Supporting information

Predictive Fabrication of Ni Phosphide Embedded in Carbon Nanofibers as Active and Stable Electrocatalysts

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Sample preparation

Fabrication of Ni/Carbon nanofibers (CNFs)

Ni/CNFs were fabricated by electrospinning process. 0.496 g of Polyacrylonitrile (PAN, $(C_3H_3N)_n$, Sigma Aldrich, average M_w : 150,000) and 0.496 g of polyvinylpyrrolidone (PVP, $(C_6H_9NO)_n$, Sigma Aldrich, average Mw ~ 1,300,000) were dissolved in 10 g of N, N-Dimethylformamide (DMF, Sigma Aldrich, > 99.9%). PAN was typically used polymer for carbon matrix due to high carbonization ratio and PVP was mixed for higher surface area in CNFs because it could generate pore after pyrolysis. 1.4g of Nickel(II) acetate tetrahydrate ($C_4H_6NiO_4\cdot 4H_2O$, Sigma Aldrich, 98%) were used as Ni precursor. The solution was under vigorous stirring at room temperature for 24hours. The solution was electrospun through a syringe with 15.89mm diameter and metal needle (18G) (Nano NC). the distance between metal needle tip and ground collector covered with Al foil was 15cm. The rate of electrspinning was 0.3ml/h under applying a voltage of 15kV. 60mg of as spun nanofibers detached from Al foil were used for each carbonization step.

For Carbonization, the chamber was vacuumed to $\sim 10^{-6}$ Torr through turbomolecular pump (TMP) and sealed after injection by the specific oxygen partial pressure (pO₂). At this time, the flow rate of Ar or O₂ gas was controlled constantly by mass flow controller (MFC). pO₂ was measured by baratron guage. Under these pO₂ conditions, Ni/CNFs were fabricated through carbonization process at 700°C with the ramping ratio of 3°C/m for 5 hours.

Phosphidation of Ni/CNFs



Figure S1. Image of evacuated ampoule with various volume from 1ml to 500ml. Ni/CNFs and regulated quantity of red phosphorus were put into ampoule.

Ni/CNFs via pO₂ controlled carbonization and red phosphorus lump (Alfa aesar, 99.999%) were placed in ampoule having various volume. They were vacuumed to $\sim 10^{-3}$ Torr by rotary pump (RP) and sealed. Considering the amount of red phosphorus (3, 10, 20mg) and the volume of the ampoule (1, 5, 50, 250, 500ml), the ideal gas law could be applied to calculate the phosphorus pressure during the phosphidation at a specific temperature and volume. For low phosphidation pressure condition, the chamber was also used (V=7854 cm³).

Thermodynamic Calculations

Formation free energy of Ni-C-O system.

Ellingham diagram which show the formation free energy of the various reactions per 1mole of O_2 gas in the temperature range from 100 to 1000°C was plotted in figure 1(a) Each detailed value calculated from Reaction tab in FactsageTM is shown in the following table. Although plotting the formation free energy of Ni₂P in Ellingham diagram was not suitable because its reactant gas was not oxygen, we described it to compare the relative stability with Ni oxide.

Temperature (°C)	$2C + O_2 = 2CO$	$C + O_2 = CO_2$	$2\mathrm{CO} + \mathrm{O}_2 = \mathrm{CO}_2$	$0.8P + O_2 = 0.4P_2O_5$
0	-269.843	-396	-518.846	-587.69
100	-287.776	-396	-501.508	-566.13
200	-305.9	-396	-483.944	-544.57
300	-324.044	-396	-466.32	-523.01
400	-342.124	-396	-448.709	-501.45
500	-360.102	-396	-431.147	-479.89
600	-377.962	-396	-413.649	-458.33
700	-395.702	-396	-396.221	-436.77
800	-413.322	-396	-378.867	-415.21
900	-430.828	-396	-361.586	-393.65
1000	-448.225	-396	-344.377	-372.09

Table S1. Formation Gibbs free energy of each reaction. All reactions were considered per 1 mole of O_2 . The unit is kJ.

Temperature (°C)	$2Ni + O_2 = 2NiO$	$2\mathrm{Ni} + 0.25\mathrm{P}_4 = \mathrm{Ni}_2\mathrm{P}$
0	-428.283	-193.023
100	-409.256	-187.306
200	-390.697	-181.7
300	-372-743	-176.102
400	-355.028	-170.395
500	-337.49	-164.668
600	-320.151	-158.991
700	-302.983	-153.369
800	-285.959	-147.801
900	-269.053	-142.285
1000	-252.247	-136.817

Table S2. Formation Gibbs free energy of each reaction. All reactions were considered per 2 mole of Ni. The unit is kJ.

