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H₂ In-situ Inducing Strategy on Pt Surface Segregation over Low Pt
Doped PtNi₅ Nanoalloy with Superhigh Alkaline HER Activity

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Abstract: Surface segregation constitutes an efficient approach to enhance the alkaline hydrogen evolution reaction (HER) activity of the bimetallic Pt_xNi_y nanoalloys. Herein, we propose a new strategy by utilizing the small gas molecule of H_2 as the structure directing agent (SDA) to in-situ induce Pt surface segregations over a series of PtNi_{5-n} samples with extremely low Pt dopings ($\text{Pt/Ni} = 0.2$). Impressively, the sample of $\text{PtNi}_{5-0.3}$ synthesized under 0.3 MPa H_2 delivers an unprecedentedly low overpotential of 12.8 mV (-10 mA cm^{-2}) and Tafel slop of 14.1 mV dec^{-1} , which is superior than most of previously reported Pt_xNi_y electrocatalyst. This is closely related to the strong in-situ inducing effect of H_2 (0.3 MPa) leading to an obvious Pt-rich@Ni-rich core-shell nanostructure which can efficiently reduce the reaction Gibbs free energies. Finally, the specific mechanistic effects of H_2 during PtNi_{5-n} synthesis process are well illustrated based on the combined experimental and theoretical studies.

Keywords: PtNi_5 nanoalloy, H_2 structure directing agent (SDA), Pt surface segregation, alkaline hydrogen evolution reaction (alkaline-HER), DFT calculation

Electrochemical water splitting to produce hydrogen has drawn great attentions to reduce the reliance on fossil fuels for the human beings, owing to the massive resources of the water as well as the negligible greenhouse gas emissions of the reaction.¹⁻³ However, the development of energy production system based on hydrogen evolution reaction (HER) is currently limited by either high cost or low efficiency of the electrode catalyst.⁴ For example, although the platinum (Pt) is widely accepted as the best HER catalyst in acid medium, the high cost greatly hinders its wide applications; additionally, as for the alkaline-HER the Pt however shows low reaction efficiency due to the sluggish activity in the Volmer step ($\text{H}_2\text{O} + * + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$).^{5,6}

To overcome these problems, considerable efforts have been devoted to making the Pt electrocatalysts being less costly but more efficient, especially for the scenario of the alkaline-HER due to its relatively mild reaction condition which allows the non-Pt group metals being incorporated into the Pt electrocatalyst to lower its cost and simultaneously enhance its alkaline-HER activity.⁷⁻⁹ Typically, the surface segregation has been reported to be an efficient approach to synthesize highly active Pt-based bimetallic nanoalloy electrocatalysts for the alkaline-HER.¹⁰⁻¹² Large amounts of works have been recently focused on the synthesis of the surface segregated Pt_xNi_y bimetallic nanoalloys, due to the excellent water splitting activity of the dopant Ni in Volmer step.¹³⁻¹⁶ For example, Cao et al.¹⁴ fabricated one type of PtNi nanoalloy with a Pt-rich@Ni-rich core-shell nanostructure, which achieved much higher activity than that of the commercial Pt/C by displaying an overpotential of 104 mV (10 mA cm^{-2}) and Tafel slope of 73 mV dec^{-1} . Zhang et al.¹⁵ reported one type lotus-thalamus-shaped PtNi nanoalloy with a Pt-rich surface, which exhibited an even lower overpotential of 27.7 mV (10 mA cm^{-2}) and Tafel slope of 27 mV dec^{-1} .

Various types of approaches have been reported to realize the surface segregations.¹⁶⁻²³ For example, based on the chemical leaching or deposition techniques, the Pt-rich trimetallic surface,¹⁶ Pt-Rich_{core}/Sn-Rich_{subsurface}/Pt_{skin} nanocubes,¹⁷ Pt-skin on AuCu,¹⁸ or multilayered

Pt-skin surfaces catalyst¹⁹ can be formed. Additionally, employing the thermal annealing approach,²⁰ the Ni-segregated surface can be produced over the PtNi nanoalloy under a vacuum condition; while the Pt-rich surface can be evolved after the CO post-treatment due to the stronger binding energy of CO to Pt. Similarly, taking the advantage of the strong interaction of H₂ with Pt, the Pt segregated Pt-M (M = Au,²¹ Ni,²² Co²³) bimetallic nanoalloys were successfully synthesized after the post treatment by H₂.

Inspired by the above literature reports as well as the basic design principle of enhancing the Pt utilization efficiency, herein we propose a simple one-pot synthesis strategy by simultaneously introducing the H₂ into the synthesis system of PtNi₅, which possesses an extremely low Pt/Ni mole ratio of 0.2, to in-situ induce Pt surface segregation for the alkaline HER. Following this idea, a range of PtNi_{5-n} (n = 0, 0.1, 0.3, 0.5, 0.7 MPa, representing the H₂ pressure) nanoalloys were successfully synthesized. Among them, the PtNi_{5-0.3} delivering an unprecedentedly low overpotential of 12.8 mV (10 mA cm⁻², 1 M KOH) and Tafel slope of 14.1 mV dec⁻¹ reaches a record-high alkaline HER activity relative to the previously reported alkaline-HER electrocatalysts (See Supplementary Fig. S1 and Tables S1). Deep mechanistic insights into the H₂ in-situ induced Pt segregation as well as the structure-activity relationship of the PtNi_{5-n} were well illustrated based on the combined experimental (H₂-assisted metal precursor reduction kinetics) and theoretical [density function theory (DFT) simulations] approaches. Finally, we would like to emphasize that the developed H₂ in-situ inducing surface segregation strategy is simple (one-pot synthesis without tedious post treatment), environmentally friendly (H₂ as the SDA) and what is most important is efficient to synthesize highly active and economical PtNi₅ nanoalloy as a promising candidate for the industrial application.

