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### Title

Amorphous nickel hydroxide shell tailors local chemical environment on platinum surface for alkaline hydrogen evolution reaction

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# 1 **Amorphous nickel hydroxide proton **conductive shell**** 2 **tailors local chemical environment on Pt surface for high-** 3 **performance alkaline hydrogen evolution reaction**

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17 **In analogy to natural enzymes, an elaborated design of catalytic systems with a specifically**  
18 **tailored local chemical environment could substantially improve reaction kinetics,**  
19 **effectively combat **catalyst poisoning effect** and boost catalyst lifetime under unfavorable**  
20 **reaction conditions. Herein, we report a unique design of “Ni(OH)<sub>2</sub>-clothed Pt-tetrapods”**  
21 **with an amorphous Ni(OH)<sub>2</sub> shell as a water dissociation catalyst and a proton **conductive****  
22 **layer to ensure abundant proton supply while isolating the Pt core from bulk alkaline**  
23 **electrolyte and rejecting undesired poisoning species. This design creates a favorable local**  
24 **chemical environment **with efficient proton supply** to the active Pt sites, resulting in acidic-**  
25 **like HER kinetics with a lowest Tafel slope of 27 mV/decade and a record-high specific**  
26 **activity and mass activity in alkaline electrolyte. The proton **conductive** Ni(OH)<sub>2</sub> shell**  
27 **effectively rejects impurity ions and retards the Oswald ripening, endowing a **high****  
28 **tolerance to solution impurities and long-term durability that is difficult to achieve in the**  
29 **naked Pt-catalysts. The markedly improved alkaline HER activity and durability promise**

- 1 **an attractive catalyst material for alkaline water electrolyzers and renewable chemical fuel**
- 2 **generation.**

1 Water electrolysis is of increasing interest for converting intermittent renewable electricity  
2 (from solar cells and windmills) into high purity hydrogen. The electrochemical water-splitting  
3 reaction is comprised of two half-reactions: the cathodic hydrogen evolution reaction (HER) and  
4 anodic oxygen evolution reaction (OER). In general, the HER and OER display distinct kinetics  
5 in acidic and basic electrolytes and often require costly platinum group metal (PGM) catalysts.  
6 Platinum (Pt) is regarded as the best element to catalyze HER for its optimal hydrogen binding  
7 energy (HBE).<sup>1-6</sup> In particular, the Pt catalysts feature a rather small overpotential for HER in the  
8 acidic condition where the cathodic HER is usually regarded as a trivial challenge. However, for  
9 the complete water electrolysis, the anodic OER in the acidic condition is considerably more  
10 challenging and often features large overpotential and limited durability even with the most  
11 advanced design of PGM catalysts.<sup>7</sup> On the other hand, the OER in the alkaline condition is  
12 much more friendly and can be readily facilitated with non-precious metal (Ni, Fe, Co, etc.)  
13 oxide/hydroxide catalysts, offering considerable kinetic and cost benefits.<sup>8</sup> With the continued  
14 development of anion exchange membrane (AEM) of lower resistance and lower hydrogen  
15 diffusivity,<sup>9</sup> alkaline electrolysis is becoming an increasingly attractive alternative for  
16 commercial electrolyzers.<sup>10,11</sup>

17 However, the HER kinetics in the alkaline condition is considerably slower. Even with the  
18 Pt catalysts, the HER rate is orders of magnitude lower than that in the acidic electrolyte because  
19 of the sluggish water dissociation step and the **poor** proton supply rate (Extended Data Fig. 1).<sup>12</sup>  
20 Therefore, **unlike the commonly perceived “easy” HER in the acidic electrolyte, the HER in**  
21 **the alkaline condition represents a major challenge for alkaline water electrolyzers.**<sup>13,14</sup>  
22 Considerable efforts have been placed on tailoring the Pt active sites to optimize HBE and HER  
23 kinetics. **Beyond the active sites**, the local chemical species can compete for adsorption for  
24 active sites, inactivate (poison) the catalytic sites, or profoundly affect the mass transfer of  
25 feedstocks/products.<sup>15,16</sup> Additionally, catalysts are inherently dynamic materials whose  
26 structures may evolve continuously during the adsorption of reactants and desorption of  
27 products, which could dictate the catalyst stability and lifetime.

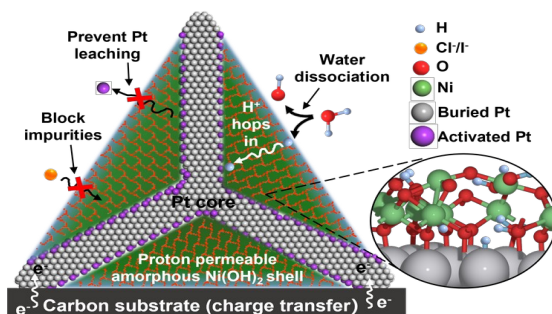
28 In general, the local chemical environment plays a fundamental role in determining the  
29 reaction pathway and kinetics on the catalytic surface. A practical water electrolysis requires the  
30 concerted supply of the reactants and removal of the products under specific operating conditions

1 to achieve high activity, tolerance to impurities in water, and long lifetime. To this end, a  
2 **comprehensive approach that integrates electrocatalytic active site design with rational**  
3 **strategies to manipulate nanoscale mass/charge transport, ion separation, or structural**  
4 **evolution is critical for designing high-performing electrocatalysts that can facilitate**  
5 **efficient electron transfer and** chemical transformations under practical conditions. This is  
6 **analogous to the natural enzymes where precisely tailored micro-environment works in**  
7 **concert with the active sites to ensure superior activity, selectivity, and durability under**  
8 **practical solution conditions.** Such an elaborate design is particularly important for alkaline  
9 water electrolysis where the local chemical environment near the active Pt sites in alkaline  
10 electrolytes is far more complex than that in an acidic electrolyte due to the limited **proton supply**  
11 **rate**, competitive adsorption of positively charged alkali metal cations (vs. protons) or other  
12 **undesirable** strong binding impurities (e.g., Cl<sup>-</sup>) **that could poison** the catalytic **sites**.

13 Surface decoration has been recognized as an effective approach for tailoring the local  
14 chemical environment near the active sites. For example, the decoration of crystalline NiO or  
15 NiS<sub>x</sub> particles on Pt surface has been reported to improve HER specific activity (SA, activity  
16 normalized by electrochemical surface area: ECSA) in the alkaline electrolyte,<sup>17,18</sup> which has  
17 been mostly attributed to enhanced water dissociation kinetics facilitated by the Ni species.  
18 However, such crystalline Ni species are less permeable to protons and partly block the surface  
19 active sites (Extended Data Fig. 2) to reduce proton-accessible ECSA and compromise the  
20 overall mass activity (MA, activity normalized by mass loading);<sup>5</sup> Additionally, the protons  
21 generated from Ni-catalyzed water dissociation could be rapidly consumed within ~1 nm (See  
22 Supplementary Note 1) through reassociation with the abundant hydroxyl in alkaline electrolyte.  
23 Thus, only a small fraction of Pt sites in close proximity of the decorated Ni species can benefit  
24 from the improved water dissociation kinetics on decorated Ni species, while most Pt sites  
25 **farther away** from Ni species are barely impacted (Extended Data Fig. 2). In this way, although  
26 the surface decoration with the crystalline Ni species could facilitate the water dissociation and  
27 partly accelerate the HER kinetics, **most of the surface Pt sites in such decorated catalysts**  
28 **remain exposed to the bulk alkaline electrolyte, and the HER kinetics largely retain the**  
29 **alkaline HER characteristics with the Volmer- and Heyrovsky-step limited kinetics**

1

1 (Extended Data Table 1). Moreover, the exposed Pt surface sites could undergo severe Oswald  
2 ripening during HER and gradually lose the designed nanostructure and the original activity.



3

4 **Figure 1| “Ni(OH)<sub>2</sub>-clothed Pt-tetrapod” with the proton conductive amorphous**  
5 **Ni(OH)<sub>2</sub> to tailor local chemical environment for optimum HER in bulk alkaline**  
6 **electrolyte:** (i) the “Ni(OH)<sub>2</sub>-clothed Pt-tetrapod” structure offers an ideal geometry for  
7 isolating most of the Pt surface sites from the bulk alkaline electrolyte and rejecting  
8 undesired poisoning species while allowing the less encapsulated “feet” to make robust  
9 electrical contacts with the carbon support for efficient electron transport to the catalytic  
10 sites; (ii) the amorphous Ni(OH)<sub>2</sub> shell functions as an effective water dissociation catalyst  
11 and a low-barrier proton conductive layer to ensure efficient proton supply to the  
12 interfacial Pt sites, creating a proton-enriched local environment and fundamentally altering  
13 the HER to kinetics to the acidic-like Tafel-step limited pathway; (iii) the proton  
14 Ni(OH)<sub>2</sub> shell effectively rejects impurity ions and retards Oswald ripening process,  
15 endowing a high tolerance to water impurities and long-term durability not attainable in the  
16 naked Pt-catalysts.

17 Herein we report a unique design of “Ni(OH)<sub>2</sub>-clothed Pt-tetrapod” core/shell  
18 nanostructure [Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>] to create a local chemical environment that can provide efficient  
19 proton (H<sup>+</sup>) supply to the Pt active sites and greatly boost HER performance in alkaline medium  
20 (Fig. 1B). The designed [Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>] consists of a Pt nano-tetrapod (Pt<sub>tet</sub>) core as the HER  
21 catalyst and an amorphous Ni(OH)<sub>2</sub> shell as the water dissociation (WD) catalysts and proton  
22 conductive layer. In particular, the hydrogen-bond framework in the amorphous Ni(OH)<sub>2</sub> layer  
23 stabilizes the intermediate state of the WD step and facilitates water dissociation into OH<sup>-</sup> and  
24 H<sup>+</sup>, with OH<sup>-</sup> diffusing into the alkaline electrolyte and the H<sup>+</sup> efficiently transporting to the Pt  
25 surface through the amorphous Ni(OH)<sub>2</sub> matrix following a low-barrier cascade pathway  
26 (Grotthuss-like mechanism).<sup>19,20</sup> The rapid water dissociation and low-barrier proton permeation  
27 through amorphous Ni(OH)<sub>2</sub> matrix provide abundant proton supply to the active Pt sites,<sup>19,20</sup>  
28 fundamentally altering the HER kinetics to the acidic-like Tafel step limited pathway.  
29 Meanwhile, the tetrapod feet feature intrinsically thinner Ni(OH)<sub>2</sub> decoration layer and

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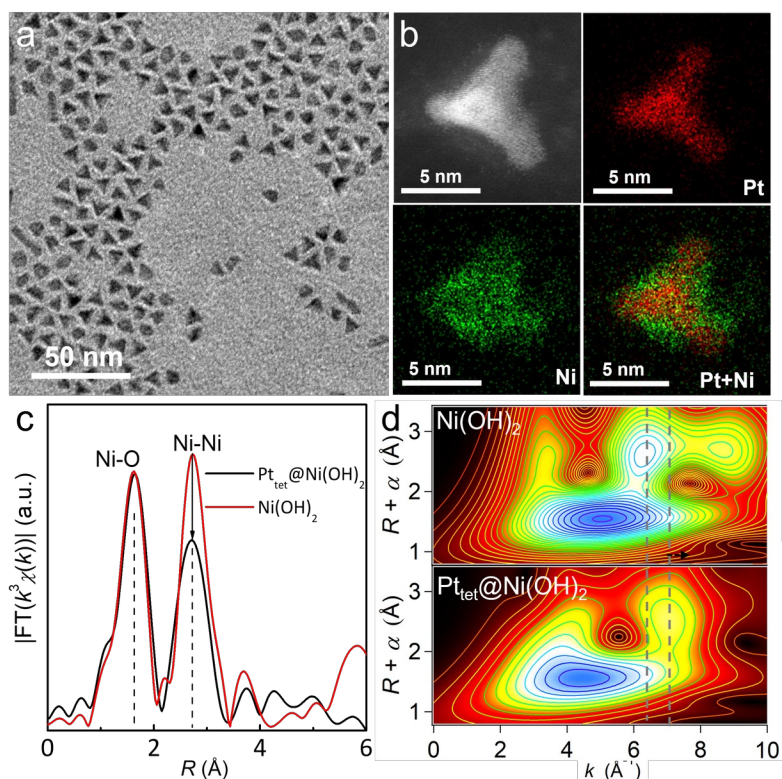
1 geometrically and electrically favorable contacting point with the carbon support<sup>21</sup> to ensure  
2 efficient electron transfer to the catalytic sites for electrocatalytic process. Additionally, the  
3 encapsulation by the proton conductive Ni(OH)<sub>2</sub> efficiently rejects water impurity ions (e.g., Cl<sup>-</sup>  
4 and I<sup>-</sup>) and suppresses Pt atom leaching, leading to significantly enhanced tolerance to water  
5 impurities, long-term operation durability, and the overall catalyst lifetime. Together, the  
6 designed Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> catalysts display acidic-like HER kinetics, achieving a lowest Tafel  
7 slope of 27 mV/dec, a record-high specific activity, and mass activity ( $27.7 \pm 0.5$  mA/cm<sup>2</sup> Pt and  
8  $13.4 \pm 0.4$  A/mg<sub>Pt</sub> at -70 mV vs. reversible hydrogen electrode: RHE) in alkaline electrolyte,  
9 along with excellent durability and tolerance towards halide anions not attainable in conventional  
10 naked Pt catalysts.

### 11 **Structure characterizations of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>**

12 The Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> nanoparticles were prepared through a facile one-pot synthesis (see  
13 Methods). Transmission electron microscopy (TEM) studies reveal the resulting nanoparticles  
14 exhibit uniformly dispersed tetrahedral shapes (Fig. 2a). The high-angle-annular-dark-field  
15 scanning TEM (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) mapping  
16 studies (Fig. 2b) reveal the tetrahedral nanoparticle is composed of a Pt tetrapod core  
17 encapsulated in a Ni-containing shell to form an overall tetrahedral shape, with a total Pt/Ni  
18 atomic ratio of 1.0:2.3 (Extended Data Fig. 3). High-resolution STEM images reveal the Pt  
19 tetrapods grow along <111> directions (Extended Data Fig. 4), while the Ni-containing shell  
20 shows no apparent crystalline order, indicating an amorphous nature (Extended Data Fig. 5). X-  
21 ray photoelectron spectroscopy (XPS) studies show Pt emission peaks can be assigned to Pt (0)  
22 with minor Pt(+2) species; while that of Ni are consistent with Ni(OH)<sub>2</sub> (Extended Data Fig.  
23 6).<sup>22-26</sup> X-ray diffraction (XRD) studies show all diffraction peaks can be assigned to face-  
24 centered cubic Pt (Extended Data Fig. 6), with no apparent diffraction peaks for nickel species,<sup>27-</sup>  
25 <sup>29</sup> further confirming the amorphous nature of the Ni(OH)<sub>2</sub> shell. It is interesting to note that  
26 STEM EDS mapping studies (Fig. 2b) indicate the Pt-tetrapod body is well encapsulated by the  
27 amorphous Ni(OH)<sub>2</sub> shell, while the Pt-tetrapods feet (tips) are less encapsulated. Previous  
28 studies suggested that the Ni adatoms tend to fill the concave sites of the Pt multi-pod structure  
29 following a step-site induced layer-by-layer deposition process.<sup>30</sup> Such a concave-site filling  
30 process on Pt-tetrapods would eventually saturate all concave sites of four (111) faces, forming

1

1 tetrahedral structures with intrinsically less encapsulated tetrapod feet on four convex corners,  
 2 producing a unique structure of “Ni(OH)<sub>2</sub>-clothed Pt-tetrapods”, which is ideally suited for  
 3 isolating most of the Pt surface from the bulk alkaline electrolyte while allowing the less  
 4 encapsulated tetrapod-feet to make robust electrical contacts with the carbon support for  
 5 efficient electron transport to the catalytic sites (Fig. 1).



6

7 **Figure 2| Structural characterizations of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> nanocatalysts.** **a**, The TEM  
 8 image of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>. **b**, HAADF image of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>, and STEM-EDS mapping images of  
 9 Pt, Ni, and Pt+Ni. **c**, Ni K edge EXAFS-FT signals of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and α-Ni(OH)<sub>2</sub>. The  
 10 significantly lower peak intensity and broader peak width at half maximum for the Ni-Ni peak  
 11 in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> vs. crystalline α-Ni(OH)<sub>2</sub> reference indicate the amorphous nature of the  
 12 Ni(OH)<sub>2</sub> shell. **d**, Wavelet transform (WT) for the Ni k<sup>3</sup>-weighted EXAFS signals of α-Ni(OH)<sub>2</sub>  
 13 and Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>. The positive shift of the Ni-Ni coordination signal from 6.4 to 7.0 Å<sup>-1</sup> in the  
 14 k-space indicates Ni is also coordinated with a heavier element, which should be the Pt.