Formation free energy of Ni phosphide

To compare the relative stability between various phase of Ni phosphide and elicit the equilibrium phosphorus pressure, the formation free energy was calculated. All reactions were considered per 1 mole of P_4 .

Temperature (°C)	$12Ni + P_4 = 4Ni_3P$	$16\mathrm{Ni}_3\mathrm{P} + \mathrm{P}_4$ $= 4\mathrm{Ni}_{12}\mathrm{P}_5$	$4\mathrm{Ni}_{12}\mathrm{P}_5 + \mathrm{P}_4$ $= 24\mathrm{Ni}_2\mathrm{P}$	$\frac{20}{_{3Ni_2P}} + P_4 = \frac{8}{_{3Ni_5P_4}}$	$\frac{2}{_{3Ni_5P_4}} + \frac{P_4}{_{10}} = \frac{10}{_{3NiP_2}}$
0	-850.162	-786.237	-445.6725	-136.494	-136.058
100	-829.3465	-757.669	-420.3047	-119.892	-118.165
200	-808.808	-729.874	-395.710	-104.062	-101.045
300	-788.019	-702.669	-371.705	-88.822	-84.516
400	-766.350	-675.933	-348.169	-74.052	-68.455
500	-744.363	-649.583	-325.018	-59.667	-52.780
600	-722.509	-623.558	-302.194	-45.608	-37.431
700	-700.849	-597.815	-279.651	-31.830	-22.364
800	-679.392	-572.320	-257.356	-18.300	-7.544
900	-658.132	-547.047	-235.283	-4.9923	7.054
1000	-637.059	-521.995	-213.388	8.116	21.452

Table S3. Formation free energy of Ni phosphide. The unit of value is kJ.

Ni-C-O Ternary phase diagram

As the oxygen partial pressure changes, the pressure of the system changes. The ternary phase diagram at each atmosphere was drawn from Phase diagram tab in FactsageTM (Figure S2) and the molar ratio at conditions were marked in phase diagram with stars. All ternary phase diagram could be overlapped. (Figure 2(a)) The mole ratio of Ni-C-O at each oxygen partial pressure condition was calculated from the recipe of the as spun nanofibers and injected O_2 quantity into chamber (V=7854cm³).



Figure S2. Calculated Ni-C-O ternary phase diagram at 700°C for each pressure condition.

Theoretical calculation of surface energy for Ni phosphide

Phase Facet	Ni ₂ P	Ni ₅ P ₄	NiP ₂
(100)	45.6477	82.4524	75.1513
(111)	66.1254	23.9589	22.6096

Table S4. Surface energies of Ni phosphide depending on the phases and facets. All values were calculated from DFT calculations and detailed method is described in DFT calculation section. The unit of the value is meV/Å². The calculated surfaces correspond to Figure S3 for (100) facets and Figure S5 for (111) facets.

 $\begin{array}{l} R \ a \ d \ io \ fN \ in \ a \ n \ o \ p \ a \ r(r) : 11:92 \times 10^{\ \ \ \square} \ m \ (experimental \ data) \\ N \ u \ m \ bo \ fN \ in \ a \ r \ t \ p \ e \ 1cm \ \sigma \ l: \frac{V_{\square,\square\square}}{4_{\square_3} \ \pi r^\square} \\ S \ u \ r \ f \ a \ r \ \sigma \ fN \ in \ a \ n \ o \ p \ a \ r \ p \ e \ 1cm \ \sigma \ l(S_\square) : 4\sigma r^\square \times \frac{V_\square}{4_{\square_3} \ \pi r^\square} = \frac{3V_\square,\square\square}{r} \end{array}$