Results

Physiochemical Characterizations of PtNi_{5-n}. Fig. 1a displays the X-ray diffraction (XRD) patterns of the as-synthesized samples PtNi_{5-n}. As can be seen, all the samples exhibit the

characteristic diffraction patterns of the face centered cubic (fcc) structure type; and the PtNi nanoalloys can be verified to be formed according to the diffraction patterns of the pure Pt fcc (ICSD 04-0802) and Ni fcc (ICSD 04-0850). Specifically, only the diffraction patterns belonging to the Ni-rich phase PtNi nanoalloy ($2\theta = \sim 43.7, 50.7$ and 74.5°) can be observed for the sample of PtNi₅-0; while an additional diffraction pattern belonging to the Pt-rich phase PtNi nanoalloy ($2\theta = \sim 40.5 - 42.1^\circ$) is evolved for the samples of PtNi₅-n ($n = 0.1, 0.3, 0.5$ and 0.7 MPa),²⁴ which verifies the strong in-situ inducing effect of H₂ on Pt surface segregations, especially for the scenario of P_{H_2} of 0.3 MPa displaying the strongest peak intensity at 2θ of $\sim 40.8^\circ$. Moreover, the specific ratios of the Pt and Ni in Pt-rich and Ni-rich phases of the PtNi₅-n were further predicted based on the Vegard's rule,²⁵ as shown in Fig. 1b (or see Supplementary Table S2). Obviously, the PtNi₅-0.3 possesses the highest Pt ratio of 79% over the Pt-rich phase nanoalloys, quantitatively confirming the strongest Pt segregation effect of H₂ of 0.3 MPa.

Fig. 1| Nanocrystal structure of the synthesized PtNi₅-n ($n = 0, 0.1, 0.3, 0.5$ and 0.7 MPa).

a, XRD diffraction patterns of the PtNi₅-n. **b**, Predicted elemental (Pt and Ni) ratios in Pt-rich (red and green) and Ni-rich (blue and gray) phases of PtNi₅-n based on the Vegard's rule and the XRD results.

Fig. 2| Structural morphologies and surface elemental distributions of PtNi₅-n (n = 0, 0.3 and 0.5 MPa). **a-c**, Cs-corrected HAADF-STEM images of PtNi₅-0 (**a**), PtNi₅-0.3 (**b**) and PtNi₅-0.5 (**c**). **d-f**, EDS mapping results of PtNi₅-0 (**d**), PtNi₅-0.3 (**e**) and PtNi₅-0.5 (**f**). Insert images in panels (**a-c**) represent the statistics of nanoparticle size distributions; and the insert images in panels (**d-f**) represent the corresponding HAADF-STEM images.

Figs. 2a-2c show the Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (Cs-corrected HAADF-STEM) images of the PtNi₅-n (n = 0, 0.3 and 0.5 MPa), which clearly display the well-alloyed nanoparticles (NP) in the truncated octahedral shapes and with the average NP sizes of 6.7, 27.5 and 32.6 nm, respectively. The gradually increased NP sizes along with increasing of H₂ pressures (0-0.5 MPa) can be related to the accelerated metal precursor reduction rate by higher pressure H₂ (as will be discussed later), which greatly favors the PtNi₅ growth. To further specify the surface elemental distributions, the energy dispersive X-ray spectroscopy (EDS) mapping was thereby conducted, as shown in Figs. 2d-2f. It can be found that i) the Ni surface content is obviously higher than that of Pt

for PtNi₅-0 (Fig. 2d); ii) on the contrary, much higher amounts of Pt emerge on the surface of PtNi₅-0.3 (Fig. 2e) and PtNi₅-0.5 (Fig. 2f) owing to the strong in-situ inducing effect of H₂, especially for the scenario of PtNi₅-0.3 exhibiting an obvious Pt-rich@Ni-rich core-shell nanostructure and with the Pt-rich phase of Pt₇₉Ni₂₁ as the shell and Ni-rich phase of Pt₁₁Ni₈₉ as the core (as quantified by XRD of Fig. 1b). As noted, the Pt-rich@Ni-rich nanostructure of PtNi₅-0.5 was less obvious (Fig. 2f), which can be related to the comparable Pt (53%) and Ni (47%) ratios of the Pt-rich phase of PtNi₅-0.5 (see Fig. 1b).

Fig. 3| Validation of Pt-rich@Ni-rich cor-shell nanostructure of PtNi₅-0.3. a-c, Nanostructure characterization of PtNi₅-0.3 by applying TEM (a), HRTEM (b), Cs-corrected HAADF-STEM (c). **d,** Elemental intensity analysis along the directions of Line 1 and Line 2 marked in panel (c).