15 The Fourier transform (FT) extended X-ray absorption fine structure (EXAFS) signal of  
 16 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> exhibits a major peak of Ni-O at 1.66 Å, and a second major peak of Ni-Ni at 2.69  
 17 Å (Fig. 2c). We note that the corresponding peak intensities for the Ni-Ni peaks (second  
 18 coordination sphere) are considerably lower than that of standard α-Ni(OH)<sub>2</sub>, suggesting  
 19 abundant Ni defects in the Ni(OH)<sub>2</sub> shell and the high level of structural disorder. Additionally,  
 20 the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> features a notably broader Ni-Ni peak at half maximum with a considerably

2  
3



1 larger Debye-Waller factor than that of the standard crystalline  $\alpha$ -Ni(OH)<sub>2</sub> (Extended Data Table  
2 2), further suggesting the amorphous nature of the Ni(OH)<sub>2</sub> in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and consistent with  
3 the results obtained in TEM and XRD studies. The X-ray absorption near edge structure  
4 (XANES) spectra of Ni K-edge and Pt L<sub>3</sub>-edge suggest that the oxidation state of Ni is slightly  
5 lower than +2, while the oxidation state of Pt is slightly higher than 0 (Extended Data Fig. 7 and  
6 8), indicating a partial charge transfer from Pt to the Ni(OH)<sub>2</sub> at the interface. This charge  
7 transfer is also confirmed by the density functional theory (DFT) calculations of the Bader  
8 charge of interfacial Pt and Ni atoms in the next section.

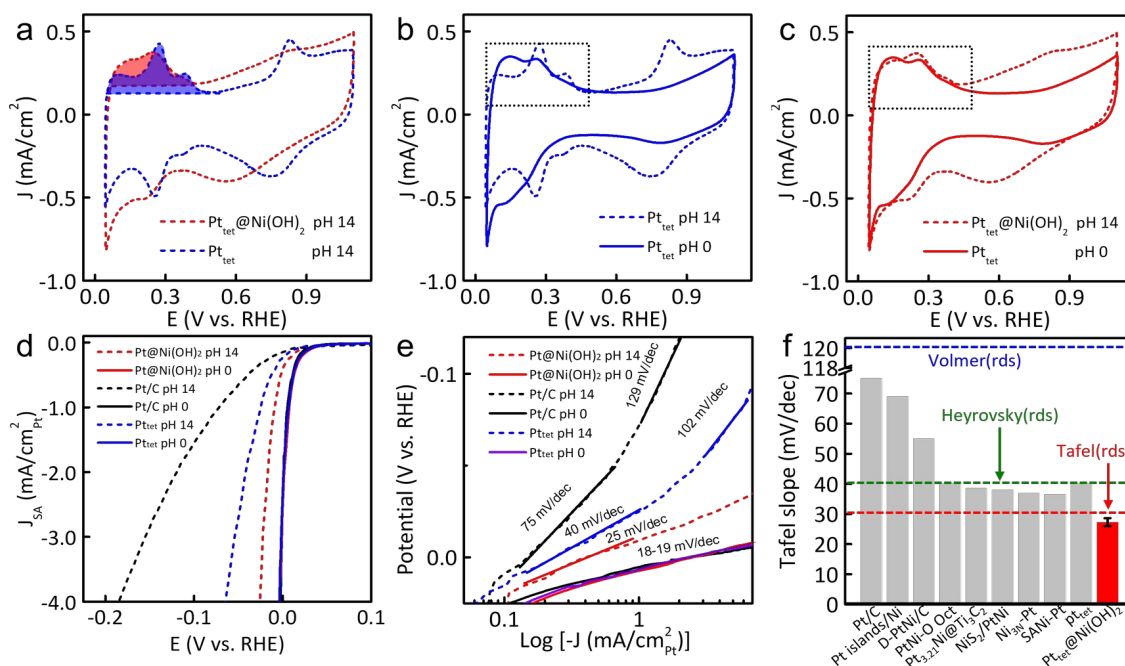
9 EXAFS wavelet transform (WT) analysis is powerful for discriminating the backscattering  
10 atoms. The main signal of Ni-Ni coordination lies at 6.4 Å<sup>-1</sup> in the k-space for standard Ni(OH)<sub>2</sub>  
11 reference (Fig. 2D), which shifts towards higher values (7.0 Å<sup>-1</sup>) for Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>, indicating the  
12 existence of Ni-Pt coordination. This is also consistent with the negative shift of Pt-Pt *k* value  
13 observed in Pt-L<sub>3</sub> edge EXAFS-WT analysis for Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> (Extended Data Fig. 9). Based on  
14 the EXAFS-WT results, the EXAFS spectrum of the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> was analyzed by quantitative  
15 least-square EXAFS curve-fitting using backscattering paths of Ni-Pt, Ni-Ni, and Ni-O  
16 (Extended Data Fig. 10 and Table 2 and 3). The best-fitting results show that the bonding  
17 distance of Ni-Pt coordination is 3.10 Å, considerably larger than the 2.66 Å Ni-Pt distance in  
18 the PtNi alloy, indicating that the Ni and Pt atoms in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> are likely bridged by O  
19 atoms. This is further confirmed by the DFT studies in the following section. Proton permeability  
20 through Ni(OH)<sub>2</sub> shell and acidic-like local environment on Pt surface

### 21 **Proton permeability through Ni(OH)<sub>2</sub> shell and acidic-like local environment on Pt surface**

22 Since it is difficult to directly evaluate the proton permeability through the amorphous  
23 Ni(OH)<sub>2</sub> layer, we have compared cyclic voltammetry (CV) characteristics of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and  
24 the naked Pt<sub>tet</sub> in the alkaline electrolyte to evaluate the proton accessibility of the Ni(OH)<sub>2</sub>  
25 encapsulated Pt core in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> (Fig. 3a). The naked Pt<sub>tet</sub> was obtained by completely  
26 etching the Ni(OH)<sub>2</sub> shell in the acidic electrolyte (Extended Data Fig. 4). Based on the CV  
27 curves, the proton-accessible ECSA can be quantified by the integration of the hydrogen  
28 desorption region (0.05-0.45 V vs. RHE). Interestingly, the ECSA of the original Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>  
29 with full Ni(OH)<sub>2</sub> encapsulation is about 80% of the naked Pt<sub>tet</sub> obtained after completely  
30 removing the surface Ni(OH)<sub>2</sub>, indicating that **the Pt sites in the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> coreshell**

1 structures are mostly accessible to the  $H^+$  even with the encapsulation by the  $Ni(OH)_2$  shell,  
 2 suggesting the proton permeability of the  $Ni(OH)_2$  shell.

3 Most Pt catalysts typically exhibit notably different CV in acidic or alkaline electrolytes  
 4 with highly distinct behavior in the hydrogen desorption region ( $H_{up,d}$ ) region due to distinct local  
 5 proton concentration and different hydrogen adsorption/desorption potential.<sup>28,31,32</sup> Indeed, the  
 6 naked  $Pt_{tet}$  shows a rather different CV behavior in the alkaline vs. acidic conditions (Fig. 3b),  
 7 consistent with previous studies. On the other hand, it is interesting to note that the CV curves  
 8 of the  $Pt_{tet}@Ni(OH)_2$  in the alkaline electrolyte show rather similar behavior in the  $H_{up,d}$   
 9 region to that of the naked  $Pt_{tet}$  in the acidic electrolyte (Fig. 3c), indicating a largely  
 10 comparable proton supply near the Pt sites in  $Pt_{tet}@Ni(OH)_2$  even in bulk alkaline  
 11 electrolyte.



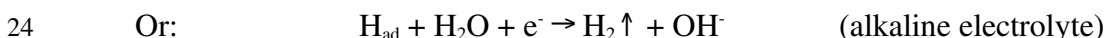
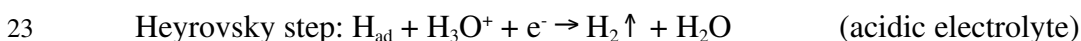
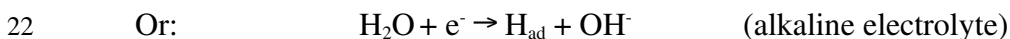
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13 **Figure 3| Electrochemical characterizations of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> nanocatalysts.** **a**, The  
 14 CV of the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and naked Pt<sub>tet</sub> in 1.0 M KOH. The Pt ECSA of the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> with  
 15 full Ni(OH)<sub>2</sub> shell is about ~80 % of the ECSA of the naked Pt<sub>tet</sub>, confirming the proton  
 16 permeability through the amorphous Ni(OH)<sub>2</sub> shell. **b**, The CV curves of the naked Pt<sub>tet</sub> under  
 17 pH 0 and 14 show distinct characteristics in the hydrogen adsorption/desorption region. **c**,  
 18 The CV curves of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> under pH 0 and 14 show highly comparable characteristics in  
 19 hydrogen adsorption/desorption region, indicating a largely comparable proton supply near  
 20 the Pt sites in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> even in bulk alkaline electrolyte. **d**, Polarization curves (specific  
 21 activity) of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>, Pt<sub>tet</sub>, and Pt/C in pH 0 and 14, respectively. **e**, Tafel slopes of  
 22 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>, Pt<sub>tet</sub> and Pt/C pH 0 and 14, respectively. **f**, Comparison of the Tafel slopes of  
 23 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> with the state-of-the-art alkaline HER catalysts. The dotted lines represent the

1 Tafel slopes determined by three distinct rate-determining steps (rds): Volmer step (blue);  
 2 Heyrovsky step (green), and Tafel step (red). All previous studies of Pt or modified Pt  
 3 catalysts show a Tafel slope of  $\sim 40$  mV/dec or above in alkaline electrolytes, consistent with  
 4 a Volmer step or Heyrovsky limited mechanism, while the Tafel slope achieved with our  
 5  $\text{Pt}_{\text{tet}}@Ni(OH)_2$  catalysts is below 29.6 mV/dec, comparable to the typical values observed in  
 6 the acidic electrolyte, suggesting abundant proton supply near Pt surface in our unique  
 7 design of  $\text{Pt}_{\text{tet}}@Ni(OH)_2$  catalysts despite the bulk alkaline electrolyte.

8 The efficient proton supply could lead to considerably improved HER kinetics. To this end,  
 9 we have conducted linear scan voltammetry (LSV) and compared the HER polarization curves  
 10 (normalized by hydrogen desorption area) of  $\text{Pt}_{\text{tet}}@Ni(OH)_2$ , naked  $\text{Pt}_{\text{tet}}$ , and Pt/C in pH 14 and  
 11 pH 0 (Fig. 3d). Expectedly, the Pt/C under pH 14 shows a markedly lower current than under pH  
 12 0. Similarly, the naked  $\text{Pt}_{\text{tet}}$  without the  $Ni(OH)_2$  shell also shows considerably lower HER  
 13 current in the alkaline electrolytes than that in acidic conditions. In contrast, **the  $\text{Pt}_{\text{tet}}@Ni(OH)_2$**   
 14 **shows a much more comparable HER polarization curve between the alkaline condition**  
 15 **and the acidic condition, further suggesting a similar local chemical environment**  
 16 **regardless of the entirely different bulk electrolytes.** Additionally, the uninterrupted increase  
 17 of the HER current from the  $\text{Pt}_{\text{tet}}@Ni(OH)_2$  catalysts during the cathodic LSV scan (Fig. 3d)  
 18 indicates that the amorphous  $Ni(OH)_2$  layer is also  $H_2$  permeable.

19 These specific HER kinetics can be highlighted by the Tafel slope analysis. The HER  
 20 reaction follows three basic steps, with distinct rate-determining steps (rds) and Tafel slopes:<sup>12</sup>



27 Depending on the electrolyte conditions, we expect distinct reaction kinetics. In the acidic  
 28 electrolyte, the sufficient  $H^+$  supply ensures a Tafel-step limited HER pathway, with the Tafel  
 29 step as the rds and an ideal Tafel slope of 29.6 mV/dec. In the alkaline electrolyte where the  $H^+$   
 30 is supplied by water dissociation, the HER reaction typically follows Volmer- or Heyrovsky-step  
 31 limited pathway, with the Volmer step or Heyrovsky step as the rds, and ideal Tafel slopes of  
 32 118.4 and 39.5 mV/dec, respectively.

1 The Pt/C, naked Pt<sub>tet</sub>, and Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> show a low and comparable Tafel slope of around  
2 18-19 mV/dec at pH 0 (Fig. 3e), consistent with previous reports in the acidic environment and  
3 the well-accepted HER mechanism with the Tafel-step limited pathway described above.<sup>33-36</sup> The  
4 smaller than 29.6 mV/dec Tafel slope is possibly ascribed to the backward HOR reaction with H<sub>2</sub>  
5 *in-situ* generated on the Pt surface at a small HER overpotential regime and has also been  
6 commonly observed in previous works.<sup>33-36</sup> On the other hand, the Pt/C, naked Pt<sub>tet</sub>, and  
7 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> show distinct Tafel slopes of 75-129 mV/dec, 40-102 mV/dec, and 27 mV/dec at  
8 pH 14 (Fig. 3e). We note that Tafel slope derivation can be tricky in some situations,<sup>37,38</sup> and  
9 have taken extra caution in deriving the Tafel slopes (See Supplementary Note 2) to ensure a fair  
10 and robust comparison. The much higher Tafel slopes observed for Pt/C and Pt<sub>tet</sub> at pH 14 are  
11 consistent with the Volmer or Heyrovsky limited kinetics expected in the alkaline electrolyte,  
12 **while the much lower Tafel slope of 27 mV/dec observed for Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> at pH 14**  
13 **suggests a distinct Tafel step limited mechanism more similar to that in an acidic**  
14 **environment.**<sup>39-42</sup> Indeed, a closer comparison of the HER activity of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> in pH 14  
15 with that of Pt/C under pH 0-3 condition indicate that the HER activity of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> in pH  
16 14 is largely comparable to that of Pt/C under pH 1 (Extended Data Fig. 11). **These HER**  
17 **polarization analyses further suggest that the Pt sites in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> feature a proton**  
18 **supply rate closed to that of an acidic environment (pH 1-2), consistent with the CV**  
19 **analyses discussed above.**

20 It is interesting to note that the HER Tafel slope of 27 mV/dec achieved with Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>  
21 represents the lowest value achieved in the alkaline electrolyte, which is notably lower than those  
22 achieved previously with Pt or modified Pt catalysts in alkaline conditions (Fig. 3f).<sup>4,43-48</sup>  
23 Although it has been well reported that the surface decoration with Ni species may facilitate the  
24 water dissociation and partly accelerate the HER kinetics on Pt, **most of the surface Pt sites in**  
25 **such decorated catalysts remain exposed to the bulk alkaline electrolyte, and the HER**  
26 **kinetics largely retain the alkaline HER characteristics with the Volmer and Heyrovsky step**  
27 **limited kinetics and an overall Tafel slope ~40 mV/dec or larger** (see Extended Data Table  
28 1). In contrast, a full encapsulation of Pt surface with a proton permeable amorphous Ni(OH)<sub>2</sub> in  
29 our Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> core-shell catalysts isolates most active Pt sites from bulk alkaline electrolyte

1 while ensuring sufficient proton supply to all Pt sites, thus fundamentally altering the HER  
2 pathway to acidic-like Tafel-step limited kinetics.