 $s \ u \ r \ f \ a \ r \ eo \ fN \ \underline{i} \ \underline{R} \ n \ a \ n \ o \ p \ a \ r \ f \ t \ p \ hoes \ p \ hi \ d \left(S_{\underline{PP}} \ \underline{R}_{\underline{P}}\right) : \frac{\underline{PP}_{\underline{P},\underline{PP}}}{\underline{P}} \times \left(\frac{\underline{PPP}}{\underline{PP}}\right)^{\underline{P}_{\underline{P}}}$ $S \ u \ r \ f \ a \ r \ eo \ fN \ \underline{i} \ \underline{R}_{\underline{4}} \ n \ a \ n \ o \ p \ a \ r \ f \ t \ p \ hoes \ p \ hi \ d \left(S_{\underline{PP}} \ \underline{R}_{\underline{P}}\right) : \frac{\underline{PP}_{\underline{P},\underline{PP}}}{\underline{P}} \times \left(\frac{\underline{PPP}}{\underline{PP}}\right)^{\underline{P}_{\underline{P}}}$ $S \ u \ r \ f \ a \ r \ eo \ fN \ \underline{i} \ \underline{R}_{\underline{4}} \ n \ a \ n \ o \ p \ a \ r \ f \ t \ p \ hoes \ p \ hi \ d \left(S_{\underline{PP}} \ \underline{R}_{\underline{P}}\right) : \frac{\underline{PP}_{\underline{P},\underline{PP}}}{\underline{P}} \times \left(\frac{\underline{PPP}}{\underline{PP}}\right)^{\underline{P}_{\underline{P}}}$ $S \ u \ r \ f \ a \ r \ eo \ fN \ \underline{i} \ \underline{R}_{\underline{4}} \ n \ a \ n \ o \ p \ a \ r \ f \ t \ p \ hoes \ p \ hi \ d \left(S_{\underline{PP}} \ \underline{R}_{\underline{R}}\right) : \frac{\underline{PP}_{\underline{P},\underline{PP}}}{\underline{P}} \times \left(\frac{\underline{PPP}}{\underline{PP}}\right)^{\underline{P}_{\underline{P}}}$

 $\Delta G_{\text{Product}}^{\text{Product}} = \gamma_{\text{Product}} \times S_{\text{Product}}$

$$= 75.1513 \times 10^{2} \times 1.6 \times 10^{2} \times 10^{2} \times 10^{2} \times \frac{2 \times 2.22 \times 22^{2}}{22.22 \times 22^{2}} \times \left(\frac{22.22}{2.22}\right)^{2}/_{2}$$
$$= 4.7756 \times 10^{2} \left(\frac{2}{2.22}\right)$$

$$\Delta G^{\text{PP}}_{\text{PP}}(\text{PP}) = 1.0170 \times 10^{\text{P}} \left(\frac{J}{m \ o}\right) \qquad l$$
$$\Delta G^{\text{PP}}_{\text{PP}}(\text{PP}) = 2.5553 \times 10^{\text{P}} \left(\frac{J}{m \ o}\right) \qquad l$$

$$\Delta G_{\mathbb{Z} \oplus \mathbb{P}}^{\mathbb{Z}} = 1.4368 \times 10^{\mathbb{Z}} \left(\frac{J}{m \ o} \right) \qquad l$$

$$\Delta G^{\text{22}}_{\text{22,(222)}} = 3.7016 \times 10^{\text{2}} \left(\frac{J}{m \ o}\right) \qquad l$$

$$\frac{20}{3} N \dot{P}_{(2)} + P_{2(2)} = \frac{8}{3} N \dot{P}_{2(2)}$$

 $\Delta G = \Delta G^{\circ} + R \ T \ Q_{\Xi} = \Delta G^{\circ,\Xi\Xi} + \Delta G^{\circ,\Xi\Xi} + R \ T \ Q_{\Xi} = \begin{pmatrix} \frac{8}{3} \mu_{\Xi,\Xi\Xi,\Xi}^{\circ}(\Xi) - \frac{20}{3} \mu_{\Xi,\Xi\Xi,\Xi}^{\circ}(\Xi) - \mu_{\Xi,\Xi}^{\circ}(\Xi) \end{pmatrix} + \begin{pmatrix} \frac{8}{3} \Delta G_{\Xi,\Xi\Xi,\Xi}^{\Xi\Xi}(\Xi) - \frac{20}{3} \Delta G_{\Xi,\Xi\Xi,\Xi}^{\Xi\Xi}(\Xi) \end{pmatrix} + R \ T \ \frac{a_{\Xi,\Xi\Xi,\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)} + R \ T \ \frac{a_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)} + R \ T \ \frac{a_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)} + R \ T \ \frac{a_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi}^{\Xi\Xi}(\Xi)} + R \ T \ \frac{a_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi}^{\Xi\Xi}(\Xi)} + R \ T \ \frac{a_{\Xi,\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi}^{\Xi\Xi}(\Xi)} + R \ T \ \frac{a_{\Xi,\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi}^{\Xi\Xi}(\Xi)} + R \ T \ \frac{a_{\Xi,\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi}^{\Xi}(\Xi)} + R \ T \ \frac{a_{\Xi,\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi}^{\Xi}(\Xi)} + R \ T \ \frac{a_{\Xi,\Xi}^{\Xi}(\Xi)}{a_{\Xi,\Xi}^{\Xi}(\Xi)} + R \ \pi \ \frac{a_{\Xi,\Xi}^{\Xi}(\Xi)}{a_{\Xi,\Xi}^{\Xi}(\Xi)} + R \ \frac{a_{\Xi,\Xi}^{\Xi}(\Xi)}{a_{\Xi}^{\Xi}(\Xi)} + R \ \frac{a_{\Xi,\Xi}^{\Xi}(\Xi)}{a_{\Xi}^{\Xi}(\Xi)} + R \ \frac{a_{\Xi,\Xi}^{\Xi}(\Xi)}{a_{\Xi}^{\Xi}(\Xi)} + R \ \frac{a_{\Xi}^{\Xi}(\Xi)}{a_{\Xi}^{\Xi}(\Xi)} + R \ \frac{a_{\Xi}^{\Xi}(\Xi)}{a_{\Xi}^{\Xi}(\Xi)}$