To further characterize the generated Pt-rich@Ni-rich core-shell nanostructures of PtNi₅-0.3 and 0.5, the HRTEM and Cs-corrected HAADF-STEM were conducted and with the PtNi₅-0 as a reference (see Fig. 3 and Supplementary Fig. S2). Obviously, two types of fcc-(111) lattice spacings with the values of 2.21 Å (edge-site) and 2.06 Å (inner-core site) can be clearly observed for the PtNi₅-0.3 (Fig. 3b, HRTEM), which agree well with the values derived from the XRD for the Pt-rich phase (2.21 Å) and Ni-rich phase (2.06 Å) of PtNi₅-0.3 (see Supplementary Table S2). This quantitatively validates the Pt-rich@Ni-rich core-shell nanostructure of PtNi₅-0.3. Similar findings can also be observed for the PtNi₅-0.5 (see Supplementary Figs. S2f), whereas only one lattice spacing of 2.10 Å [fcc-(111)] can be found for PtNi₅-0 (Supplementary Fig. S2b) indicating the uniforming growth of PtNi₅-0. In addition to that, the Cs-corrected HAADF-STEM (Fig. 3c) and combined elemental intensity analysis (Fig. 3d) can also support the Pt-rich@Ni-rich nanostructure of PtNi₅-0.3: i) the bright and dark spots regions respectively representing the Pt-rich shell and Ni-rich inner core can be clearly observed in Fig. 3c; ii) and the element intensity gradually grew up along the direction of Line 1 (inner-core → edge sites) due to the Pt surface segregations to generate the Pt-rich shell. (Fig. 3d).

Due to the fact of that the alkaline-HER majorly occurs on the surface of the catalyst, it is thereby significantly important to specify the surface elemental chemical states as well as contents of the synthesized samples. In light of that, the X-ray photoelectron spectroscopy (XPS) was conducted over the PtNi₅-n samples (see Figs. 4a-4d). As shown in Fig. 4b, the peaks centered at around ~71.3 and ~74.7 eV can be respectively assigned to be Pt⁰ 4f_{7/2} and Pt⁰ 4f_{5/2}, which indicates that the metallic Pt constitutes as the dominant Pt species on the surface of PtNi₅-n, being greatly favorable for the alkaline-HER. As noted, the slight peak shifts of the Pt 4f toward the lower binding energies can be related to the gradually increased Pt surface content of the PtNi₅-n (n = 0.1, 0.3, 0.5 and 0.7 MPa) samples relative to that of PtNi₅-0.²⁶ As for the surface Ni, two types Ni species of the metallic Ni (852.6 eV) and

Ni(OH)₂ (855.6 eV) can be found on the surface of PtNi_{5-n} (see Fig. 4b of Ni 2p), wherein the formation of Ni(OH)₂ can be related to the strong water splitting effect of the surface Ni⁰ during the synthesis process.²⁷

Fig. 4| Surface elemental chemical states and contents of PtNi_{5-n} (n=0, 0.1, 0.3, 0.5 and 0.7 MPa). **a-c,** XPS survey spectra (**a**), Pt 4f (**b**), Ni 2p (**c**). **d,** Surface Pt contents detected by XPS compared with the bulk content determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

The Pt surface contents derived by XPS were further profiled in Fig. 4d, being with the bulk content of Pt as a reference (see Supplementary Table S3). As can be seen, the surface content of Pt is comparable to that of bulk Pt, verifying the uniform growth of PtNi₅₋₀. However, much higher surface Pt contents can be found for the PtNi_{5-n} (n = 0.1, 0.3, 0.5 and 0.7 MPa), which decrease following the order of 46% (PtNi_{5-0.3}) > 42% (PtNi_{5-0.1}) > 38.4%

(PtNi₅-0.5) > 36.3% (PtNi₅-0.7). This finding quantitatively validates the availability of the H₂ in-situ inducing strategy of present work to synthesize highly surface segregated PtNi₅-n bimetallic nanoalloy, especially for the scenario of PtNi₅-0.3 exhibiting an ultrahigh surface Pt content of 46% due to the strongest in-situ inducing effect of H₂ at 0.3 MPa.

Alkaline-HER Activity Measurement. The alkaline-HER activities of the PtNi₅-n and commercial Pt/C were evaluated in this section (see Figs. 5a-5f and Supplementary Table S4). Specifically, the obvious peak shifts of H_{upd} (underpotentially detected H) toward the lower potentials can be clearly observed for the PtNi₅-n samples in comparison to that of the commercial Pt/C (0.28 and 0.38 V, see Fig. 5a), which implies the significantly improved alkaline-HER activities of PtNi₅-n owing to the extensively weakened H⁺ adsorption energy,²⁸ especially for the scenario of PtNi₅-0.3 displaying the lowest H_{upd} value of ~0.1 eV. This finding can be further verified by the derived linear sweep voltammetry curves of Fig. 5b displaying an obvious decreasing of the overpotentials (η) at -10 mA cm⁻² for the PtNi₅-n with respect to that of the commercial Pt/C; noteworthy, the PtNi₅-0.3 delivers an unprecedentedly low overpotential of 12.8 mV (-10 mA cm⁻²). Moreover, the volcano shapes can be clearly observed for the derived mass activity (MA) and specific activity (SA) (see Fig. 5c) at an overpotential of 70 mV versus reversible hydrogen electrode (RHE), wherein the PtNi₅-0.3 presents the highest values of 6.0 mA μ g_{Pt}⁻¹ (MA) and 20.8 mA cm_{Pt}⁻² (SA), being respectively of 3.5 and 10.4 fold higher than those of the commercial Pt/C (1.7 mA μ g_{Pt}⁻¹ and 2.0 mA cm_{Pt}⁻², see Supplementary Table S4). In addition to that, the PtNi₅-0.3 also exhibits the highest TOF (Fig. 5d) and lowest Tafel plot (14.1 mV dec⁻¹, Fig. 5e), which further confirms its highest activity. Finally, the long-term test was further conducted to evaluate the reaction stability of PtNi₅-0.3 as shown in Fig. 5f, wherein only a slight current loss of 3% can be found after 10 h's test, reflecting the excellent reaction durability of PtNi₅-0.3.