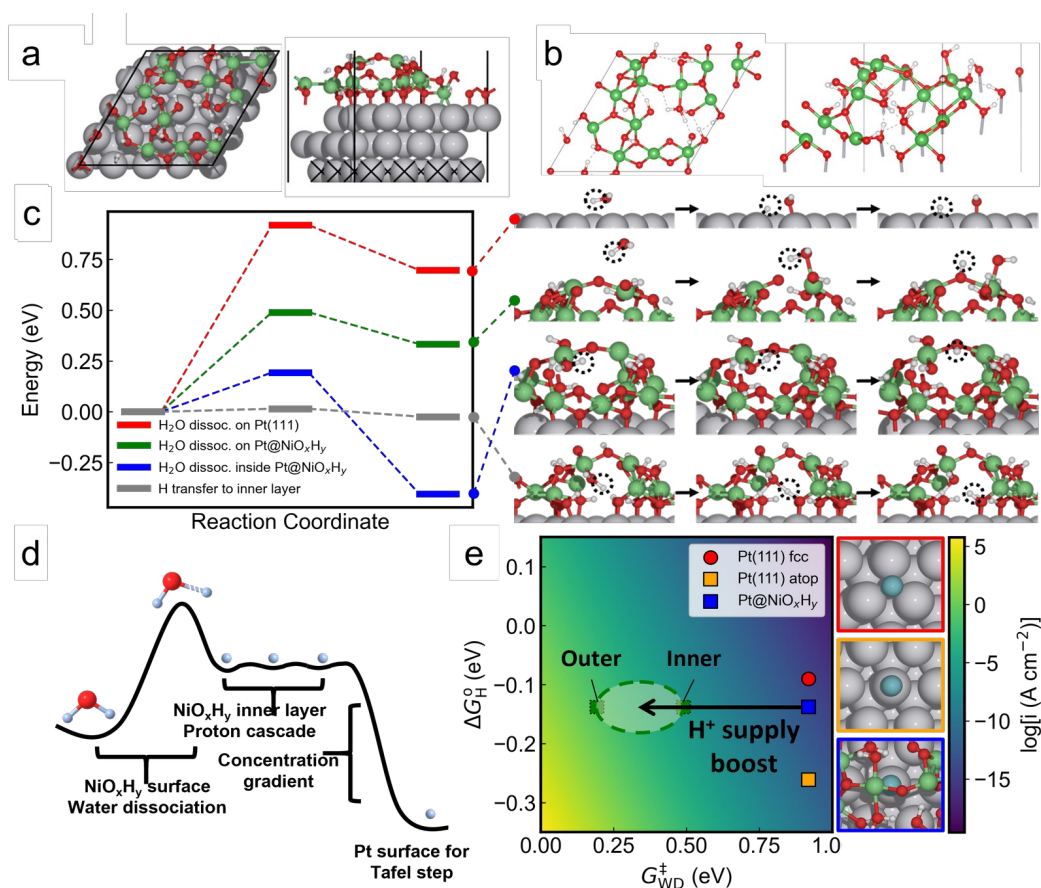
### 3 **Theoretical study on the water dissociation and proton transfer at Pt/Ni(OH)<sub>2</sub> interface**

4 To understand the intriguing acidic-like HER kinetics at Pt/Ni(OH)<sub>2</sub> interface observed in  
5 our experiments, we established an atomistic model of the Pt/Ni(OH)<sub>2</sub> interface using grand  
6 canonical genetic algorithm at the DFT level (see Methods, Extended Data Fig. 12 and 13 for  
7 sampling details), and obtained a highly disordered NiO<sub>x</sub>H<sub>y</sub> layer over 4-layer 4x4 supercell of  
8 Pt(111) as the global minimum configuration (Ni<sub>12</sub>O<sub>25</sub>H<sub>13</sub> (Fig. 4a). The nonstoichiometric H/O  
9 ratio in the Ni<sub>12</sub>O<sub>25</sub>H<sub>13</sub> model is due to the formation of Pt-O-Ni bonds that replace part of the H  
10 atoms in the simulated model, while keeping a finite number of H-O-Ni moieties near the  
11 interface. The coordination number and the bonding length are consistent with the EXAFS  
12 results, confirming the accuracy of this model in simulating the local chemical environment  
13 (Extended Data Table 4). The non-crystalline NiO<sub>x</sub>H<sub>y</sub> has an outer layer that is not directly  
14 linked to Pt, and directly interfaces with bulk electrolyte; and an inner layer representing the  
15 Pt/NiO<sub>x</sub>H<sub>y</sub> interface. The inner layer of NiO<sub>x</sub>H<sub>y</sub> is directly bonded to Pt(111) via the Ni-O-Pt  
16 bonds and occasional Ni-Pt linkages, in agreement with EXAFS studies. Overall, the NiO<sub>x</sub>H<sub>y</sub>  
17 film contains a more flexible Ni-O framework and hydrogen bond matrix featuring a coexistence  
18 of Ni-bonded OH, adsorbed H<sub>2</sub>O, bridging O, and bridging O-H<sup>+</sup> species (Fig. 4b), which is  
19 significantly different from the crystalline layered double hydroxide (LDH) where the Ni-O  
20 framework is more rigid and all the hydroxyls point normal to the basal planes of the crystalline  
21 layers.

22 The NiO<sub>x</sub>H<sub>y</sub> layer influences the electronic structure of surface Pt sites, with the Bader  
23 charges of the surface Pt atoms changing from slightly negative to positive (Extended Data  
24 Fig. 14), in agreement with the XANES results. The surface Pt atoms directly bonded to O atoms  
25 undergo the most significant charge transfer of *circa* +0.40 *e* to NiO<sub>x</sub>H<sub>y</sub>. The exposed Pt atoms  
26 also exhibit a slightly positive charge shift to +0.11 *e*. The reduced electron density on those  
27 exposed Pt makes them no longer able to chemisorb \*H on an *fcc* site but only on the atop site.  
28 The atop H adsorption on an exposed Pt atom has  $\Delta G_H^o$  of -0.14 eV, which is weaker than on the  
29 atop sites (-0.26 eV) on bare Pt(111) but still stronger than the *fcc* sites (-0.09 eV) on bare  
30 Pt(111) (see Extended Data Table 5). Considering the pH of the alkaline electrolyte, the  $\Delta G_H$  of

1 Pt (111) atop, Pt(111) *fcc* sites, and Pt@NiO<sub>x</sub>H<sub>y</sub> atop sites are 0.57 eV, 0.74 eV, and 0.69 eV at  
2 pH 14. They are all on the right side of the Sabatier volcano and far away from the volcano top,  
3 resulting in a significant activity drop compared with that of the acidic condition. (Extended Data  
4 Fig. 15). The relatively small  $\Delta G_H$  difference of 0.05 eV between Pt@NiO<sub>x</sub>H<sub>y</sub> atop sites and  
5 bare Pt *fcc* sites cannot fully account for the experimentally observed drastic HER activity boost  
6 in Pt@NiO<sub>x</sub>H<sub>y</sub>, suggesting additional factors in play.

7 The alkaline HER activity largely relies on the proton generation rate from WD step and the  
8 proton supply rate to the catalytic sites. There have been reports that nanostructured metal  
9 catalysts could enrich local proton concentration without affecting the nature of the active sites to  
10 enhance the HER activity.<sup>32</sup> Since the main H<sup>+</sup> source in the alkaline medium is water, we  
11 investigate the water dissociation pathways on two different NiO<sub>x</sub>H<sub>y</sub> sites (Fig. 4c). For the  
12 reference, water dissociation on Pt(111) has an activation barrier of 0.92 eV and a  $\Delta G$  of 0.70  
13 eV (Fig. 4c red). At the outer layer of NiO<sub>x</sub>H<sub>y</sub>, water gets dissociated at the 4-coordinated Ni,  
14 transferring one H<sup>+</sup> to a neighboring bridging O, with a lower activation barrier of 0.49 eV and a  
15  $\Delta G$  of 0.33 eV (Fig. 4c green), which is similar to the energetics of water dissociation on  
16 crystalline Ni(OH)<sub>2</sub> surface (Extended Data Fig. 16a). Note that the bridging O in Ni-O-Ni is  
17 coordinatively saturated, and the H<sup>+</sup> thus forms a loosely held O-H<sup>+</sup> bridge. The H<sup>+</sup> on such  
18 bridging O-H<sup>+</sup> in top-layer Ni could readily detach and move to other bridging O within NiO<sub>x</sub>H<sub>y</sub>,  
19 which is equivalent to injecting an H<sup>+</sup> into NiO<sub>x</sub>H<sub>y</sub> matrix. After the water dissociates at the  
20 unsaturated Ni sites and transfers the H<sup>+</sup> to the bridging O, the remaining OH<sup>-</sup> on Ni can diffuse  
21 away from the electrode via proton exchange with nearby free water molecules to initiate a new  
22 WD catalytic cycle and maintain charge balance. Deeper into the NiO<sub>x</sub>H<sub>y</sub> layer, water can more  
23 readily dissociate with the assistance of the H-bonding network, by transferring H<sup>+</sup> to nearby  
24 bridging O, showing a lower barrier of 0.19 eV (Fig. 4c blue), 0.3 eV smaller than the case of  
25 crystalline Ni(OH)<sub>2</sub>.



1

2 **Figure 4| DFT calculations of the Pt@NiO<sub>x</sub>H<sub>y</sub> interface.** **a**, The top and side views of the  
 3 global minimum geometry of the disordered NiO<sub>x</sub>H<sub>y</sub> layer on Pt surface from the GCGA  
 4 search. **b**, The hydrogen bond network in the NiO<sub>x</sub>H<sub>y</sub> layers. The Pt(111) substrate is hidden  
 5 for clarity. **c**, Energy profiles of the water dissociation processes on bare Pt(111), the outer  
 6 surface of Pt@NiO<sub>x</sub>H<sub>y</sub>, inside the NiO<sub>x</sub>H<sub>y</sub> matrix, and the proton transfer to the inner layer.  
 7 The geometries of the initial, transition and final states are shown to the right of the  
 8 diagram. Note that due to the Pt-O-Ni linkages nearby, the *fcc* sites cannot stably host an \*H  
 9 as on bare Pt(111), and the atop site is the only available type on Pt covered by NiO<sub>x</sub>H<sub>y</sub>.  
 10 Atomic color code: H, white; O, red; Ni, green; Pt, grey; \*H, blue. **d**, The schematic of the  
 11 reaction pathway on Pt@NiO<sub>x</sub>H<sub>y</sub>. The water dissociates at the NiO<sub>x</sub>H<sub>y</sub> surface to generate  
 12 protons that migrate through the H-bond network in NiO<sub>x</sub>H<sub>y</sub> layer to reach the active Pt  
 13 surface. **e**, HER activity colormap showing log(*j*) at the investigated HER sites as a function  
 14 of ΔG<sub>H</sub><sup>‡</sup> WD and ΔG<sub>H</sub><sup>‡</sup>. The geometries of the \*H are shown on the right.

15 The efficient transport of protons to the interfacial Pt sites is critical for sustained HER. Our  
 16 model of the Pt/Ni(OH)<sub>2</sub> interface indicates that the NiO<sub>x</sub>H<sub>y</sub> is non-stoichiometric and  
 17 amorphous, featuring a complex H-bond network with three relevant deprotonation/protonation  
 18 states including oxo, hydroxyl, and adsorbed water, in which both hydroxyl/oxo and  
 19 water/hydroxyl pairs can facilitate proton transfer through protonation/deprotonation process  
 20 with a rather low activation barrier of 0.02 eV (Fig. 4c) and 0.03 eV (Extended Data Fig. 17).  
 21 These are in sharp contrast to the much higher barrier for intra- and inter-layer proton migration

1 (1.09 and 0.54 eV, respectively) in crystalline Ni(OH)<sub>2</sub> (Extended Data Fig.16 B and C), where  
2 the Ni-O framework is much more rigid and an interwoven H-bond matrix is not present.  
3 Notably, in the final state a proton transfer process in the NiO<sub>x</sub>H<sub>y</sub> matrix, the H<sup>+</sup> is located 1.24 Å  
4 and 1.15 Å from the donor and acceptor O sites, respectively, i.e., longer than a typical O-H  
5 bond (~0.98 Å) but significantly shorter than a typical O · · · H hydrogen bond (~1.97 Å). This  
6 structure is similar to the oxonium ion (H<sub>3</sub>O<sub>2</sub><sup>+</sup>), where the shared proton is located ~1.21 Å from  
7 the O atoms.<sup>49</sup> Therefore, at the thermodynamic equilibrium state, the protons inside  
8 NiO<sub>x</sub>H<sub>y</sub> are delocalized between the donor and the acceptor sites, and follow the Grotthuss-  
9 type mechanism to cascade from the NiO<sub>x</sub>H<sub>y</sub>/electrolyte interface to the Pt/NiO<sub>x</sub>H<sub>y</sub>  
10 interface.

11 In this picture, the water or hydroxyl near the Pt surface gets dissociated and adsorbed by Pt  
12 sites to form Pt-H, leaving a “proton-hole” (hydroxyl or oxo) in the interfacial NiO<sub>x</sub>H<sub>y</sub>, which  
13 provides the effective driving force for the H<sup>+</sup> generated from the water dissociation at the  
14 NiO<sub>x</sub>H<sub>y</sub>/electrolyte interface to cascade inwards to reach the interfacial Pt sites through H-bond  
15 network in NiO<sub>x</sub>H<sub>y</sub> (Fig. 4d). Considering the substantial size difference and more substantial  
16 structural reorganization needed to accommodate water or OH<sup>-</sup> transfer in the NiO<sub>x</sub>H<sub>y</sub> matrix, the  
17 direct transfer of OH<sup>-</sup> or H<sub>2</sub>O would be considerably more sluggish. In this way, the NiO<sub>x</sub>H<sub>y</sub>  
18 layer behaves as a proton selective sieve to effectively isolate the inward diffused H<sup>+</sup> from  
19 the abundant OH<sup>-</sup> in bulk alkaline electrolyte to create an artificially proton-enriched  
20 environment near the Pt catalytic surface.

21 By assuming the WD (alkaline Volmer) step to be the rate-limiting step of the HER at  
22 pH=14, the exchange current density corrected by the promoted WD kinetics can be estimated as  
23 an HER activity descriptor. The WD barriers on the outer surface or inside the NiO<sub>x</sub>H<sub>y</sub> are lower  
24 than on the bare Pt(111) by 0.43 or 0.73 eV, respectively. The accelerated WD kinetics, together  
25 with the proton-permeability of the NiO<sub>x</sub>H<sub>y</sub> matrix, boosts the effective proton supply to the Pt  
26 surface for the later Tafel step. The activity of the Pt@NiO<sub>x</sub>H<sub>y</sub> system is hence substantially  
27 increased from the 10<sup>-11.2</sup> A/cm<sup>2</sup> of bare Pt(111) to the range of 10<sup>-6.1</sup> to 10<sup>-1.1</sup> A/cm<sup>2</sup> (mixed  
28 contribution from inner and outer WD sites in NiO<sub>x</sub>H<sub>y</sub>, respectively) (Fig. 4e), largely  
29 comparable to the performance of Pt(111) at pH=0 (10<sup>-3.2</sup> A/cm<sup>2</sup>).



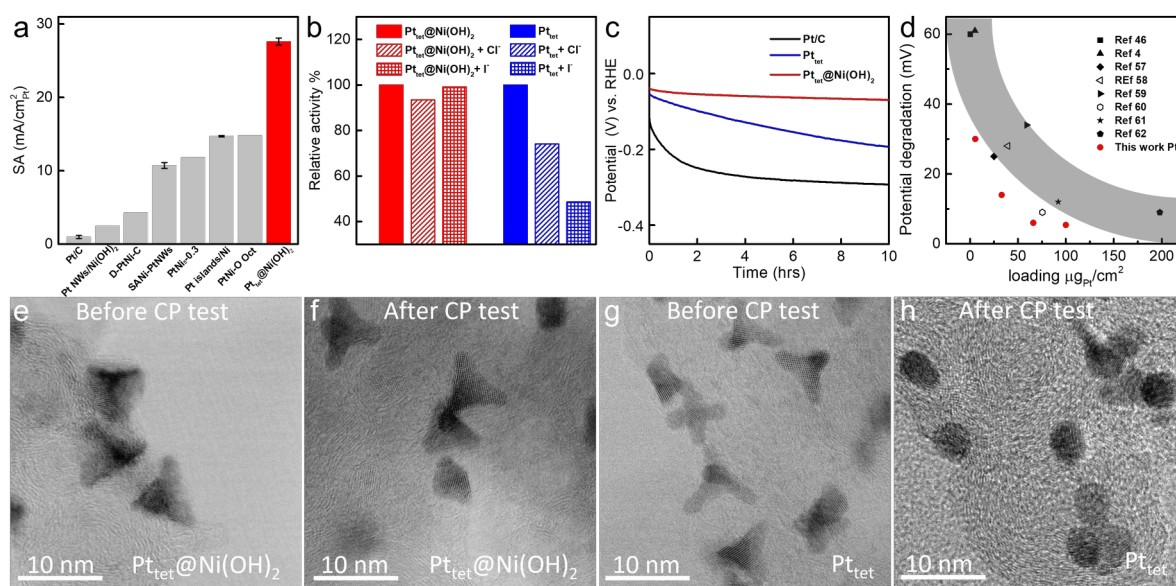
1 Although the WD kinetics of transition metal hydroxides have been suggested to explain the  
2 enhanced HER activity of Pt/transition metal oxide catalysts, a direct measurement of the  
3 enhanced WD steps on electrocatalyst is challenging due to the difficulties to decouple with  
4 subsequent hydrogen production steps. To directly elucidate the role of the **amorphous** Ni(OH)<sub>2</sub>  
5 shell as an efficient WD catalyst, we tested the WD activity of the Ni(OH)<sub>2</sub> shell by using bipolar  
6 membrane (BPM) electrolysis. The BPM electrolysis is conducted in an H-cell where a  
7 combination of AEM and PEM is used to separate the acidic HER half-cell (pH=0) and alkaline  
8 OER half-cell (pH=14). The Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> or Pt<sub>tet</sub> were uniformly dispersed at the interface  
9 between the PEM and AEM as the WD catalysts. The standard potential required to drive WD is  
10 0.83 V<sup>50,51</sup>, above which the WD current increases exponentially until reaching the mass transport  
11 limit. The WD polarization curves (**Extended Data Fig. 18**) reveal that the pure BPM with no  
12 catalyst, with the naked Pt<sub>tet</sub> core or with **crystalline Ni(OH)<sub>2</sub> nanoplates** require an overpotential  
13 of 1.64 V, 0.97 V, and 0.64 V, respectively, to reach the 50 mA/cm<sup>2</sup>, while that with the  
14 amorphous Ni(OH)<sub>2</sub> shell (in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>) only needs 0.18 V overpotential to reach 50  
15 mA/cm<sup>2</sup>, demonstrating a much faster WD kinetics, and experimentally confirming the  
16 exceptional WD catalytic activity of the amorphous Ni(OH)<sub>2</sub>.