$$a \ te \ q \ ui \ \lim_{\square_{\overline{U}_{\overline{U}}}} a \ te \ q \ ui \ \lim_{\square_{\overline{U}_{\overline{U}}}} a \ \overline{ui}_{\square_{\overline{U}_{\overline{U}}}} = a \ \underline{a}_{\square \square_{\overline{U}}} = e \ p \left(-\frac{\Delta G^{\circ,\underline{m}} + \Delta G^{\circ,\underline{m}}}{R \ T} \right)$$

$$(a_{\underline{m} \square_{\overline{U}}} = a_{\underline{m} \square_{\overline{U}}} = 1)$$

$$\therefore \ P_{\underline{U}_{\underline{n}}}^{\underline{m}} = e \ p \left(\frac{\Delta G^{\circ,\underline{m}} + \Delta G^{\circ,\underline{m}}}{R \ T} \right)$$

 $\begin{array}{l} F \ o \ (100) \ f \ a \ c \ o \ Neightarrow \ h \ s \ p \ h \ i \\ \Delta G^{\circ, \square\square} = \frac{8}{3} \times 1.0170 \times 10^{\square} - \frac{20}{3} \times 2.5553 \times 10^{\square} = 1.0085 \times 10^{\square} \ (\frac{J}{m \ o}) \ l \end{array}$

$$\begin{array}{l} F \ o \ (111) f \ a \ co \ fN \ dp \ ho \ sp \ h \ i \\ \Delta G^{\circ \square\square} = \frac{8}{3} \times 2.9586 \times 10^{\square} - \frac{20}{3} \times 3.7016 \times 10^{\square} = -1.2588 \times 10^{\square} \ (\frac{J}{m \ o}) \ l \end{array}$$

$$\frac{2}{3} N i P_{\mathbb{Z}} + P_{\mathbb{Z}} = \frac{10}{3} N i_{\mathbb{Z}}$$

$$\Delta G = \Delta G^{\circ} + R T Q_{\Xi} = \Delta G^{\circ,\Xi\Xi} + \Delta G^{\circ,\Xi\Xi} + R T Q_{\Xi} = \left(\frac{10}{3}\mu_{\Xi,\Xi\Xi}^{\circ}(\Xi) - \frac{2}{3}\mu_{\Xi,\Xi\Xi}^{\circ}(\Xi) - \mu_{\Xi_{\Xi}}^{\circ}(\Xi)\right) + \left(\frac{10}{3}\Delta G_{\Xi,\Xi\Xi}^{\odot\Xi}(\Xi) - \frac{2}{3}\Delta G_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)\right) + R T \frac{a_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)}{a_{\Xi,\Xi\Xi}^{\Xi\Xi}} + R T Q_{\Xi} = \left(\frac{10}{3}\mu_{\Xi,\Xi\Xi}^{\circ}(\Xi) - \frac{2}{3}\mu_{\Xi,\Xi\Xi}^{\circ}(\Xi)\right) + \left(\frac{10}{3}\Delta G_{\Xi,\Xi\Xi}^{\odot\Xi}(\Xi) - \frac{2}{3}\Delta G_{\Xi,\Xi\Xi}^{\Xi\Xi}(\Xi)\right) + R T Q_{\Xi} = \left(\frac{10}{3}\mu_{\Xi,\Xi\Xi}^{\circ}(\Xi) - \frac{2}{3}\mu_{\Xi,\Xi\Xi}^{\circ}(\Xi)\right) + R T Q_{\Xi} = \left(\frac{10}{3}\mu_{\Xi,\Xi}^{\circ}(\Xi) - \frac{2}{3}\mu_{\Xi,\Xi\Xi}^{\circ}(\Xi)\right) + R T Q_{\Xi} = \left(\frac{10}{3}\mu_{\Xi}^{\circ}(\Xi) - \frac{2}{3}\mu_{\Xi}^{\circ}(\Xi)\right) + R T Q_{\Xi} = \left(\frac{10}{3}\mu_{\Xi}^{\circ}(\Xi) - \frac{2}{3}\mu_{\Xi}^{\circ}(\Xi)}\right) + R T Q_{\Xi} = \left(\frac{10}{3}\mu_{\Xi}^{\circ}(\Xi)}\right) + R T Q_{\Xi}^{\circ}(\Xi) + R$$