Fig. 5| Alkaline-HER activity measurements of PtNi_{5-n} and commercial Pt/C. The alkaline-HER was carried out in a H₂-saturated 1 M KOH solution (PH = 14) with the catalyst sample being directly spread onto the glassy carbon electrode (diameter of 5 mm) under a loading of 10 μg cm⁻². The polarization curves were obtained based on the linear voltammetry sweeping approach under a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. **a-f**, Cyclic voltammetry curves (**a**), *iR*-corrected polarization curves (**b**), comparison of the mass activity

(MA) and specific activity (SA) at 70 mV vs RHE (c), calculated turnover frequency (TOF) (d), the corresponding Tafel plots (e) and potentiostatic electrolysis study at 50 mV vs RHE in 1 M KOH (f).

Mechanistic insight into specific effects of H₂. As stated above, the H₂ in-situ induced Pt surface segregation is verified to be an efficient strategy to produce highly active PtNi₅ nanoalloy for the alkaline-HER. In this section, the specific in-situ inducing effects of H₂ (kinetically and thermodynamically) during PtNi₅-n synthesis were systematically investigated based on the combined experimental and theoretical approaches.

Kinetic Effect of H₂ on Metal Precursor Reduction. Inspired by the literature report²⁹ suggesting that the metal precursor reduction rate differences determine the final nanostructures of the bimetallic nanoalloy as well as our previous study³⁰ finding that the H₂ behaving as a reductant greatly favored the metal precursor reductions, herein we further investigated the H₂-mediated metal precursor reduction kinetics based on the Finke-Watzky model^{31,32} to illustrate the kinetic effect of H₂ on Pt surface segregations to generate the Pt-rich@Ni-rich nanostructures (see Figs. 6a-6f). As can be seen, the H₂ can efficiently promote the metal precursor (both Ni²⁺ and Pt²⁺) reductions (Figs. 6a-6b), wherein the experimental data points can be well fitted by the constructed kinetic models represented by the curve lines. Furthermore, the metal precursor reduction rate ratio (R_{Ni} / R_{Pt}) of PtNi₅-0 (Fig. 6c) was obviously lower than the stoichiometric Ni/Pt ratio of PtNi₅ (Ni/Pt = 5); whereas much higher reduction rate differences ($R_{Ni} / R_{Pt} > 5$) can be clearly observed for the scenarios of PtNi₅-0.3 and 0.5 (Figs. 6d-6e) at $t = (0.5-1.0)$ and $(0.25-0.5)$ h, respectively, which are greatly favorable for the Pt-rich@Ni-rich core-shell nanostructure formations. This can be majorly related to that the quickly reduced metallic Ni atoms relative to Pt ($R_{Ni} / R_{Pt} > 5$) can be preferentially nucleated to generate the Ni-rich core, based on which the subsequently reduced metallic Pt would be nucleated onto the Ni-rich core eventually generating the Pt-rich shell. A R_{Ni} - R_{Pt} distribution diagram is further depicted in Fig. 6f to illustrate the uniform

growth and core-shell growth regions for the PtNi_{5-n} samples according to the criteria of $R_{Ni} / R_{Pt} = 5$ (based on the data points profiled in Figs. 6c-6e). Obviously, all the data points were located in the uniform growth region ($R_{Ni} / R_{Pt} < 5$) for the PtNi₅₋₀; while three and two points were located in the core-shell growth regions ($R_{Ni} / R_{Pt} > 5$) for PtNi_{5-0.3} and 0.5. More data points being located in core-shell growth regions being associated with higher R_{Ni} / R_{Pt} values leads to much more obvious core-shell nanostructure of PtNi_{5-0.3} related to that of PtNi_{5-0.5}.

Fig. 6| Correlation between H₂-mediated metal precursor reduction kinetics and

generated Pt-rich@Ni-rich nanostructure. a,b, H₂-mediated metal precursor (Ni²⁺ and Pt²⁺) reduction kinetic results of PtNi₅-0, 0.3 and 0.5: the concentrations of ionic Ni²⁺ (**a**) and Pt²⁺ (**b**) remaining in the solutions as a function of time t , wherein the point data represents the experiment results and the line data represents the simulation results based on the Finke-Watzky model. **c-e,** The derived reduction rates of Ni²⁺ (R_{Ni}), Pt²⁺ (R_{Pt}) and (R_{Ni} / R_{Pt}) ratios as functions of reaction time (t) under different H₂ pressures of 0 MPa (**c**), 0.3 MPa (**d**) and 0.5 MPa (**e**). **f,** A R_{Ni} - R_{Pt} distribution diagram based on the data points of Figs. 6c-6e to illustrate the correlations between reduction rate differences of (R_{Ni} / R_{Pt}) and finally evolved nanostructure according to the criterion of $R_{Ni}/R_{Pt} = 5$ being of stoichiometric Ni/Pt ratio of PtNi₅.

Thermodynamic Effect of H₂ on Pt Surface Content Adjustment by DFT. In this part, the thermodynamic effect of H₂ during PtNi₅-n (n = 0.3 and 0.5 MPa) synthesis ($T = 453$ K) was further investigated based on the ab initio thermodynamic analysis. Initially, according to the XPS characterization results of PtNi₅-0.3 (Pt = 46%) and 0.5 (Pt = 38.4%), two types of PtNi₅ models respectively with the surface Pt content of 50% (being close to 46%) and 38% were constructed, as shown in Fig. 7a. Based on that, the Gibbs surface free energies (γ) were calculated under the diverse surface hydrogen coverages ($\theta_H = 0 - 1$ ML, see Supplementary Fig. S5) and H₂ pressures (0.3 and 0.5 MPa), as profiled in Figs. 7b-7e. As can be seen, the θ_H of 1/2 ML leads to PtNi₅-38% achieving the most thermodynamically stable state (Figs. 7b and 7d); while the θ_H of 1/16 ML results in PtNi₅-50% being of the most stable state (Figs. 7c and 7e) under the PtNi₅ synthesis conditions ($P_{H_2} = 0.3$ and 0.5 MPa, $T = 453$ K). Further comparing the γ of PtNi₅-38% and PtNi₅-50% related to the most thermodynamically stable states at $T = 453$ K (see Fig. 7f), one can find that the PtNi₅-50% possesses the lower γ than that of PtNi₅-38% under the H₂ pressure of 0.3 MPa, which however became converse under the higher H₂ pressure of 0.5 MPa. This finding unravels that the H₂ prefers adjusting the Pt surface content of PtNi₅-0.3 and PtNi₅-0.5 to be respectively 50 and 38% to achieve the

255 thermodynamically stable state, which agrees well with the experimental results.