### 17 **Electrochemical HER performance of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>**

18 With greatly improved HER kinetics from the selective enrichment of proton by the  
19 Ni(OH)<sub>2</sub> proton sieve, the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> coreshell catalysts show a record-high specific activity  
20 (SA) of 27.7 mA/cm<sup>2</sup> Pt at -70 mV vs. RHE at pH 14, which is 28 times and 6 times that of Pt/C  
21 and naked Pt<sub>tet</sub>, respectively; and considerably higher than the previous state-of-art (14.8 mA/cm<sup>2</sup>  
22 Pt@ -70 mV vs. RHE) (Fig. 5a).<sup>3,4,43,46,47,52</sup> We note the SA achieved with Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> is also  
23 higher than that of the recently reported Pt-shell catalysts with elaborate strain engineering on Pd  
24 nanocubes.<sup>53</sup> Further, since the Ni(OH)<sub>2</sub> shell only moderately reduces the ECSA, such a high SA  
25 observed in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> has also directly led to a record-high MA of 13.4 A/mg<sub>Pt</sub> @ -70 mV  
26 vs. RHE, which is 18-fold higher than that of the commercial Pt/C, and 4.6-fold of that of naked  
27 Pt<sub>tet</sub>; and represent the best among the state-of-the-art Pt-based HER catalysts in the alkaline  
28 electrolyte (Extended Data Table 6).<sup>3,4,6,17,18,43,46,47,52,54</sup> Additionally, considering the greatly  
29 reduced Tafel slope with the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> design, the relative benefit of the increased SA and  
30 MA could be further amplified at higher overpotential in practical HER conditions.

1

1 The proton **conductive** Ni(OH)<sub>2</sub> **shell** could help isolate the active Pt sites from the bulk  
 2 electrolyte environment and thus improve the catalytic tolerance to water impurities with  
 3 competitive adsorption or capability of etching. For example, halide anions (e.g., Cl<sup>-</sup>) represent  
 4 common impurity anions that can strongly bind with Pt sites and partly suppress the catalytic  
 5 activity. **In this regard, the amorphous Ni(OH)<sub>2</sub> shell may help block halide anions from the**  
 6 **active Pt sites due to the lack of transport path and Donnan exclusion effect.**<sup>55</sup> To this end, we  
 7 have evaluated the Cl<sup>-</sup> and I<sup>-</sup> tolerance of the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and the naked Pt<sub>tet</sub> catalysts. Notably,  
 8 the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> maintains essentially the same HER current level in the presence of 0.5 M Cl<sup>-</sup>  
 9 or 0.25 M I<sup>-</sup> in electrolyte, while the Pt<sub>tet</sub> shows a substantial current drop by 26% and 52%,  
 10 respectively (Fig. 5b and Extended Data Fig. 19). **Such a high tolerance to ionic impurities**  
 11 **could help relax the water purity requirements in practical water electrolysis, which is a**  
 12 largely unaddressed matter but could be significant since the **cost of ultrapure water and the**  
 13 **relevant circulation system constitutes a significant fraction** (up to 13%) of the total hydrogen  
 14 production cost.<sup>56</sup>



15 **Figure 5| Evaluation of HER activity and stability** **a**, Comparison of the specific activity  
 16 (SA) of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> with the state-of-the-art alkaline HER catalysts. Error bar is added  
 17 unless they are not provided in the cited literature. **b**, Relative activity of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and  
 18 Pt<sub>tet</sub> in pure 1.0 M KOH, 1.0 M KOH + 0.5 M Cl<sup>-</sup>, and 1.0 M KOH + 0.25 M I<sup>-</sup>. **c**,  
 19 Chronopotentiometry (CP) stability test of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>, Pt<sub>tet</sub>, and Pt/C. **d**, Comparison of the  
 20 stability of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> with different loading with the state-of-the-art alkaline HER  
 21 catalysts. We should note that there are numerous parameters in the stability tests,  
 22 including Pt loading amount, current density, operation time, etc. It is extremely difficult to  
 23 have all the parameters identical when compared with the literature data. Here we  
 24

2  
3

1 specifically selected the stability results from the literature which conduct the CP test with a  
2 fixed current density at 10 mA/cm<sup>2</sup> (Ref 59 is under 20 mA/cm<sup>2</sup>) and duration longer than 10  
3 hours. Only the potential degradation data within the first 10 hours are taken into  
4 consideration. (e-h) Representative HRTEM images of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and Pt<sub>tet</sub> before and after  
5 the stability tests.

6 Additionally, the Ni(OH)<sub>2</sub> encapsulation can also prevent the Pt surface from dissolution,  
7 leaching, ripening or aggregation. Chronopotentiometry (CP) tests were conducted to evaluate  
8 the durability of the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> catalysts at a constant current of 10 mA/cm<sup>2</sup> (normalized by  
9 electrode geometrical area). Our CP studies show that Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> coreshell catalysts exhibit  
10 only a 30 mV overpotential increase over the 10-hour continuous test (Fig. 5c), much lower than  
11 those of naked Pt<sub>tet</sub> and Pt/C under the same test conditions (140.5 mV and 177 mV potential  
12 degradation in 10 hours, respectively). We note that such CP test evaluation of HER catalyst  
13 durability is highly dependent on the catalyst loading amount. To more comprehensively  
14 compare the stability of our Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> catalysts with other Pt HER catalysts under similar  
15 operation conditions, we plotted the potential degradation vs. the loading amount of different  
16 catalysts reported in recent literature (Fig. 5d and Extended Data Fig. 20).<sup>4,46,57-62</sup> It is apparent  
17 that the potential degradation decreases substantially with the increasing Pt loading. This is not  
18 surprising since higher loading usually comes with more active surface sites, which reduces the  
19 average catalytic current per active site and thus reduces the chemical stress or slows the surface  
20 degradation process. Indeed, our Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> catalysts with 4 different loading amounts show  
21 a similar trend with a notably smaller potential degradation at the higher catalyst loading levels  
22 (Fig. 5d and Extended Data Fig. 20). More importantly, the potential degradation of  
23 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> catalysts is considerably below the reference curve, demonstrating the more stable  
24 nature of the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> coreshell catalysts (Fig. 5d).

25 In general, the Pt nanocatalysts typically feature a relatively high surface energy, and may  
26 readily undergo surface reconstruction or ripening process to minimize the total surface energy,<sup>63</sup>  
27 particularly under HER conditions where the dynamic interaction with surface bonded H atoms  
28 (Pt-H) was found to considerably accelerate surface Pt atom diffusion<sup>64</sup>. Such surface  
29 reconstruction or ripening process could lead to the loss of originally designed surface structure  
30 and the irreversible activity degradation. In this regard, the encapsulating Ni(OH)<sub>2</sub> proton  
31 conductive shell in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> can effectively retard Pt surface atom migration to ensure  
32 high structural stability and durable activity durability. Indeed, our studies demonstrate that the

1 tetrahedral shape of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and the embedded Pt tetrapods are well-retained (Fig. 5e, f;  
2 and Extended Data Fig. 21) with little Pt loss after the long-term durability test. In contrast, the  
3 naked Pt<sub>tet</sub> without Ni(OH)<sub>2</sub> shell undergoes severe ripening with higher Pt loss during the  
4 stability test and turns into nearly spherical nanoparticles (Fig. 5g, h and ; and Extended Data  
5 Fig. 22). Our additional stability test with periodic surface cleaning reveal that the activity loss  
6 observed in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> can be largely recovered after surface cleaning, indicating little  
7 irreversible catalyst degradation, which is consistent with the well-retained coreshell  
8 morphology. On the other hand, the Pt<sub>tet</sub> and Pt/C show considerable irreversible degradation due  
9 to the severe surface reconstruction and ripening behavior (Extended Data Fig. 22).

## 10 Conclusion

11 In summary, we have reported a unique design of “Ni(OH)<sub>2</sub>-clothed Pt-tetrapod” coreshell  
12 nanostructure, in which the amorphous Ni(OH)<sub>2</sub> shell functions as a water dissociation catalyst  
13 and proton conductive shell to isolate the catalytic Pt surface from the bulk alkaline electrolyte  
14 while ensuring efficient proton supply to Pt sites. It delivers an acidic-like HER kinetics in bulk  
15 alkaline electrolyte, with the lowest Tafel slope and the highest alkaline HER activity among all  
16 Pt-based catalysts reported to date. Moreover, the encapsulation of the catalytic surface by the  
17 proton conductive shell considerably slows the dissolution/diffusion of Pt atoms from catalytic  
18 surfaces and suppresses the undesirable poisoning effect from impurity ions, thus ensuring high  
19 structural stability and activity durability that is difficult to achieve in the naked Pt-catalyst  
20 designs. The markedly improved alkaline HER activity and presents an attractive catalyst  
21 material for alkaline water electrolyzers and renewable chemical fuel generation. Additionally,  
22 the demonstrated capability to fundamentally modify the reaction kinetics by tailoring the local  
23 chemical environment may be expanded as a general strategy for the design of a new generation  
24 of electrocatalysts with a favorable reaction environment and high selectivity or durability for a  
25 wide range of fundamentally and technologically important electrochemical reactions.

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## 7 **Methods**

8 **Chemicals.** Platinum(II) acetylacetonate [Pt(acac)<sub>2</sub>, Pt 48.0%], nickel(II) acetylacetonate  
9 [Ni(acac)<sub>2</sub>, 95%], glucose, tungsten(0) hexacarbonyl (W(CO)<sub>6</sub>, 97%), oleylamine (> 98%), 1-  
10 octadecene (ODE, > 90%), nickel(II) nitrate hexahydrate [Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], Cetrimonium  
11 bromide ([C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>]Br and Nafion® 117 solution (~ 5%) were purchased from Sigma  
12 Aldrich. Commercial Pt/C catalyst (10 wt% Pt, and particle size ~ 2 nm) was purchased from  
13 Alfa Aesar. Ethanol (200 proof) was obtained from Decon Labs, Inc. Potassium hydroxide  
14 (KOH) was purchased from Fisher Chemical. All the above reagents were used as received  
15 without further purification. Carbon black (Vulcan XC-72) was received from Cabot Corporation  
16 and was annealed for 2 hours under Ar gas environment at 400 °C before being used. The  
17 deionized water (18 MΩ/cm) was obtained from an ultra-pure purification system (Milli-Q  
18 advantage A10). The Naftion™ 117 (PEM) and the Fumasep Fas-50 (AEM) were purchased  
19 from the Fuel cell Store.

20 **Synthesis.** In a 30 mL glass vial, 20 mg Pt(acac)<sub>2</sub>, 25.6 mg Ni(acac)<sub>2</sub>, 32 mg W(CO)<sub>6</sub> and 135  
21 mg glucose were dissolved in a mixture of 3 mL oleylamine and 2 mL octadecene. The mixture  
22 was sonicated for 1 hour and the resulting homogenous solution was kept at 80 °C for 2.5 hours  
23 and then heated to 140 °C for another 8 hours. After the reaction, the precipitate was centrifuged  
24 out at 12100 r.p.m. and washed by ethanol/hexane (25 mL/5 mL) three times. The final product  
25 was suspended in 10 mL cyclohexane. In a 30 mL glass vial, 30 mg carbon black (the carbon  
26 black was annealed under Ar at 200 °C for 1 hour before use) was sonicated in 15 mL ethanol for  
27 1 hour. 5 mL Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> hexane solution was then added into the carbon black/ethanol  
28 solution and the mixture was sonicated for another 1 hour. The catalysts were centrifuged out at  
29 12100 r.p.m. and washed with cyclohexane/ethanol solution three times, followed by being dried  
30 in the vacuum oven for 1 hour. The Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>/C were then annealed in the air at 200 °C for  
31 2 hours to fully remove the surface remaining ligands. The Pt yield is about 40%, on the scale of  
32 6 mg<sub>Pt</sub>/ batch. It has been scaled up to 120 mg<sub>Pt</sub> per batch. The crystalline Ni(OH)<sub>2</sub> nanoplates

1 were synthesized via adding 0.5 mL 30 wt% ammonia water drop by drop into 100 mL Ni(NO)<sub>3</sub>  
2 solution (10g/L) with 0.25 g CTAB as the surfactant.

3 **Characterizations.** Transmission electron microscopy (TEM) images were taken on an FEI T12  
4 operated at 120 kV. Atomic resolution high angle annular dark-field scanning transmission  
5 electron microscopy (HAADF-STEM) images and X-ray energy dispersive spectroscopy (EDS)  
6 mapping were taken on FEI Titan Cubed Themis G2 300 at 200 kV and JEOL Grand ARM  
7 300CF TEM/STEM with double spherical aberration-correctors operated at 300 kV. Samples for  
8 TEM measurements were prepared by dropping 10-20  $\mu$ L nanoparticles dispersion in hexane on  
9 a carbon-coated copper grid (Ladd Research, Williston, VT). Powder X-ray diffraction patterns  
10 (PXRD) were collected on a Panalytical X'Pert Pro X-ray Powder Diffractometer with Cu-K $\alpha$   
11 radiation. The composition of catalysts was determined by inductively coupled plasma atomic  
12 emission spectroscopy (ICP- AES, Shimadzu ICPE-9000) as well as SEM-EDS (JEOL JSM-  
13 6700F FE-SEM). X-ray photoelectron spectroscopy (XPS) tests were done with Kratos AXIS  
14 Ultra DLD spectrometer.

15 **X-ray adsorption data analysis.** Ni K-edge and Pt L<sub>3</sub>-edge X-ray absorption spectra were  
16 acquired under ambient conditions in fluorescence and transmission modes at beamline 1W2B of  
17 the Beijing Synchrotron Radiation Facility(BSRF), using a Si (111) double-crystal  
18 monochromator. The storage ring of BSRF was operated at 2.5 GeV with a maximum current of  
19 250 mA in top-up mode. While the energy was calibrated using Ni/Pt foil, the incident,  
20 transmitted and fluorescent X-ray intensities were monitored by using standard ion chambers and  
21 Lytle-type detector, respectively.

22 XAS analysis was performed according to standard procedures using the ATHENA and  
23 ARTEMIS modules implemented in the IFEFFIT software package.<sup>65</sup> The EXAFS signal was  
24 first obtained by background-subtraction and normalization, then the  $\chi(k)$  data were Fourier-  
25 transformed to real (R) space using a Hanning window. To obtain the quantitative structural  
26 parameters around the central atoms, a least-squares curve-fitting analysis of the EXAFS  $\chi(k)$   
27 data was carried out based on the EXAFS equation in R-space. The structural models were  
28 constructed based on the crystal structures of Ni(OH)<sub>2</sub>, with the scattering amplitudes, phase  
29 shifts, and photoelectron mean free path for all paths calculated with the ab initio code FEFF  
30 8.5.<sup>66</sup>

1 **Electrochemical Measurements.** To obtain a homogeneous catalyst ink, 1 mg of dried  
2 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>/C was mixed with 1 mL ethanol and sonicated for 5 minutes. Then, 10  $\mu$ L (20  $\mu$ L  
3 for stability test) of Nafion (5 wt%) was added to the solution. After sonication, 20  $\mu$ L of the  
4 homogeneous ink was dropped onto a 5 mm diameter glassy carbon electrode (0.196 cm<sup>2</sup>, Pine  
5 Research Instrumentation). The ink was dried under ambient air before electrochemical testing.

6 All electrochemical tests were carried out in a three-electrode cell from Pine Research  
7 Instrumentation. The working electrode was a glassy carbon rotating disk electrode (RDE)  
8 coated with corresponding catalysts. The reference electrode was a Hg/HgO electrode from CH  
9 Instrument and was calibrated in 1.0 M KOH with saturated H<sub>2</sub>. A graphite rod was used as the  
10 counter electrode. Cyclic voltammetry was conducted in 1.0 M KOH and 1.0 M HClO<sub>4</sub> between  
11 50 mV to 1100 mV vs. RHE at a sweep rate of 100 mV/s. The polarization curves were tested  
12 between -200 mV to 100 mV vs. RHE at a sweep rate of 5 mV/s in 1.0 M KOH and 1.0 M  
13 HClO<sub>4</sub> with a Pt loading of 5.1  $\mu$ g/cm<sup>2</sup> for Pt/C and 5.6  $\mu$ g/cm<sup>2</sup> for Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and Pt<sub>tet</sub>, under  
14 a rotation speed of 1600 r.p.m. The solution resistances were measured via impedance test.  
15 ECSA was measured through the hydrogen desorption region in N<sub>2</sub> saturated 1 M KOH. The  
16 bipolar membrane test was conducted in the H-cell. The BPM was fabricated by wet pressing the  
17 Nafion 117 PEM and the Fumasep Fas-30 AEM and removing all the bubbles in between two  
18 films. When desired, the WD catalysts were pre-deposited on the PEM and the press together  
19 with AEM to form BPM with sandwiched WD-CL. The stability test was performed with  
20 chronopotentiometry under 10 mA/cm<sup>2</sup> in Ar purged KOH for 10 hours.

