Р	P/Pt ratio
as-prepared PtNi NWs	34.6%	65.4%	0	0
PtNi NWs	47.5%	52.5%	0	0
PtNiP-0.03 NWs	50.3%	48.2%	1.5%	0.03
PtNiP-0.11 NWs	43.1%	52.2%	4.7%	0.11
PtNiP-0.81 NWs	36.6%	33.6%	29.8%	0.81

Table S1. The atomic percentage of PtNi NWs and P-doped counterparts based ICP-AES.

Table	S2.	Comparison	of	the	HER	activity	for	PtNiP-0.11	NWs	with	other	reported
electro	catal	ysts in alkaline	e me	ediun	n (corre	esponding	g to F	Fig. 3f).				

Catalysts	Loading (µg)	η ₁₀ (mV)	Tafel slope (mV dec ⁻¹)	Reference
PtNiP-0.11 NWs	3.6	12	26.6	This work
(Ru-N)@Pt	/	15	25	[13]
Pt-Te ₂ -600	31.8	22	29.9	[14]
Pt-Ni(N)	11	25	29	[15]
Dr-Pt	/	26	52	[16]
PtNi ₅ -0.3	2	26.8	19.2	[17]
20%Pt-Ni(HCO ₃) ₂	8	27	52	[18]
Pt-Ni ASs	1.2	27.7	27	[19]
Pt-Ni ASs/C	0.39	28	47	[20]
Pt-NiO@Ni/NF	/	34	39	[21]
Pt/NiRu-OH	16	38	39	[22]
Pt/MMC	1.59	45	30	[23]
SA In-Pt NWS/C	2.5	46	32.4	[24]
MoC1-X/Pt-600-NPs	12	67	64	[25]
Ru-Mo ₂ C@CNT	/	15	26	[26]
Ru/np-MoS2	/	30	31	[27]
NiRu _{0.13} -BDC	/	34	32	[28]
2DPC-RuMo NSs	/	18	25	[29]
RuCo NSs	/	26	26.3	[30]
2.2wt% Ru SAs-Ni ₂ P	/	57	71	[31]

Catalysts	Loading (µg)	MA (A mg ⁻¹ _{Pt})	η (mV)	Reference	
PtNiP-0.11 NWs	3.6	5.79	70	This work	
PtNiP-0.11 NWs	3.6	6.91	80	This work	
PtNiP-0.11 NWs	3.6	8.14	90	This work	
PtNiP-0.11 NWs	3.6	9.58	100	This work	
Dr-Pt	/	1.16	50	[16]	
20%Pt-Ni(HCO ₃) ₂	8	1.77	100	[18]	
Pt/NiRu-OH	16	2.08	77	[22]	
Pt/MMC	1.59	2.16	80	[23]	
PtNi ₅ -0.3	2	2.36	70	[17]	
Pt-Ni ASs	1.2	2.80	70	[19]	
Pt-Ni NTAs	/	4.27	50	[32]	
Pt ₄ /Co	44	5.10	80	[33]	

Table S3. Comparison of the HER mass activity for PtNiP-0.11 NWs with other reported electrocatalysts in alkaline medium (corresponding to Fig. 3g).

	Potential (mV)	$R_{s}\left(\Omega ight)$	T (F s ⁿ⁻¹)	n 1	$R_{CT}(\Omega)$	Сф (F)	$R_H(\Omega)$
Pt/C	0	6.028	0.0016	0.79	116.2	0.0004	117.7
	-10	5.925	0.0016	0.78	29.87	0.0001	121.8
	-20	5.849	0.0015	0.79	13.01	0.0001	98.37
	-30	5.772	0.0013	0.8	11.57	0.0001	71.37
	-40	5.768	0.0012	0.81	11.11	0.0001	54.31
	-50	5.751	0.0011	0.82	10.62	0.0001	41.95
	-60	5.759	0.001	0.83	12.69	0.0002	32.46
	-70	5.769	0.0009	0.85	12.46	0.0002	25.49
	-80	5.741	0.0009	0.85	13.99	0.0002	18.64
PtNi NWs	0	5.766	0.0016	0.7	6.385	0.0004	120.3
	-10	5.772	0.0031	0.64	9.227	0.0004	48.1
	-20	5.746	0.0042	0.63	16.27	0.0012	13
	-30	5.667	0.0049	0.59	13.11	0.0048	5.77
	-40	5.664	0.0038	0.62	8.276	0.0092	3.257
	-50	5.716	0.003	0.65	6.524	0.0124	2.187
	-60	5.764	0.0018	0.71	5	0.0095	1.537
	-70	5.772	0.0015	0.73	4.427	0.0085	1.105
	-80	5.79	0.0014	0.74	4.024	0.0089	0.78
PtNiP-0.11 NWs	0	6.002	0.0034	0.73	29.86	0.0052	23.45
	-10	5.868	0.0045	0.68	12.09	0.0178	0.11
	-20	5.857	0.0045	0.68	11.91	0.0368	E-7
	-30	5.8	0.0033	0.69	4.63	0.031	~0

Table S4. The fitted parameters of the EIS data of various catalysts under HER conditions.

-40	5.746	0.0035	0.66	3.68	0.022	~0
-50	5.737	0.0034	0.66	3.201	0.02	~0
-60	5.704	0.0039	0.63	2.889	0.021	~0
-70	5.74	0.0041	0.62	2.905	0.018	~0
-80	5.305	0.0108	0.44	3.319	0.023	~0

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