Fig. 7| Thermodynamic effects of H₂ on Pt surface adjustment for the PtNi₅-0.3 and 0.5.

a, Optimized models of PtNi₅ with Pt surface contents of 38 and 50% [with a $p(4 \times 4)$ unit cell of four layers and being enclosed by (111) facet]; as noted, these two models were respectively selected from 5 different PtNi₅ models (with diverse Ni and Pt distributions, Fig. S4) based on the geometry optimization results. **b-e**, Gibbs surface free energies as a function

of temperature (T) under surface H coverages of (0-1 ML) and H_2 pressures of 0.3 MPa over PtNi₅-38% (b) and PtNi₅-50% (c); and under H_2 pressure of 0.5 MPa over PtNi₅-38% (d) and PtNi₅-50% (e). f, Gibbs surface free energy comparisons of PtNi₅-38% and PtNi₅-50% of most thermodynamically stable state under the PtNi₅-n synthesis conditions of $T = 453$ K and H_2 pressure of 0.3 and 0.5 MPa, respectively.

Short summary. In light of the above investigations, the H_2 in-situ inducing effect on Pt surface segregations to generate Pt-rich@Ni-rich nanostructure can be summarized in two aspects. Kinetically, the H_2 working as the reductant results in the metal precursor reduction rate difference being much higher than the stoichiometric ratio of PtNi₅ ($R_{Ni} / R_{Pt} > 5$), especially for the scenario of 0.3 MPa H_2 , eventually leading to the generation of Pt-rich@Ni-rich core-shell nanostructure. Thermodynamically, the H_2 working as the SDA can adjust the surface Pt content through influencing the surface free energy of the exposed facet in the manner of dissociatively adsorption mode: the H_2 of 0.3 MPa leading to the surface Pt of 50% being under the stable state, while further increasing the H_2 to 0.5 MPa leading to decreasing of the surface Pt (38%) to achieve its thermodynamically stable state.

Alkaline-HER Simulations by DFT and In-depth Insight. In this part, the alkaline-HER activity of PtNi₅-n ($n = 0, 0.3$ and 0.5 MPa) and commercial Pt/C were simulated by DFT based on the constructed models of PtNi₅-18% (Supplementary Fig. S6a), 38%, 50% (Fig. 7a) and Pt(111) (Supplementary Fig. S6b). According to the literature reports,³³ the real reaction route can be justified by the Tafel slope. For the scenario of present work, the the reaction would prefer to follow the Volmer-Tafel mechanism due to the low Tafel slopes (< 30 mV dec⁻¹, Fig. 5e). Fig. 8a displays the calculated adsorption Gibbs free energies of the H_2O (ΔG_{H_2O}) and H_{ad} (ΔG_H), being of two types of key activity indicators for Volmer and Tafel steps, respectively.³⁴ Obviously, the PtNi₅-n samples exhibit much lower absolute values of ΔG_{H_2O} and ΔG_H than those of Pt/C (see Fig. 8b), which indicates much higher HER activity.³⁵ Moreover, the derived activity decreasing order (PtNi₅-0.3 > PtNi₅-0.5 > PtNi₅-0 > Pt/C) is in

good agreement with the experimental activity measurement results (Figs. 5b-5e). This finding unravels that the significantly improved activity of the synthesized PtNi₅-n samples can be related to the effective capabilities to reduce the absolute values of $\Delta G_{\text{H}_2\text{O}}$ and ΔG_{H} during alkaline-HER, especially for the best performed sample of PtNi₅-0.3 displaying much lower values (0.48 and 0.04 eV) in comparison to those of the commercial Pt/C (0.75 and 0.30 eV).

Fig. 8| Alkaline-HER simulations based on DFT and in-depth mechanistic insight unraveled by d band center theory. a, DFT simulated Gibbs free energy diagram for alkaline-HER over PtNi₅-n (n = 0, 0.3 and 0.5 MPa) samples represented by the constructed models of PtNi₅-18%, PtNi₅-38% and PtNi₅-50%, respectively; as noted, the PtNi₅-18% is also selected from 5 different PtNi₅-18% models with a minimum optimization energy (see Fig. S7); and a four layered Pt(111) with a unite cell of $p(4 \times 4)$ is constructed to represent the

commercial Pt/C (Supplementary Fig. S6b). **b**, Comparisons of the derived adsorption Gibbs free energies of H₂O ($\Delta G_{\text{H}_2\text{O}}$) and H⁺ (ΔG_{H}). **c**, The projected d band density of states (PDOS) of the Pt active site of PtNi₅-18%, PtNi₅-38% and PtNi₅-50% and Pt(111) (see Supplementary Fig. S8d), wherein the PDOS of Ni site of Ni(111) was taken as a reference; the black dash line represents the Fermi level (ε_{F}) and colored dash lines represent the derived d band center (ε_{d}); $\varepsilon_{\text{d}}-\varepsilon_{\text{F}}$ represents the energy of d band center relative to the Fermi level; as noted, the derived ($\varepsilon_{\text{d}}-\varepsilon_{\text{F}}$) of the atomic Pt (-2.44 eV) and Ni (-1.78 eV) over Pt(111) and Ni(111) were comparable to the values reported in the benchmark work of Ref. 37 [-2.75 eV of Pt(111) and -1.48 eV of Ni(111)]. **d**, Linear correlation between the derived ΔG_{H} and ($\varepsilon_{\text{d}}-\varepsilon_{\text{F}}$) of PtNi₅-18, 38 and 50%.