21 **Computational Methods: GCGA sampling.** To sample the non-stoichiometric chemical  
22 subspace efficiently, we use the grand canonical genetic algorithm (GCGA) as implemented in  
23 our open-source Python package GOCIA (<https://github.com/zishengz/gocia>). The GA is an  
24 evolutionary global optimization algorithm that has been successfully applied to various fields  
25 including molecular design and structural search of gas-phase and supported clusters,<sup>67-69</sup> and the  
26 GC feature in our program allows variation of both the compositional and geometrical degrees of  
27 freedom to explore a larger chemical space of surface restructuring and adsorbates interactions,  
28 with minimal prior knowledge.<sup>70,71</sup> GCGA has been employed to efficiently explore the non-  
29 stoichiometric restructuring, under a certain chemical potential, of ternary alloys, 2D materials,  
30 supported metal clusters, etc.<sup>70,72</sup>

1 In the GCGA algorithm, the grand canonical free energy (grand potential) instead of the potential  
2 energy is the quantity to optimize. The grand potential is approximated by:

$$3 \quad \Delta G = E(\text{slab}) - E(\text{substrate}) - \sum N_i \mu_i \quad (1)$$

4 Where  $E(\text{slab})$  is the electronic energy of the whole optimized slab;  $E(\text{substrate})$  is the  
5 electronic energy of the Pt(111) substrate;  $N_i$  is the number of element  $i$  atoms in the adlayer;  $\mu_i$   
6 is the chemical potential of element  $i$  which are estimated from reference species as follows:

$$7 \quad \mu_c = E_c \quad (2)$$

$$8 \quad \mu_H = \frac{1}{2} E(H_2) + 2.3 k_B T \text{pH} \quad (3)$$

$$9 \quad \mu_O = E(H_2O) - 2 \mu_H \quad (4)$$

10 A population size of 30 and a mutation rate of 30% are chosen for the GCGA sampling. The pool  
11 of initial candidates is generated using the bond length distribution algorithm (BLDA) which is a  
12 random structure generation method based on the covalent radii of the atoms.<sup>73</sup> A pre-  
13 optimization with Hookean potential is performed to produce reasonable starting geometries  
14 before they are fed to electronic structure method codes for local optimization and energy  
15 evaluation. Mating between the candidates alive to create offspring by the Split-and-splice  
16 operation,<sup>74</sup> in which the parent slabs are cut along a random plane and then spliced together. The  
17 fitness factor is assigned to each candidate based on the mating counts and the grand canonical  
18 free energy. Candidates with higher fitness are more probable to mate. The similarity check  
19 against the current population is performed before adding any new candidate to remove  
20 duplicates. Mutation of the randomly chosen offspring by adding or removing an adatom or  
21 adsorbate, or by rattling the surface atoms along random vectors drawn from a normal  
22 distribution. If an offspring is too similar to its parent, its mutation rate is raised to 100%. Upon  
23 the addition of each offspring to the population, the candidate with the lowest fitness is archived  
24 to maintain the population size. The structures with detached  $\text{NiO}_x\text{H}_y$  layers or unbound water  
25 molecules are removed from the population to avoid sampling into chemically irrelevant regions  
26 of the PES. A flowchart summarizing the workflow of the automated GCGA sampling is  
27 provided in Extended Data Fig. 11.

1 Note that the ratio of exposed surface Pt atoms (1/16 for the GM structure) may be  
 2 underestimated due to sampling constraints as described in the last paragraph to focus the GCGA  
 3 search direction on the interfacial structures. However, this model could well reflect (1) the  
 4 interfacial structure where the Pt core and NiO<sub>x</sub>H<sub>y</sub> shell make the most contact and (2) the  
 5 reactivity of NiO<sub>x</sub>H<sub>y</sub> and the hydrogen bond matrix that is still present even above the surface Pt  
 6 regions that are less directly bonded to the NiO<sub>x</sub>H<sub>y</sub> layer.

7 **Model set-up and DFT methods.** The Pt surface is modeled by a 4-layer 4x4 supercell of  
 8 Pt(111) surface termination with the upper two layers relaxed as a surface region while the  
 9 bottom two layers are constrained as bulk region (Extended Data Fig. 11). A vacuum of 15 Å  
 10 thickness is added in the Z direction to avoid spurious interactions between periodic images. The  
 11 coverage of Ni was chosen to be 12 atoms per supercell for the production run, according to the  
 12 lattice parameters of Pt (2.812 Å) and Ni(OH)<sub>2</sub> (3.165 Å):

$$13 \quad 16 \text{ atoms/supercell} \times \left( \frac{2.812 \text{ \AA}}{3.165 \text{ \AA}} \right)^2 \approx 12 \text{ atoms/supercell} (5)$$

14 Which is the estimated minimal Ni coverage to fully cover the Pt(111) at the direct interface and  
 15 to capture the interfacial chemistries while not heavy sample into the Ni(OH)<sub>2</sub>-like regions.

16 The local optimization and energy evaluation of the generated structures are performed with the  
 17 PBE functional<sup>75</sup> and PAW pseudopotentials<sup>76</sup> using the VASP program.<sup>77-80</sup> D3 correction is  
 18 used to account for the dispersion interactions,<sup>81</sup> and dipole corrections are applied to remove the  
 19 artificial electrostatic fields arising from asymmetric slabs in periodic boundary conditions. The  
 20 convergence criteria for geometry (SCF) are set to 10<sup>-5</sup> (10<sup>-6</sup>) eV and 10<sup>-2</sup> eV/Å for forces. Due to  
 21 the relatively large system and sampling size, only the  $\Gamma$  *k*-point is sampled in the reciprocal  
 22 space of the Brillouin zone throughout, and the cutoff energy for the kinetic energy of the plane-  
 23 waves was 400 eV. Reaction energies are refined at higher cutoff energy of 500 eV and with the  
 24 implicit solvation model using the VASPsol code.<sup>27,82</sup> The Bader charges are calculated from the  
 25 charge density output using the Bader Charge Analysis code.<sup>83</sup>

## 26 **Calculation of adsorption free energy and activation barriers.**

27 The adsorption energy is calculated by:

$$28 \quad \Delta E_H = E(\dot{i}H) - E(\dot{i}) - E(H) \quad (6)$$

1

1 where the \* stands for the adsorption site. The adsorption free energy of H is calculated by:

$$2 \quad \Delta G_H^o = \Delta E_H + ZPE(\ddot{H}) - T \Delta S_H \quad (7)$$

3 where the  $(ZPE - T \Delta S_H)$  term at room temperature is taken from literature to be +0.24 eV<sup>84</sup>.

4 The term is pH-independent and reflects the intrinsic adsorption property of the site at standard  
5 condition.

6 The pH-corrected adsorption free energy of H is calculated by shifting the chemical potential of  
7 the reference state of proton by the concentration dependence of the entropy,  $-k_B T \ln[H^+] = \ln 10$   
8  $k_B T \text{pH}$ ,<sup>85</sup> which yields:

$$9 \quad \Delta G_H = \Delta G_H^o + \ln(10) k_B T \text{pH} \quad (8)$$

10 The exchange current densities  $i_0$  are calculated from  $\Delta G_H$  following the procedures described in  
11 Ref<sup>84</sup>. The preexponential factors are treated as the same for all the elementary steps.

12 Since the rate-limitng step of alkaline HER is the Volmer step, the kinetics of water dissociation  
13 is expected to induce a direct boost on the overall HER rate by controlling the rate of proton  
14 supply. Such thermochemistry-independent contribution is approximated by:

$$15 \quad i' = \exp\left(\frac{-\Delta G_1^\ddagger - \Delta G_0^\ddagger}{k_B T}\right) \cdot i_0 \quad (9)$$

16 Where  $\Delta G_0^\ddagger$  and  $\Delta G_1^\ddagger$  represents the free enegy barrier of the water dissociation process on the  
17 reference system Pt(111) and other sites of interest in the restructured slab. The  $i'$  is the  
18 corrected exchange current density. The estimation assumes (i) that water dissociation on  
19 different sites shares the same preexponential factor; (ii) the HER rate is solely determined by the  
20 kinetics of the Volmer step, and the produced \*H are consumed by Tafel step at Pt surface within  
21 a much shorter time scale; (iii) there are no significant recombination of proton and hydroxide  
22 from water dissociation because the hydrogen permeable NiOxHy effectively seperates the H<sup>+</sup>  
23 from the recombination with the OH<sup>-</sup>.

## 24 **Data availability**

25 The data that support the plots within this paper and other findings of this study are available  
26 from the corresponding author upon reasonable request.

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3

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12 **Author contributions.** X.D. and Y.H. designed the research. C.W. performed the synthesis,  
13 most of the structural characterizations, and electrochemical tests. J.D. and T.H. performed the  
14 XAS measurement and analyzed the EXAFS and XANES data. Z.Z. and A.N.A. conducted DFT  
15 calculations. S.W., H.P., J.H., A.H.S. assisted in the synthesis. Z.L. and B.D. assisted in the  
16 SEM-EDS and XRD analysis. M.X. conducted the aberration-corrected STEM characterization  
17 under the supervision of X.P. The paper was co-written by C.W., X.D., J.D., Z.Z., A.N.A. and  
18 Y.H. The research was supervised by X.D., Y.H. and A.N.A. All authors discussed the results  
19 and commented on the manuscript. **Competing interests:** The authors declare that they have no  
20 competing interests.

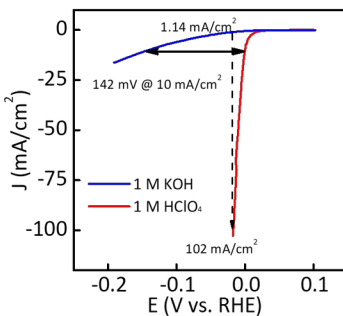
21 | **Competing financial interests. The authors declare no competing financial interests.**

22 | **Additional information**

23 Extended data is available for this paper.



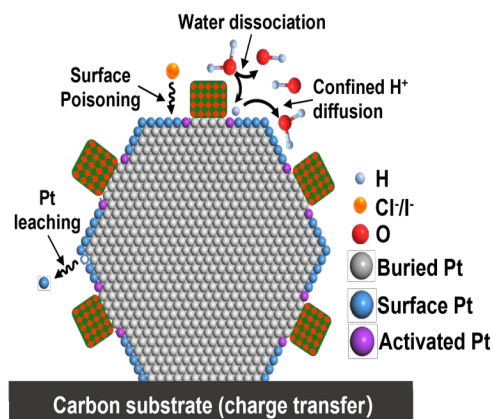
## 1 Extended data



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### 3 Extended Data Fig. 1| The comparison of Pt/C HER activity in acid and base.

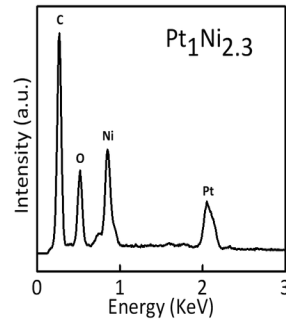
4 There is a 142 mV difference between the activity of Pt/C (5.1  $\mu\text{g}_{\text{Pt}}/\text{cm}^2$ ) in acid and base  
 5 at a current density of 10 mA/cm<sup>2</sup>. In a real application, the current is always on the  
 6 scale of 500 mA/cm<sup>2</sup>-1000 mA/cm<sup>2</sup>, and the Tafel slopes in the acidic case and basic  
 7 case are 29.6 mV/dec and 118.4 mV/dec respectively. Thus this potential difference will  
 8 be significantly amplified at higher current density in the real application. Moreover, at -  
 9 20 mV vs. RHE, the activity under pH 0 is about 89.5 times higher than that under pH  
 10 14, almost two orders of magnitude. For the same reason, the activity difference will  
 11 also be amplified in the real application and will potentially be enlarged to 2-3 orders of  
 12 magnitude, or even bigger.



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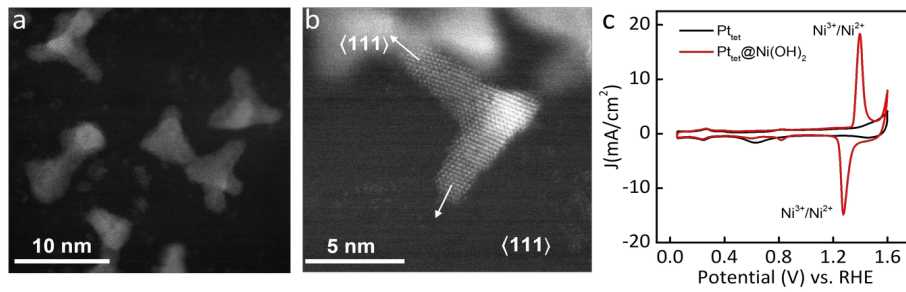
2 **Extended Data Fig. 2 | Pt NPs decorated with crystalline Ni species.** The  
 3 decoration of Pt surface with crystalline NiO<sub>x</sub> or NiS<sub>x</sub> species can partly facilitate water  
 4 dissociation and activate nearby Pt for improved HER activity, but with two potential  
 5 limitations that could compromise the overall activity: (i) Pt atoms buried under the  
 6 crystalline NiO<sub>x</sub> are not accessible to the electrolyte and hence cannot participate in the  
 7 surface reaction; (ii) only the Pt sites in close proximity to the Ni sites can benefit from  
 8 the enhanced water dissociation kinetics. The diffusion length of the generated H<sup>+</sup> is  
 9 estimated to be ~1 nm in the alkaline electrolyte and cannot benefit Pt sites farther  
 10 away from the Ni species can further migrate on the Pt surface to neighboring Pt sites,  
 11 the adsorbed H will be consumed immediately once being adsorbed due to the much  
 12 faster Tafel step than the Volmer step during HER, and thus has a low possibility to spill  
 13 over. Therefore despite partly enhanced kinetics, the majority of Pt sites are exposed to  
 14 alkaline electrolyte and the HER and follow a typical Volmer- or Heyrovsky-step limited  
 15 pathway with Tafel slopes of 40 mV/dec or larger. Moreover, the exposed Pt surface  
 16 sites will undergo severe Oswald ripening during HER and gradually lose the designed  
 17 nanostructure and the original activity.

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2 **Extended Data Fig. 3 | SEM-EDS analysis of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>.** The SEM-EDS result of  
3 the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> shows the Pt:Ni atomic ratio is around 1:2.3.

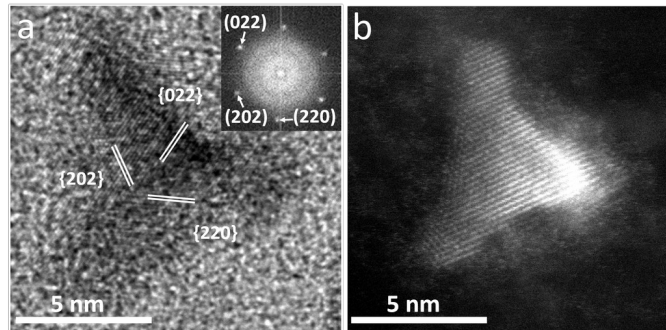


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1 **Extended Data Fig. 4| The Pt tetrapod core. a,** Low-resolution STEM image of Pt  
2 tetrapods remained after completely removing the Ni(OH)<sub>2</sub> shell in acidic condition. **b,**  
3 The HAADF-STEM image of Pt tetrapod. The Pt core has a unique tetrahedral structure  
4 with four Pt pods grown along the <111> directions. **c,** The CV of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and Pt  
5 tetrapod. The redox peaks at 1.39 V vs. RHE in the anodic scan and 1.28 V vs. RHE in  
6 the cathodic scan represent the redox process of Ni<sup>3+</sup>/Ni<sup>2+</sup> on the surface of  
7 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>, while disappearing after in pure Pt<sub>tet</sub>, indicating complete removal of the  
8 Ni(OH)<sub>2</sub> shell.

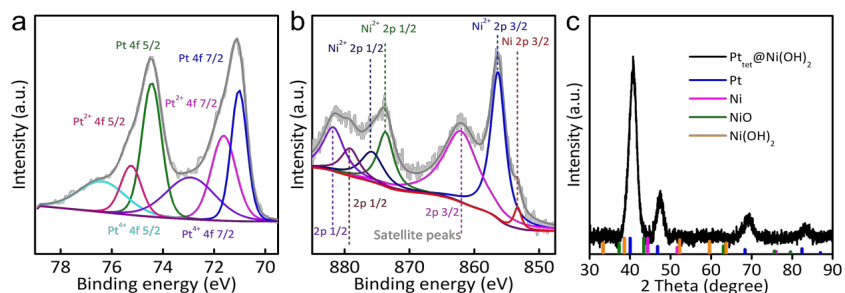
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2 **Extended Data Fig. 5| High-resolution TEM Characterization of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>.**  
3 **a**, TEM images and FFT pattern of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>. Only the FFT pattern of Pt core can be  
4 observed and there is no FFT pattern of Ni(OH)<sub>2</sub>, indicating the amorphous feature of  
5 Ni(OH)<sub>2</sub> shell. **b**, Representative HAADF-STEM images of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>. It can be  
6 overserved that the crystalline core is covered by a blurry amorphous shell.

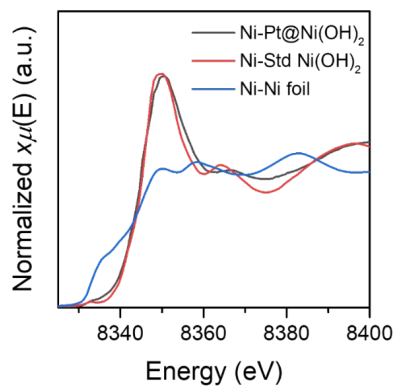
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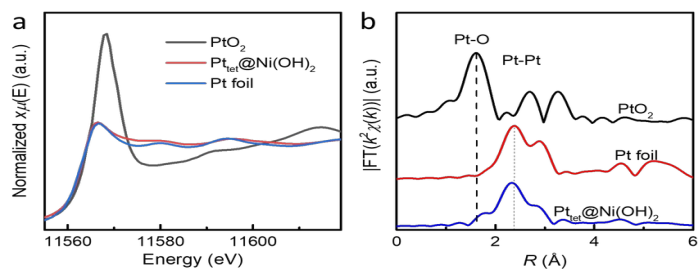
2 **Extended Data Fig. 6 | XPS and XRD characterization of  $\text{Pt}_{\text{tet}}@ \text{Ni}(\text{OH})_2$ .** **a**, The Pt  
3 4f XPS spectra of  $\text{Pt}_{\text{tet}}@ \text{Ni}(\text{OH})_2$ . Two main peaks at around 74.4 (Pt 4f5/2) and 71.1 eV  
4 (Pt 4f7/2) indicate that most of the Pt atoms are in the metallic phase. **b**, The Ni 2p XPS  
5 spectra of  $\text{Pt}_{\text{tet}}@ \text{Ni}(\text{OH})_2$ . The two main peaks at 856.1 eV and 873.7 eV belong to the  
6  $\text{Ni}(\text{OH})_2$  2p3/2 and  $\text{Ni}(\text{OH})_2$  2p1/2 orbitals respectively, and the characteristic spin-  
7 energy separation of 17.6 eV between  $\text{Ni}(\text{OH})_2$  2p3/2 and  $\text{Ni}(\text{OH})_2$  2p1/2 is also in consist  
8 with other literature, delivering a clear result of  $\text{Ni}(\text{OH})_2$  dominated shell composition.  
9 The singlet feature of the  $\text{Ni}(\text{OH})_2$  2p1/2 also strengthens the conclusion of  $\text{Ni}(\text{OH})_2$  as  
10 the main composition in the shell since the NiO 2p1/2 peak possesses a doublet peak  
11 feature. **c**, The XRD pattern of  $\text{Pt}_{\text{tet}}@ \text{Ni}(\text{OH})_2$ . Only symmetric peaks were found at  $40.7^\circ$   
12 the XRD pattern of  $\text{Pt}_{\text{tet}}@ \text{Ni}(\text{OH})_2$ , which was assigned to the Pt-rich tetrapod skeleton.  
13 No  $\text{Ni}(\text{OH})_2$  peak was observed at around  $37^\circ$ .

1



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2 **Extended Data Fig. 7 | The Ni K-edge XANES experimental spectra of**  
3 **Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> along with reference materials.** The oxidation state of Ni in  
4 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> is slightly lower than the standard Ni(OH)<sub>2</sub>, indicating the charge transfer  
5 at the interface from Pt to Ni.

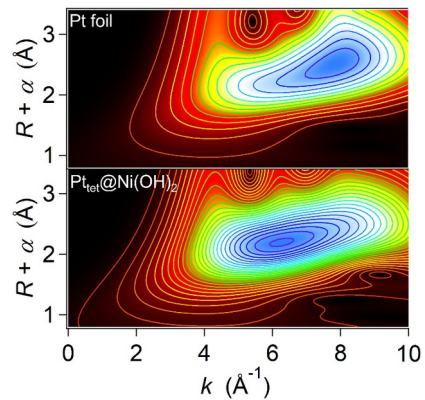


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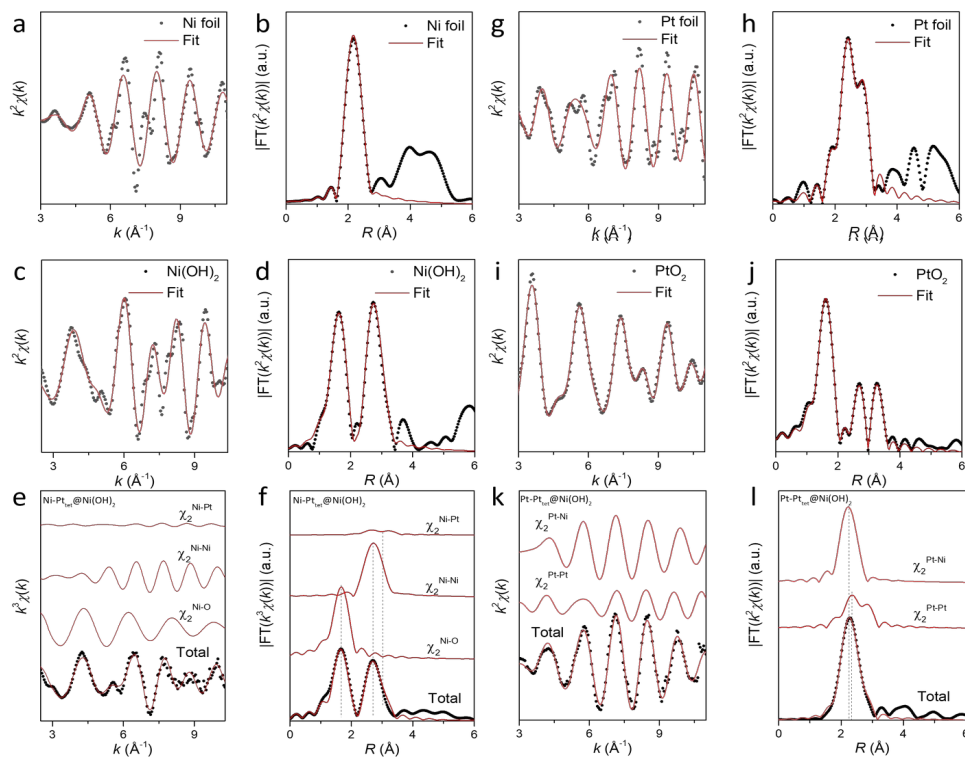
1 **Extended Data Fig. 8| XAS results of Pt L3 edge. a,** The Pt L<sub>3</sub>-edge XANES  
2 experimental spectra. The Pt of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> has a slightly higher oxidation state than  
3 the standard Pt foil, indicating the charge transfer from Pt to Ni at the interface,  
4 consistent with the Ni XANES spectra result. Note that the XAS signal is an average of  
5 all the targeted atoms, thus the change of XANES intensity resulting from the charge  
6 transfer between the interfacial atoms is diluted by the bulk signal from non-interfacial  
7 atoms, and thus is always not very obvious. **b,** Fourier transform magnitudes of the Pt  
8 L<sub>3</sub>-edge EXAFS experimental signal of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> along with reference materials.





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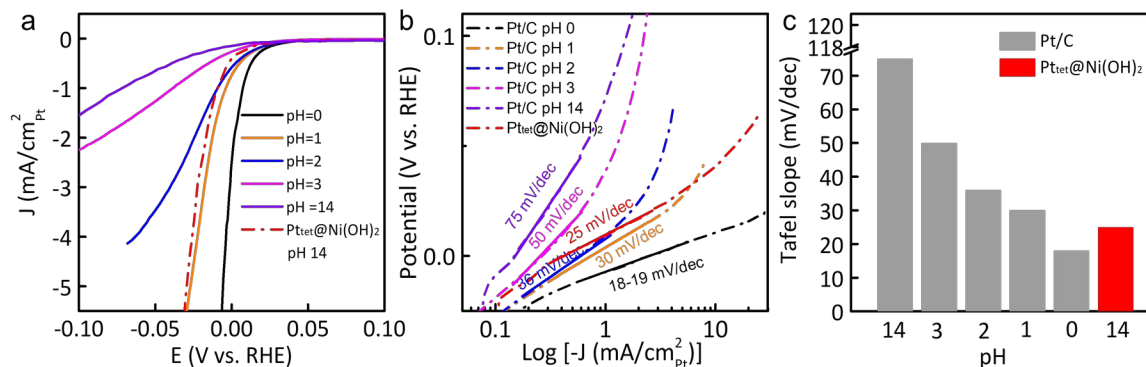
2 **Extended Data Fig. 9 | WT EXAFS signal of Pt and Pt foil.** The negative shift of the  
 3 maxima in the K space from Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> to Pt foil reveals that the Pt is coordinated  
 4 with a lighter transition metal, which should be Ni in our case.



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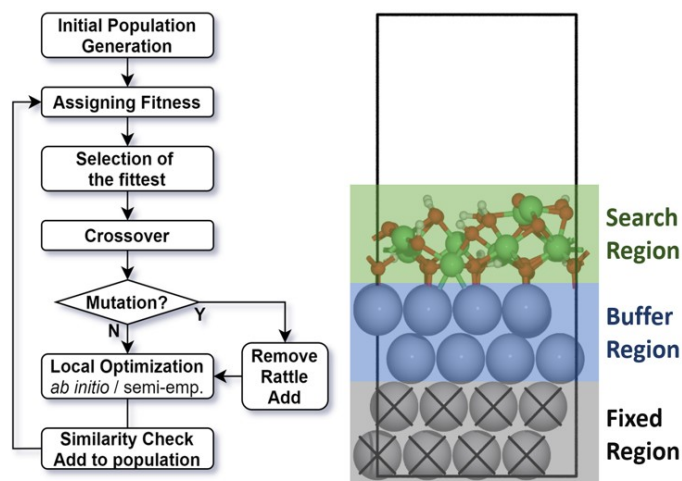
1 **Extended Data Fig. 10| The Fourier-transformed magnitude of Ni K-edge**  
2 **EXAFS and Pt L-edge spectra in k and R space. a and b, Ni foil, c and d, Ni(OH)<sub>2</sub>,**  
3 **and e and f, Ni K-edge Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>. g and h, Pt foil. i and j, PtO<sub>2</sub>. k and l, Pt L-edge**  
4 **Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>. Measured and calculated spectra are well matched for all samples. The**  
5 **best-fit parameters are shown in Extended Data Tables 1 and 2.**

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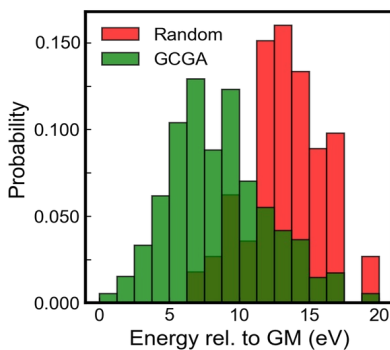
2 **Extended Data Fig. 11 | Kinetics comparison of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> and Pt/C.** **a** LSV curve  
 3 of Pt/C at pH 0-3 and 14, and Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> at pH 14. The specific activity of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> in  
 4 pH 14 lies in between that of Pt/C in pH 1 and 3, indicating that the H<sup>+</sup> supply rate to the Pt  
 5 core of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> is close to the Pt/C in the pH 1-3. More specifically, its initial activity  
 6 near the 0 V vs. RHE is slightly worse than that of pH 2, but it rapidly surpasses the pH 2  
 7 curve after 0.02 V vs. RHE, indicating that the overall H<sup>+</sup> supply rate at the high current level  
 8 is even better than typical Pt/C under pH 2 and very close to pH 1. **b** and **c**, Tafel slope  
 9 analysis of Pt/C at pH 0-3 and 14, and Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> at pH 14. The Tafel analysis shows that  
 10 the Tafel slope of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> is 25 mV/dec, higher than the 36 mV/dec of pH 2 and  
 11 comparable to the 29 mV/dec of pH 1, indicating the HER kinetics of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> is  
 12 comparable to the Pt in pH 1. This further confirms our hypothesis that the Ni(OH)<sub>2</sub> shell can  
 13 provide **an acidic-like hydrogen supply rate**, although not at the level of pH 0.



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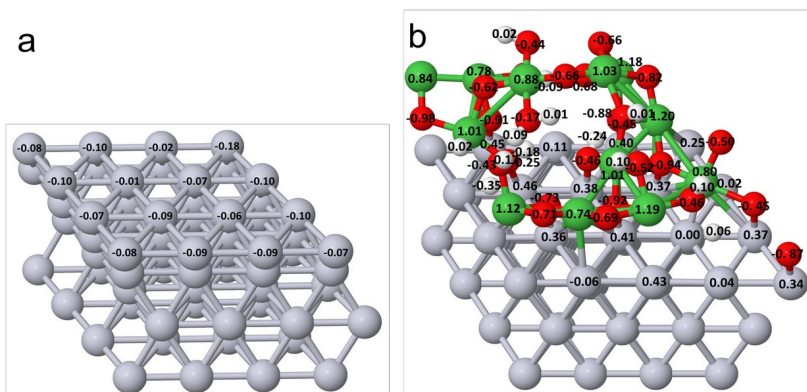
## Extended Data Fig. 12 | Workflow diagram and the model set-up of the GCGA

search. A typical GCGA search consists of the following steps: (a) Defining the substrate slab, periodic boundary conditions, the search, buffer, and fixed regions, the types (and numbers) of species to sample, and their chemical potential. (b) Random generation of the initial candidates from Bond Length Distribution Algorithm (BLDA) followed by pre-optimization with Hookean potential to produce reasonable starting geometries. (c) Local optimization and energy evaluation of the candidates through the interface to VASP. (d) The fitness factor is assigned to each candidate based on the mating counts and the grand canonical free energy. (e) A similarity check against the current population is performed before adding any new candidate to remove duplicates. (f) Selection. The candidates with low fitness or unreasonable geometries are archived to maintain the population size. (g) Mating between the candidates alive to create offspring by the Split-and-splice operation, in which the parent slabs are cut along a random plane and then spliced together. In canonical GA search, the atoms farthest to the cutting plane will be removed to maintain the composition. Candidates with higher fitness are more probable to mate. (h) Mutation of the randomly chosen offspring by adding an atom, removing an atom, or rattling the surface atoms along random vectors drawn from a normal distribution. If an offspring is too similar to its parent, its mutation rate is raised to 100%. (i) Clustering and ranking all the optimized candidates after the GCGA run and report the low-energy configurations.



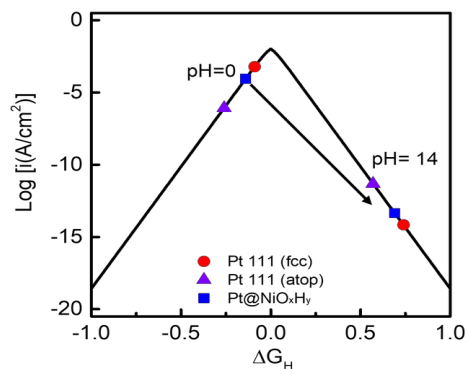
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1 **Extended Data Fig. 13| Histogram comparing the sampling efficiency of BLDA**  
2 **and GCGA in searching the low-energy surface states of the Pt@NiO<sub>x</sub>H<sub>y</sub>**  
3 **system.** We applied the GCGA combined with DFT calculations to explore the structure  
4 of the Pt/ Ni(OH)<sub>2</sub> interface in an aqueous alkaline medium by applying a corresponding  
5 set of chemical potentials and relaxing the compositional degrees of freedom for O and  
6 H. In total, over unique 1200 structures are obtained after filtering and similarity check.  
7 The histogram of the energy distribution relative to the global minimum (GM) from  
8 random and GCGA samplings, relatively, and the geometry of the obtained GM  
9 structure. The GCGA methods sample much more efficiently into the low-energy region  
10 of the chemical subspace.