Actually, it is not surprising that the PtNi₅-n samples exhibit the superior activities in Volmer step relative to that of the Pt/C, being majorly related to the higher intrinsic H₂O-splitting activity of the dopant Ni. To gain an in-depth insight into the much higher electrochemical activity of PtNi₅-n with respect to Pt/C in the subsequent Tafel step, the d band center relative to the Fermi level ($\varepsilon_{\text{d}}-\varepsilon_{\text{F}}$) of the Pt active sites of PtNi₅-n and Pt/C (see Supplementary Fig. S8d) was further calculated based on projected density of state (PDOS, see Fig. 8c), due to the fact of that the Tafel-step activity is largely determined by the specific electronic structure and coordination geometry of the exposed active site.³⁶ The d band center is efficient to evaluate the metal-adsorbate interaction strength; and the higher value of the d band center indicates more empty of the antibonding state (being less filled) which thereby leads to the stronger bonding strength (vice versa).³⁷⁻³⁹ As can be seen (Fig. 8c), the ($\varepsilon_{\text{d}}-\varepsilon_{\text{F}}$) of PtNi₅-n varying with the surface Pt content due to the ligand effect is obviously lower than that of Pt(111) (-2.44 eV). Moreover, a linear correlation between the ($\varepsilon_{\text{d}}-\varepsilon_{\text{F}}$) and the ΔG_{H} of PtNi₅-n and Pt/C can be clearly observed in Fig. 8d, which is consistent with the literature report⁴⁰ demonstrating that the d band center can be utilized as a key activity descriptor for the alkaline-HER. In light of that, we can get an in-depth insight that the significantly improved

Tafel-step activity of the PtNi_{5-n} originates from the downward-shifted d band center of the Pt active site, which can significantly weaken the Pt-H bond strength and thereby pronouncedly enhance the related electrocatalytic activity, especially for the best performed sample of PtNi_{5-0.3} possessing the lowest ($\epsilon_d - \epsilon_F$) value of -3.15 eV (PtNi_{5-50%}, Fig. 8c), being corresponding to the highest Tafel-step activity.

Conclusion

We have developed a simple one-pot synthesis strategy by utilizing the H₂ as the SDA to synthesize a series of highly active and economical (with extremely low Pt/Ni of 0. 2) PtNi_{5-n} samples for the alkaline-HER. Among them, the PtNi_{5-0.3} delivers a record-high activity ($\eta = 12.8$ mV at 10mA cm⁻², Tafel slop of 14.1 mV dec⁻¹), due to the strong H₂ in-situ inducing effect to generate Pt-rich@Ni-rich core-shell nanostructure with an ultra-high Pt surface content of 46%. The H₂ majorly functions in two aspects: i) kinetically, it significantly affects the metal precursor reduction kinetics, wherein the H₂ of 0.3 MPa resulting in the largest Ni²⁺ and Pt²⁺ reduction rate difference ($R_{Ni} / R_{Pt} > 5$) greatly favors Pt surface segregation to generate Pt-rich@Ni-rich nanostructure; ii) thermodynamically, it can adjust the Pt surface composition through alerting the surface free energy, e.g. 0.3 MPa H₂ resulting in 50% Pt surface being under the most stable state. Additionally, the DFT mechanism simulations shed a deeper mechanistic insight that the adsorption Gibbs free energy of H₂O (ΔG_{H_2O} , Volmer step) and H⁺ (ΔG_H , Tafel step) were extensively reduced due to the synergistic effect between the surface Ni and Pt, especially for the Tafel step, wherein the downward-shifted d band center of the Pt active site could efficiently reduce the Pt-H bond strength, thereby leading to the significantly low absolute values of ΔG_H . Overall, the developed H₂ in-situ inducing Pt surface segregation approach opens up a new synthesis strategy for highly efficient and economical alkaline-HER catalysis designs.

Methods

The chemicals of platinum acetate [Pt(acac)₂], nickel acetate [Ni(acac)₂], polyvinyl pyrrolidone (PVP), aniline, benzyl alcohol and ethanol were purchased from Sigma-Aldrich.

Synthesis of the PtNi₅-n catalysts: A mixing solution of Pt(acac)₂ (0.16 mmol), Ni(acac)₂ (0.80 mmol), PVP (200 mg), aniline (0.5 mL) and benzyl alcohol (20 mL) was prepared in a 50-mL Teflon-lined autoclave and under stirring for 30 min. Thereafter, the autoclave was pressurized by H₂ under diverse pressures of 0, 0.1, 0.3, 0.5 and 0.7 MPa. After that, the sealed autoclave was heated to 180 °C and maintained at this temperature for 6 h with a stirring rate of 200 rpm. After being precipitated, washed by a mixing solution of deionized water and ethanol and dried at 60 °C under vacuum for 24 h, we obtained the final products.