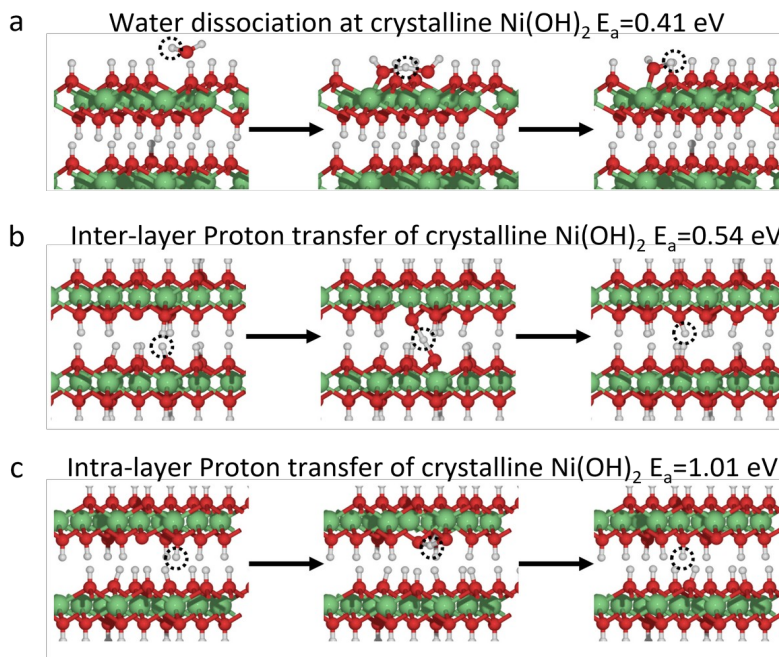
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2 **Extended Data Fig. 14| Bader charge of the surface atoms. a**, The Bader charge  
 3 of the surface atoms for Pt(111). **b**, The Bader charge of the surface atoms for  
 4 Pt@NiOxHy. The values are labeled on the corresponding atom in the structural model,  
 5 and units are in  $e$ . Compared with the Bader charge of surface atoms on Pt (111), The  
 6 surface Pt atoms of Pt@NiOxHy are more positive, indicating the charge transfer from Pt  
 7 to Ni. This is consistent with the XANES results and further proves the accuracy of our  
 8 DFT model.



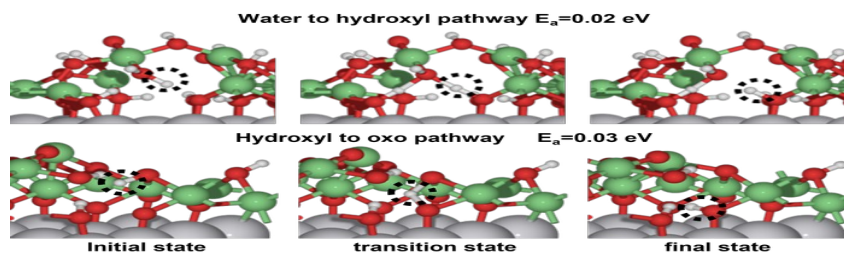
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2 **Extended Data Fig. 15| Volcano plot of HER exchange current density versus**  
 3  **$\Delta G_H$  in logarithm scale.** The positive shift of  $\Delta G_H$  after changing the electrolyte from  
 4 pH 0 to pH 14. The purple, red and blue dot mark the activity of Pt(111) atop, fcc and  
 5 Pt@NiO<sub>x</sub>H<sub>y</sub>, respectively. The positive shift of  $\Delta G_H$  to the other side of the volcano plot  
 6 from pH 0 to pH 14 results in the deviation from the volcano top and thus the decrease  
 7 of activity.



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2 **Extended Data Fig. 16| DFT calculation on proton transfer and water**  
 3 **dissociation in the crystalline beta- $\text{Ni}(\text{OH})_2$ .** **a**, The optimized geometries of the  
 4 initial, transition, and final states of water dissociation in beta- $\text{Ni}(\text{OH})_2$  with an activation  
 5 barrier 0.41 eV; **b**, inter-layer proton transfer with an activation barrier of 0.54 eV; and  
 6 **c**, intra-layer proton transfer with an activation energy barrier of 1.01 eV. Compared  
 7 with the proton transfer activation barrier of 0.02 eV in the amorphous  $\text{NiO}_x\text{H}_y$  model,  
 8 the proton transport in the crystalline  $\text{Ni}(\text{OH})_2$  is forbidden.



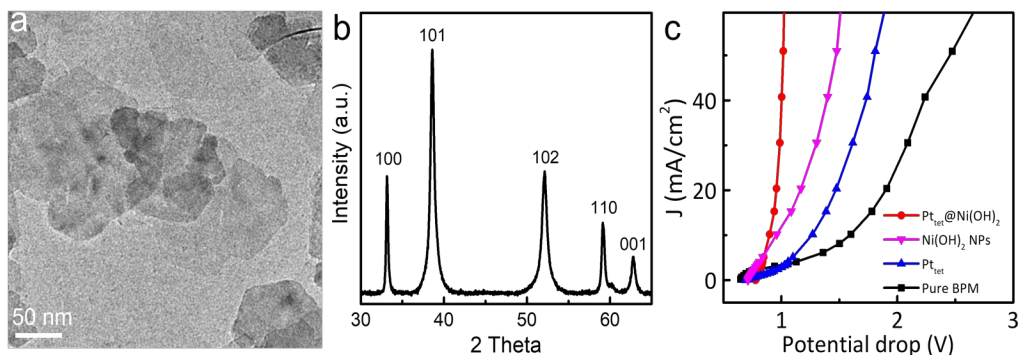
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- 1 **Extended Data Fig. 17.** Geometries of the reaction profile for proton transfer via
- 2 pathway and hydroxyl to oxo pathway, with activation energy of 0.03 eV.

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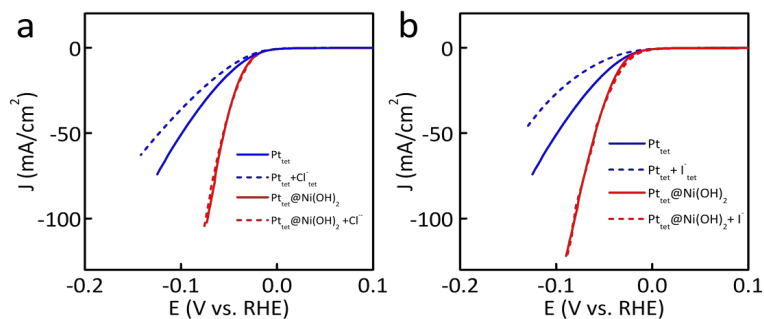
**Extended Data Fig. 18** | **a**, TEM image of crystalline Ni(OH)<sub>2</sub> nanoplate. **b**, XRD pattern of crystalline Ni(OH)<sub>2</sub> nanoplate. **c**, The water dissociation rate of Pt<sub>tet</sub>, Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>, crystalline Ni(OH)<sub>2</sub> nanoplates and pure BPM measured from BPM-based water electrolysis. The pure BPM with no catalyst, with the naked Pt<sub>tet</sub> core or crystalline Ni(OH)<sub>2</sub> nanoplates catalysts require the overpotential of 1.64 V, 0.97 V, and 0.64 V, respectively, to reach the 50 mA/cm<sup>2</sup>, while that with the amorphous Ni(OH)<sub>2</sub> shell (in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>) only needs 0.18 V overpotential to reach 50 mA/cm<sup>2</sup>, demonstrating a much faster WD kinetics, and experimentally confirming that Ni(OH)<sub>2</sub> is the primary contributor to the WD, and the amorphous Ni(OH)<sub>2</sub> shell is more active for WD.

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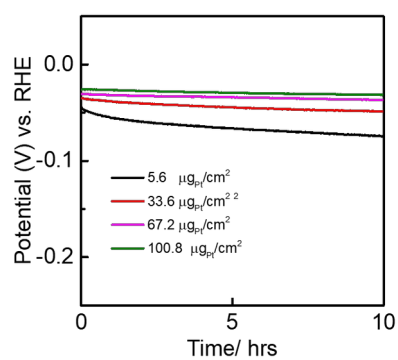
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2 **Extended Data Fig. 19| The  $\text{Cl}^-$  and  $\text{I}^-$  tolerance of  $\text{Pt}_{\text{tet}}$  and  $\text{Pt}_{\text{tet}}@Ni(\text{OH})_2$ .** **a**, in  
 3 0.5 M  $\text{Cl}^-$  and **b**, 0.25 M  $\text{I}^-$ ; the pure  $\text{Pt}_{\text{tet}}$  has a significant activity drop, while there is no  
 4 obvious change of  $\text{Pt}_{\text{tet}}@Ni(\text{OH})_2$  HER activity.

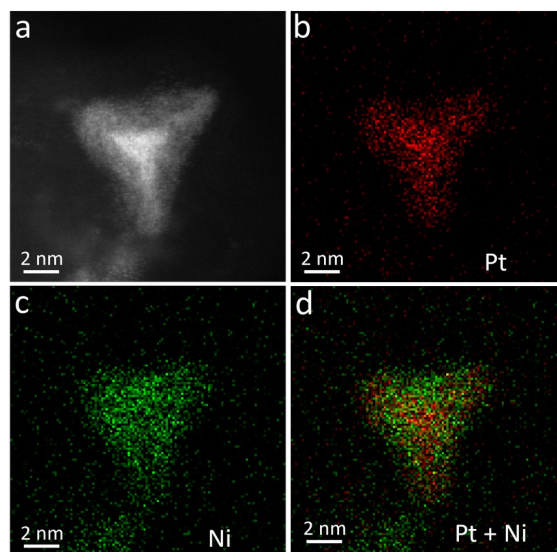


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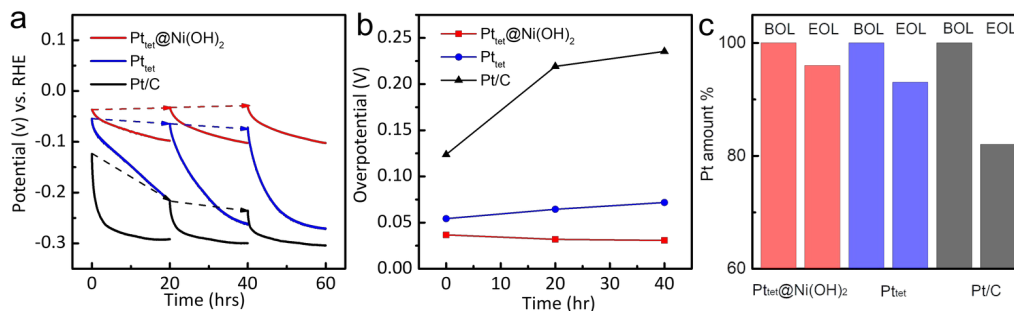
1 **Extended Data Fig. 20| The stability test of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> with a loading of 5.6,**  
2 **33.6, 67.2 and 100.8 μg<sub>Pt</sub>/cm<sup>2</sup>.** There is an obvious stability enhancement as loading  
3 increases.



1

2 **Extended Data Fig. 21| STEM image and EDS mapping of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> after**  
3 **stability test.** Both the structure and elements distribution are well maintained after  
4 the stability test.

5



1

**Extended Data Fig. 22| HER Stability test of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> with periodic interval surface cleaning. a, Chronopotentiometry stability tests of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>, Pt<sub>tet</sub> and Pt/C with periodic surface cleaning.**

A 30-cycle CV from 0.05 to 1.1 V vs. RHE was performed in between two stability tests to clean the surface. **b**, Irreversible overpotential increase of Pt<sub>tet</sub> and Pt/C after periodic surface cleaning. The activity of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> can be largely recovered after surface cleaning in repeated cycling test, indicating that the activity degradation of the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> during the HER stability test is mostly due to the accumulation of H<sub>2</sub> bubbles that cover the Pt sites or other modification of local environment, with very little catalyst degradation. Nonetheless, more severe irreversible degradations are observed in Pt<sub>tet</sub> and Pt/C control samples, in which the degraded activity can only be partially recovered with the CV scan to 1.1 V, further confirming the high durability of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> with Ni(OH)<sub>2</sub> shell protection **c**, **Pt percentage loss before and after stability test. BOL: beginning of life; EOL: end of life.** The Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> catalyst only show <4% Pt loss, which may be largely attributed to the detachment of some nanoparticles when the electrode was initially immersed into the electrolyte because the activity can be fully recovered after surface cleaning in the repeated cycling test. The loss for Pt<sub>tet</sub> and Pt/C is about 7% and 15% respectively, further confirming that the Ni(OH)<sub>2</sub> can effectively reduce the Pt loss for enhancing stability

20

1 **Extended Data Table 1** | Comparison of the Tafel slope of Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> in this work  
 2 with the state-of-the-art literature.

|     | Material   | Tafel slope (mV/dec) | Pontential range (mV vs. RHE) | Electrolyte                   | Ref                    |
|-----|--|----------------------|-------------------------------|-------------------------------|------------------------|
| 1   | Pt <sub>tet</sub> @Ni(OH) <sub>2</sub>               | <b>25</b>            | 10 to -20                     | 1.0 M KOH                     | This work <sup>a</sup> |
|     | Pt <sub>tet</sub>                                    | 40                   | 10 to -20                     |                               |                        |
|     |  | 102                  | -50 to -100                   |                               |                        |
|     | Pt/C   | 75                   | -100 to -160                  |                               |                        |
| 183 |  | 0 to -50             |                               |                               |                        |
| 2   | PtNi-O   | 40                   | 10 to -20                     | 1.0 M KOH                     | 4 <sup>b</sup>         |
| 3   | SANi-Pt  | 37                   | 10 to -20                     | 1.0 M KOH                     | 43 <sup>b</sup>        |
| 4   | Ni <sub>3</sub> N-Pt                                 | 36.5                 | 0 to -50 mV                   | 1.0 M KOH                     | 44                     |
|     | Pt/C   | 50.6                 | 0 to -50 mV                   |                               |                        |
| 5   | Pt <sub>3.21</sub> Ni@Ti <sub>3</sub> C <sub>2</sub> | 38.5                 | 20 to -20 mV                  | 0.1M KOH                      | 45                     |
|     | Pt/C   | 39.5                 | 20 to -20 mV                  |                               |                        |
| 6   | 1.9 nm Pt island                                     | 69                   | -10 to -20 mV                 | 1.0 M KOH                     | 46                     |
| 7   | D-PtNi/C   | 55                   | -5 to -25 mV                  | 1.0 M KOH                     | 47                     |
|     | Pt/C   | 56                   | -5 to -25 mV                  |                               |                        |
| 8   | NiS <sub>2</sub> /PtNi NWs                           | 20                   | -10 to -20 mV                 | <b>0.1 M HClO<sub>4</sub></b> | 48                     |
|     |  | 38                   | -10 to -20 mV                 | 0.1 M KOH                     |                        |

3 <sup>a</sup>The Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> coreshell catalysts show a Tafel slope notably smaller than those of  
 4 naked Pt<sub>tet</sub>, commercial Pt/C, and all previously reported surface decorated Pt catalysts  
 5 alkaline HER, demonstrating that this full encapsulation of Pt surface with proton  
 6 permeable Ni(OH)<sub>2</sub> shell effectively isolates the Pt surface from the alkaline electrolyte  
 7 and create a lower local pH on Pt surface, and thus fundamentally altering the HER  
 8 pathway to acidic-like kinetics with the Tafel step limited pathway, achieving a much  
 9 lower Tafel slope (< 30 mV/dec) and much higher activity.

10 <sup>b</sup>The Tafel slope is obtained from the recalculation from the original data in a different  
 11 potential range compared with the value reported in the published version.

1 **Extended Data Table 2** | Ni K-edge EXAFS curve fitting parameters.<sup>a</sup>

| sample  | path  | <i>N</i> | <i>R</i> (Å) | $\sigma^2$ (Å <sup>2</sup> ) | $\Delta E_0$ (eV) | <i>R</i> , % |
|---|-------|----------|--------------|------------------------------|-------------------|--------------|
| Ni foil <sup>b</sup>                                | Ni–Ni | 12       | 2.48         | 0.008                        | 0.5               | 0.01         |
| Ni(OH) <sub>2</sub> <sup>c</sup>                    | Ni–O  | 6        | 2.06         | 0.008                        | -7.8              | 0.6          |
|   | Ni–Ni | 6        | 3.11         | 0.008                        |                   |              |
| Ni-Pt <sub>tet</sub> (OH) <sub>2</sub> <sup>c</sup> | Ni–O  | 5.5      | 2.07         | 0.009                        | 5.4               | 0.3          |
|   | Ni–Ni | 5.0      | 3.05         | 0.010                        |                   |              |
|   | Ni–Pt | 1.0      | 3.10         | 0.010                        |                   |              |

2 <sup>a</sup>*N*, coordination number; *R*, the distance between absorber and backscatter atoms;  $\sigma^2$ ,  
3 Debye-Waller factor to account for both thermal and structural disorders;  $\Delta E_0$ , inner  
4 potential correction; *R* factor (%) indicates the goodness of the fit. Error bounds  
5 (accuracies) that characterize the structural parameters obtained by EXAFS  
6 spectroscopy were estimated as  $N \pm 20\%$ ;  $R \pm 1\%$ ;  $\sigma^2 \pm 20\%$ ;  $\Delta E_0 \pm 20\%$ .  $S_0^2$  was  
7 determined from Ni foil fitting. Bold numbers indicate fixed coordination number (*N*)  
8 according to the crystal structure.

9 <sup>b</sup>Fitting range:  $3.2 \leq k$  (/Å)  $\leq 11.0$  and  $1.0 \leq R$  (Å)  $\leq 3.0$ .

10 <sup>c</sup>Fitting range:  $2.5 \leq k$  (/Å)  $\leq 10.4$  and  $1.0 \leq R$  (Å)  $\leq 3.4$ .