Characterization. The crystalline structure of the catalyst samples were evaluated by X-ray diffraction (XRD) patterns with a Bruker D8-Advance diffractometer using Cu K α radiation. Based on the XRD, the specific ratios of Pt and Ni in Pt-rich and Ni-rich phases of the PtNi₅-n nanoalloy were predicted by Vegard's rule; and the lattice spacings were calculated based on the software of JADE 6.5. TEM, HRTEM and EDS mapping were conducted over a JEM-2100F microscope with an accelerating voltage of 200 kV to characterize the structure morphologies and surface elemental distributions of synthesized samples. The Cs-corrected HAADF-STEM images were collected on the Titan 80-300 microscope (FEI, USA). The XPS was performed over an ESCALAB 250 XPS photoelectron spectrometer with an Mg K α X-ray source (Thermo, USA) to ascertain the surface elemental contents. The C 1s at 284.5 eV was utilized as a criterion. The ICP-OES (inductively coupled plasma optical emission spectrometry) was utilized to determine the metal contents in the bulk of catalyst samples over Thermo Fisher Scientific iCAP 6000 Series.

Electrochemical measurements. An electrochemical workstation (CHI760E, CH Instruments) coupled with a three-electrode cell system was used to evaluate the alkaline-HER activities of the synthesized samples, wherein a saturated Hg/HgO electrode, carbon rod

and glassy carbon were respectively utilized as the reference, counter and working electrodes. The catalyst ink was prepared by mixing 2 mg of catalyst, 2 mg of carbon black, 0.25 mL of deionized water, 50 μ L of Nafion (5 wt%), and 0.7 mL of ethanol together, being followed by ultra-sonication in an ice bath for 0.5 h. The alkaline-HER activity measurements were carried out in a H₂-saturated 1 M KOH solution (PH = 14) with the catalyst samples being directly spread onto the glassy carbon electrode (diameter of 5 mm) with a loading of 10 μ g cm⁻². The polarization curves were obtained based on the linear sweep voltammetry (LSV) approach under a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm from 0.1 to -0.2 V. Tafel slope was obtained by fitting the linear portion to the Tafel equation: $\eta = \log(j) + a$. The potentials presented were versus the reversible hydrogen electrode (RHE) and all polarization curves were IR corrected. The chronoamperometry was measured under a constant potential of 50 mV vs RHE during the reaction stability test. The specific calculation approaches for the turnover frequency (TOF), ECSA_H and mass/ specific activity (MA and SA) were detailedly stated in Supplementary Method.

Metal precursor kinetics experiment. The metal precursor reduction kinetics were conducted according to the following procedures: i) initially, the reactor was filled with 10 mL Ni(acac)₂ (0.80 mmol) solution and heated up to 180 °C; ii) after that, the Pt(acac)₂ (0.16 mmol, 20 mL) was quickly pumped into the reactor under a flow rate of 50 mL min⁻¹; iii) then the H₂ (0.3 and 0.5 MPa) was fed into the system to start the reduction reaction; iv) the Ni²⁺ and Pt²⁺ concentrations remaining in the solution was thereby measured by ICP-OES at an time intervals 15 min. The kinetic models were constructed based on the Finke-Watzky model³⁸⁻³⁹ which was detailedly stated in Supplementary Method.

DFT calculations: All DFT calculations were performed on the Vienna ab initio simulation package (VASP) using the projector augmented wave (PAW) method and Perdew-Burke-Ernzerhof (PBE) exchange correlation functional with an energy cutoff of 400 eV. The convergence threshold was set to be 10⁻⁴ eV in energy and 0.05 eV Å⁻¹ in force. The

Brillouin zone was sampled with a $2 \times 2 \times 1$ Monkhorst-Pack k-point grid. The $p(4 \times 4)$ unit cell with four layers were employed to calculate the Gibbs surface free energy of the Pt(111) and mixed-PtNi₅ (111) surfaces. Upon slab optimization, the bottom two layers were fully fixed while the other layers were allowed to relax. To avoid unphysical influence, a 10 Å vacuum layer was added along the z direction normal to the surface. Diverse PtNi_{5-n} models with surface Pt content of 18, 38 and 50% were constructed, see detailed in Supplementary Figs. S4, S6 and S7. Based on the DFT of ab initio thermodynamic (AIT), the thermodynamic effect of H₂ (Pt surface content adjustment) during PtNi_{5-n} synthesis process were evaluated, wherein the surface free energies under diverse H surface coverages ($\theta_H = 0 - 1$ ML) were thereby calculated and with the specific calculation method being detailedly described in Supplementary Method. Additionally, the alkaline-HER activity of the PtNi_{5-n} samples were also simulated by DFT including the Volmer and Tafel steps. The adsorption Gibbs free energies of H₂O and H⁺ were thereby calculated as also detailedly described in Supplementary Method. Finally, the projected density of state (PDOS) of the active site of Pt over construed models of PtNi₅₋₁₈, 38 and 50% (see Supplementary Fig. S8d) as well as the Ni of Ni(111) (as a reference) was accordingly derived, based on which the d band centers (ε_d) were obtained.

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Conflict of Interest

The authors declare no conflict of interest.

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H_2 *in-situ* INDUCED Pt SURFACE SEGREGATION

Figures

Figure 1

Nanocrystal structure of the synthesized PtNi_{5-n} (n = 0, 0.1, 0.3, 0.5 and 0.7 MPa). a, XRD diffraction patterns of the PtNi_{5-n}. b, Predicted elemental (Pt and Ni) ratios in Pt-rich (red and green) and Ni-rich (blue and gray) phases of PtNi_{5-n} based on the Vegard's rule and the XRD results.