1 **Extended Data Table 3** | Pt L<sub>3</sub>-edge EXAFS curve fitting parameters.<sup>a</sup>

| sample   | path  | <i>N</i> | <i>R</i> (Å) | $\sigma^2$ (Å <sup>2</sup> ) | $\Delta E_0$ (eV) | <i>R</i> , % |
|--|-------|----------|--------------|------------------------------|-------------------|--------------|
| Pt foil <sup>b</sup>                                   | Pt–Pt | 12       | 2.76         | 0.004                        | 6.8               | 0.0<br>1     |
| PtO <sub>2</sub> <sup>c</sup>                          | Pt–O1 | 6        | 2.02         | 0.005                        | 4.2               | 0.0<br>2     |
|  | Pt–Pt | 6        | 3.10         | 0.006                        |                   |              |
|  | Pt–O2 | 12       | 3.70         | 0.010                        |                   |              |
| Pt-Pt <sub>tet</sub> @Ni(OH) <sub>2</sub> <sup>b</sup> | Pt–Pt | 8.9      | 2.70         | 0.004                        | 5.0               | 0.2          |
|  | Pt–Ni | 2.0      | 3.12         | 0.005                        |                   |              |

2 <sup>a</sup>*N*, coordination number; *R*, the distance between absorber and backscatter atoms;  $\sigma^2$ ,  
3 Debye-Waller factor to account for both thermal and structural disorders;  $\Delta E_0$ , inner  
4 potential correction; *R* factor (%) indicates the goodness of the fit. Error bounds  
5 (accuracies) that characterize the structural parameters obtained by EXAFS  
6 spectroscopy were estimated as  $N \pm 20\%$ ;  $R \pm 1\%$ ;  $\sigma^2 \pm 20\%$ ;  $\Delta E_0 \pm 20\%$ .  $S_0^2$  was  
7 determined from Pt foil fitting and fixed. Bold numbers indicate fixed coordination  
8 number (*N*) according to the crystal structure.

9 <sup>b</sup>Fitting range:  $3.0 \leq k$  (/Å)  $\leq 11.0$  and  $1.2 \leq R$  (Å)  $\leq 3.2$ .

10 <sup>c</sup>Fitting range:  $3.0 \leq k$  (/Å)  $\leq 11.0$  and  $1.2 \leq R$  (Å)  $\leq 3.6$ .

1 **Extended Data Table 4** | Comparison of the coordination number and bond length  
 2 fitted from EXAFS and simulated NiO<sub>x</sub>Hy model. Our model is in good accordance with  
 3 the experimental results and further confirms the accuracy and the robustness of the  
 4 following simulation results based on this model. The slight deviation of coordination  
 5 number (N) should be ascribed to much smaller numbers of atoms of the modeled motif  
 6 compared with the real structure.

| Sample                            | Path  | N <sub>XANES</sub> | N <sub>theory</sub> | R <sub>XANES</sub> (Å) | R <sub>theory</sub> (Å) |
|-----------------------------------|-------|--------------------|---------------------|------------------------|-------------------------|
| Pt@Ni <sub>x</sub> O <sub>y</sub> | Ni-O  | 5.50               | 5.17                | 2.07                   | 2.08                    |
|                                   | Ni-Ni | 5.00               | 4.50                | 3.05                   | 3.04                    |
|                                   | Ni-Pt | 1.00               | 2.17                | 3.10                   | 3.10                    |
|                                   | Pt-Pt | 8.90               | 8.00                | 2.70                   | 2.80                    |
|                                   | Pt-Ni | 2.00               | 1.67                | 3.12                   | 3.14                    |

7

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1 **Extended Data Table 5** |  $\Delta G_H^o$  of the Pt(111) fcc and atop, and Pt@Ni<sub>x</sub>O<sub>y</sub>.

| Sample                                 | $\Delta G_H^o$ | $\Delta G_H$ (pH 0) | $\Delta G_H$ (pH 14)                                    |
|--|----------------|---------------------|---|
| Pt(111) fcc                            | -0.09 eV       | -0.09 eV            | 0.74 eV   |
| Pt(111) atop                           | -0.26 eV       | -0.26 eV            | 0.57 eV   |
| Pt@Ni <sub>x</sub> O <sub>y</sub> atop | -0.14 eV       | -0.14 eV            | 0.69 eV   |
|  |                |                     | <b>-0.04-0.41 eV<br/>(proton supply rate corrected)</b> |

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1 **Extended Data Table 6** | Comparison of HER performance of the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> in this  
 2 work with state-of-the-art catalysts. Mass activity (normalized by Pt loading) and specific  
 3 activity (normalized by ECSA) were compared.<sup>a</sup>

| Catalysts   | Mass activity at -70 mV vs. RHE (mA/ $\mu$ g <sub>Pt</sub> ) | Specific activity at -70 mV vs. RHE (mA/cm <sub>2</sub> <sub>Pt</sub> ) | ECSA (m <sup>2</sup> /g) in 1 M KOH | Reference       |
|---|--|---|-------------------------------------|-----------------|
| Pt/C  | 0.75   | 0.98  | 76.4                                | This work       |
| <b>Pt<sub>tet</sub>@Ni(OH)<sub>2</sub></b>                                | <b>13.4</b>  | <b>27.7</b>   | <b>48.4</b>                         | This work       |
| SANi-JPtNWs   | 11.8   | 10.7  | 106                                 | 43              |
| PtNiO octahedra   | 7.23   | 14.8  | 48.8                                | 4               |
| Pt NWs/ SL-Ni(OH) <sub>2</sub>  | 0.679  | 2.48  | 27.3                                | 3               |
| NiO <sub>x</sub> /Pt <sub>3</sub> Ni Pt <sub>3</sub> Ni <sub>3</sub> -NWs | 2.59   | NA  | NA                                  | 18 <sup>b</sup> |
| Pt <sub>3</sub> Ni <sub>2</sub> -NWs/S C                                  | 2.48   | NA  | NA                                  | 17 <sup>b</sup> |
| Pt <sub>3,6</sub> Ni-S NWs  | 4.37   | NA  | NA                                  | 6               |
| D-PtNi/C  | 1.03   | 4.26  | 24.2                                | 47              |
| 1.9 nm Pt-island on Ni  | 7.7  | 14.7  | 52                                  | 46 <sup>c</sup> |
| PtNi5-0.3   | 2.36   | 11.8  | 20                                  | 52              |
| Pt SAs-Ni/NiO   | ~10.7  | NA  | NA                                  | 54 <sup>b</sup> |

4 <sup>a</sup>Generally, overpotential, mass activity, and specific activity are three major descriptors  
 5 when comparing the Pt catalysts' HER performance. However, the overpotential largely  
 6 depends on the Pt-loading which varies substantially among literature, making it difficult  
 7 to use overpotential as the activity descriptor without considering the Pt-loading. To  
 8 alleviate the effect of Pt-loading, it is more appropriate to use the mass activity at  
 9 certain overpotential (e.g. -70 mV vs. RHE) or the overpotential achieved at a given  
 10 current density normalized by ECSA for comparing the practical HER activity of different  
 11 noble metal catalysts in literature. Additionally, specific activity can provide a better  
 12 description of the intrinsic HER activity of a given catalyst surface.

13 <sup>b</sup>In these cases, the mass activity values were recalculated based on the reported mass  
 14 loading and the electrode geometric surface area normalized HER polarization curve  
 15 provided in the literature.

16 <sup>c</sup>The electrochemistry characterizations are conducted in 0.1 M KOH in these cases,  
 17 otherwise in 1 M KOH if not specified.

# 1 **Amorphous nickel hydroxide proton sieve tailors local chemical environment** 2 **on Pt surface for high-performance alkaline hydrogen evolution reaction**

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## 16 **Supplementary Notes**

### 17 **Table of Contents**

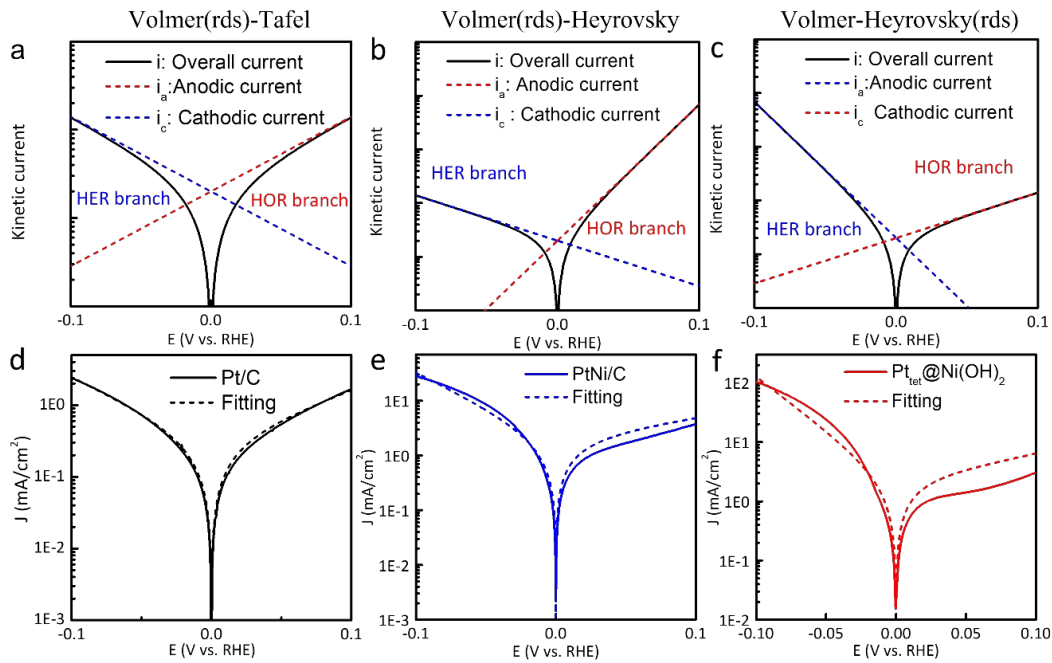
#### 18 **1. The estimation of H<sup>+</sup> diffusion distance**

#### 19 **2. Tafel slope extraction**

#### 20 **1. The estimation of H<sup>+</sup> diffusion distance**

21 The OH<sup>-</sup> concentration in the pH 14 electrolyte is 1 mol/L, which equals 1 OH<sup>-</sup> in 1.66 nm<sup>3</sup>.  
22 An H<sup>+</sup> generated from the dissociation of an H<sub>2</sub>O molecule on the Ni species can only diffuse  
23 away for about 1.18 nm (the cubic root of 1.66 nm<sup>3</sup>) before encountering and reassociating with  
24 another OH<sup>-</sup> from the bulk alkaline electrolyte. Based on this consideration, the diffusion distance  
25 of a free hydronium (H<sub>3</sub>O<sup>+</sup>) is estimated to be around 1.18 nm. This simple estimate suggests that  
26 on the Pt surface that is partially decorated with crystalline Ni species, only a small fraction of Pt  
27 atoms that are located within 1.18 nm from the Ni species can benefit from the enhanced water  
28 dissociation.

## 1 2. Tafel slope extraction



2

3 **Fig. S1**] The ideal polarization curve of HER/HOR branch for a, Volmer(rds)-Tafel pathway; b,  
 4 Volmer(rds)-Heyrovsky pathway; and c, Volmer-Heyrovsky(rds) pathway.  $\alpha=\beta=0.5$  is used in  
 5 the model. The HER branch represents the HER in the N<sub>2</sub> purged electrolyte. d, the B-V fitting  
 6 results matched properly with the experimental polarization curves for Pt/C. The best B-V  
 7 fitting results still cannot properly reconstruct the experimental polarization curves in the  
 8 case of e, PtNi/C, and f, Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>. (All the above tests are conducted under 1 M KOH,  
 9 with N<sub>2</sub> purge and 1600 r.p.m. rotating speed).

10 The quantification and comparison of the Tafel slope is a nontrivial matter and requires extra  
 11 caution to ensure a fair and consistent comparison. There are two commonly used methods to  
 12 extract the Tafel slope from the HER polarization curve: (1) Butler-Volmer (B-V) fitting of the  
 13 HER/ HOR kinetic current in the H<sub>2</sub> purged electrolyte; (2) linear fitting of the overpotential vs.  
 14 logarithm of the HER kinetic current in the N<sub>2</sub> purged electrolyte. Both methods have been used  
 15 in different literature. For the B-V fitting of Pt HER/HOR kinetic current under the H<sub>2</sub> purge,  
 16 there are three possible ideal models depending on the exact rds:

17 i) Volmer (rds)-Tafel pathway, with the cathodic HER current  $i_c = i_0 \times (-e^{-\frac{aF}{RT}\eta})$  and the

18 cathodic HOR current  $i_a = i_0 \times (e^{\frac{\beta F}{RT}\eta})$  (Fig. S1a);

1 ii) Volmer (rds)-Heyrovsky pathway, with the cathodic HER current  $i_c = i_0 \times (-e^{\frac{-aF}{RT}\eta})$  and  
 2 the anodic HOR current  $i_c = i_0 \times (e^{\frac{(1+\beta)F}{RT}\eta})$  (Fig. S1b);

3 iii) Volmer-Heyrovsky(rds) pathways, with the cathodic HER current  $i_c = i_0 \times (-e^{\frac{-(1+a)F}{RT}\eta})$   
 4 and the anodic HOR current  $i_c = i_0 \times (e^{\frac{\beta F}{RT}\eta})$  (Fig. S1c);

5 where  $i_0$  is the exchange current density,  $\alpha$  and  $\beta$  are the symmetric factors) and are set to  
 6 0.5, R is the molar gas constant, T is the temperature and  $\eta$  is the potential. Through extensive  
 7 studies with different types of HER catalysts, we found that the B-V fitting only works well for Pt/  
 8 C with a moderate alkaline HER activity and standard Volmer (rds)-Tafel mechanism (Fig. S1c  
 9 and d), while there are a number of critical issues in applying B-V fitting to the PtNi-based  
 10 catalysts such as PtNi/C and the Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> (Fig. S1e and f). Specifically, Pt/C typically  
 11 shows symmetric HER/HOR branches, and the kinetic current ( $i_k$ ) can be well fitted with the B-V  
 12 equation with an  $\alpha$  value close to 0.5 in 1 M KOH (Fig. S1a). On the other hand, for PtNi/C and  
 13 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub>, due to the existence of surface Ni species, the HER rates are considerably  
 14 enhanced while the HOR shows an abnormal passivation region at around 10-50 mV vs. RHE  
 15 (Fig. S1e, f), leading to highly asymmetric HER/HOR branches that deviate from the standard  
 16 expression of HER/HOR kinetics current. We hypothesize that the surface Ni(OH)<sub>2</sub> plays a  
 17 different role in determining the activation energy for HER and HOR, and thus reduces their  
 18 reversibility. As a result, the  $i_k$  cannot be reliably fitted with the B-V equation (Fig. S1e, f), and an  
 19 attempted fitting could lead to unphysical  $\alpha$  and  $\beta$  values (e.g.,  $\alpha > 1$ , or  $\alpha + \beta \neq 1$ ), making it  
 20 unreliable to derive or compare the Tafel slope. Additionally, we note there are also no strict rules  
 21 for selecting the proper potential window when applying the B-V fitting. More active catalysts  
 22 could reach mass transfer limitation at a lower overpotential, leading to a much smaller potential  
 23 window that can be used for B-V fitting and thus higher uncertainty in the fitting results.  
 24 Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> is clearly the case here due to its high activity.

25 Due to the above challenges associated with B-V fitting under H<sub>2</sub> purge, we have chosen to  
 26 use the linear fitting of the N<sub>2</sub> purged HER curve, which has been widely used by other  
 27 literature<sup>1,2</sup> to extract the Tafel slope for the following reasons: (i) Under the N<sub>2</sub> purging and high

1 rotating speed (1600 r.p.m.), the HOR branch is removed and thus linear fitting near the onset  
2 overpotential is not significantly affected by the HOR signal. There is a clearly linear region in the  
3 Tafel plot where the Tafel slope can be extracted. (ii) The Tafel slopes of different catalysts were  
4 extracted at similar current densities to ensure a similar mass transfer effect.

5 Lastly, we recognize there could be some level of uncertainties associated with the Tafel  
6 slope derivations. Nonetheless, a careful analysis reveals a substantially lower Tafel slope (27  
7 mV/decade) is achieved in Pt<sub>tet</sub>@Ni(OH)<sub>2</sub> in the alkaline electrolyte when compared with all  
8 other references (>36 mV/decade), which is fully validated by our internal control samples tested  
9 and evaluated with the exactly the same method. The difference is clearly beyond derivation  
10 uncertainties. Furthermore, it is important to note that our materials also deliver a record-high  
11 specific activity and a record-high mass activity, which is a directly measured number with less  
12 ambiguity. Together, our comprehensive evaluation and analysis robustly demonstrated that our  
13 unique design has enabled a superior HER catalyst in the alkaline electrolyte.

#### 14 **References**

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