Figure 2

Structural morphologies and surface elemental distributions of PtNi_{5-n} (n = 0, 0.3 and 0.5 MPa). a-c, Cs-corrected HAADF-STEM images of PtNi₅₋₀ (a), PtNi_{5-0.3} (b) and PtNi_{5-0.5} (c). d-f, EDS mapping results of PtNi₅₋₀ (d), PtNi_{5-0.3} (e) and PtNi_{5-0.5} (f). Insert images in panels (a-c) represent the statistics of nanoparticle size distributions; and the insert images in panels (d-f) represent the corresponding HAADF-STEM images.

Figure 3

Validation of Pt-rich@Ni-rich cor-shell nanostructure of PtNi_{5-0.3}. a-c, Nanostructure characterization of PtNi_{5-0.3} by applying TEM (a), HRTEM (b), Cs-corrected HAADF-STEM (c). d, Elemental intensity analysis along the directions of Line 1 and Line 2 marked in panel (c).

Figure 4

Surface elemental chemical states and contents of PtNi₅-n (n=0, 0.1, 0.3, 0.5 and 0.7 MPa). a-c, XPS survey spectra (a), Pt 4f (b), Ni 2p (c). d, Surface Pt contents detected by XPS compared with the bulk content determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Figure 5

Alkaline-HER activity measurements of PtNi_{5-n} and commercial Pt/C. The alkaline-HER was carried out in a H₂-saturated 1 M KOH solution (PH = 14) with the catalyst sample being directly spread onto the glassy carbon electrode (diameter of 5 mm) under a loading of 10 μg cm⁻². The polarization curves were obtained based on the linear voltammetry sweeping approach under a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. a-f, Cyclic voltammograms (a), iR-corrected polarization curves (b), comparison of the mass

activity (MA) and specific activity (SA) at 70 mV vs RHE (c), calculated turnover frequency (TOF) (d), the corresponding Tafel plots (e) and potentiostatic electrolysis study at 50 mV vs RHE in 1 M KOH (f).

Figure 6

Correlation between H₂-mediated metal precursor reduction kinetics and generated Pt-rich@Ni-rich nanostructure. a,b, H₂-mediated metal precursor (Ni²⁺ and Pt²⁺) reduction kinetic results of PtNi₅-0, 0.3 and 0.5: the concentrations of ionic Ni²⁺ (a) and Pt²⁺ (b) remaining in the solutions as a function of time

t, wherein the point data represents the experiment results and the line data represents the simulation results based on the Finke- Watzky model. c-e, The derived reduction rates of Ni²⁺ (R_{Ni}), Pt²⁺ (R_{Pt}) and (R_{Ni} / R_{Pt}) ratios as functions of reaction time (t) under different H₂ pressures of 0 MPa (c), 0.3 MPa (d) and 0.5 MPa (e). f, A R_{Ni}-R_{Pt} distribution diagram based on the data points of Figs. 6c-6e to illustrate the correlations between reduction rate differences of (R_{Ni} / R_{Pt}) and finally evolved nanostructure according to the criterion of R_{Ni}/R_{Pt} = 5 being of stoichiometric Ni/Pt ratio of PtNi₅.

Figure 7

Thermodynamic effects of H₂ on Pt surface adjustment for the PtNi₅-0.3 and 0.5. a, Optimized models of PtNi₅ with Pt surface contents of 38 and 50% [with a p(4×4) unit cell of four layers and being enclosed by (111) facet]; as noted, these two models were respectively selected from 5 different PtNi₅ models (with diverse Ni and Pt distributions, Fig. S4) based on the geometry optimization results. b-e, Gibbs surface free energies as a function of temperature (T) under surface H coverages of (0-1 ML) and H₂ pressures of 0.3 MPa over PtNi₅-38% (b) and PtNi₅-50% (c); and under H₂ pressure of 0.5 MPa over PtNi₅-38% (d) and PtNi₅-50% (e). f, Gibbs surface free energy comparisons of PtNi₅-38% and PtNi₅-50% of most thermodynamically stable state under the PtNi₅-n synthesis conditions of T = 453 K and H₂ pressure of 0.3 and 0.5 MPa, respectively.

Figure 8

Alkaline-HER simulations based on DFT and in-depth mechanistic insight unraveled by d band center theory. a, DFT simulated Gibbs free energy diagram for alkaline-HER over PtNi₅-n (n = 0, 0.3 and 0.5 MPa) samples represented by the constructed models of PtNi₅-18%, PtNi₅-38% and PtNi₅-50%, respectively; as

noted, the PtNi₅-18% is also selected from 5 different PtNi₅-18% models with a minimum optimization energy (see Fig. S7); and a four layered Pt(111) with a unite cell of p(4×4) is constructed to represent the commercial Pt/C (Supplementary Fig. S6b). b, Comparisons of the derived adsorption Gibbs free energies of H₂O (ΔG_{H_2O}) and H⁺ (ΔG_H). c, The projected d band density of states (PDOS) of the Pt active site of PtNi₅-18%, PtNi₅-38% and PtNi₅-50% and Pt(111) (see Supplementary Fig. S8d), wherein the PDOS of Ni site of Ni(111) was taken as a reference; the black dash line represents the Fermi level (ϵ_F) and colored dash lines represent the derived d band center (ϵ_d); $\epsilon_d - \epsilon_F$ represents the energy of d band center relative to the Fermi level; as noted, the derived ($\epsilon_d - \epsilon_F$) of the atomic Pt (-2.44 eV) and Ni (-1.78 eV) over Pt(111) and Ni(111) were comparable to the values reported in the benchmark work of Ref. 37 [-2.75 eV of Pt(111) and -1.48 eV of Ni(111)]. d, Linear correlation between the derived ΔG_H and ($\epsilon_d - \epsilon_F$) of PtNi₅-18, 38 and 50%.

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