 $F \ o \ (100) \ f \ a \ c \ o \ f \ b \ s \ p \ h \ i \ \Delta G^{\circ, \boxtimes \boxtimes} = \frac{10}{3} \times 4.7756 \times 10^{\boxtimes} - \frac{2}{3} \times 1.0170 \times 10^{\boxtimes} = 9.1387 \times 10^{\boxtimes} \ (\frac{J}{m \ o}) \ l$

 $F \circ (111) f a co f N dp ho s p h i$ $\Delta G^{\circ, \square\square} = \frac{10}{3} \times 1.4368 \times 10^{\square} - \frac{2}{3} \times 2.9586 \times 10^{\square} = 2.8169 \times 10^{\square} \left(\frac{J}{m o}\right) l$

Density functional theory (DFT) calculations

This information explains the detailed H adsorptions on the Ni_xP_y surfaces.

Computational Methods

In our theoretical results, all DFT calculations were performed using Vienna ab initio simulation package (VASP) program with the Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA).^{1, 2} We used PBE-D2 functional³ based on projector augmented wave (PAW) method⁴ with a correction to the conventional Kohn-Sham DFT energy to treat the vdW interactions for all Ni phosphide surface calculations.

For bulk calculations, the total energies of bulk Ni phosphides were converged with $6 \times 4 \times 4$, $4 \times 4 \times 8$, $4 \times 4 \times 2$, and $6 \times 6 \times 6$ k-point grids for Ni₁₂P₅, Ni₂P, Ni₅P₄, and NiP₂, respectively. The optimized lattice parameters were $a_0 = 8.629$ Å and $c_0 = 5.036$ Å for Ni₁₂P₅, $a_0 = 5.865$ Å and $c_0 = 3.360$ Å for Ni₂P, $a_0 = 6.779$ Å and $c_0 = 10.978$ Å for Ni₅P₄, $a_0 = 5.453$ Å for NiP₂. Those values are in good agreement with experimental values^{5, 6} of $a_0 = 8.646$ Å and $c_0 = 5.070$ Å for Ni₁₂P₅, $a_0 = 5.859$ Å and $c_0 = 3.382$ Å for Ni₂P, $a_0 = 6.789$ Å and $c_0 = 10.986$ Å for Ni₅P₄, $a_0 = 5.471$ Å for NiP₂.

For surface calculations, slab models for the selected four different phases of Ni phosphides were generated with 2 × 2 surface unit cells with vacuum gaps of \approx 25 Å in the z direction to avoid interactions between adjacent slabs. Accordingly, the k-point grid sampling was reduced to 3 × 3 × 1. Orbital-projected density of states (DOS) calculations were performed on the structurally optimized surfaces of the selected four catalysts using a finer k-point grid (6 × 6 × 1). We assume that the selected four catalysts are comprised of surface termination with the low Ni/P ratio due to the following reasons: The higher the number of d orbitals of Ni atoms that are not bonded to porbitals of P atoms, the less stable will be the surface because the dangling bonds formed by unbounded d orbitals increase the surface energy. Therefore, the surface enriched with dangling bonds is energetically unstable.^{7, 8} In addition, Ni phosphide surfaces of the P-enriched termination were confirmed by the results of STM and LEED experiments in the numerous literatures.⁹⁻¹³ In our DFT calculations, the four catalysts surfaces terminated with low Ni/P ratio were selected as the Ni₄P₅-terminated Ni₁₂P₅, Ni₃P₂-terminated Ni₂P, Ni₄P₃-terminated Ni₅P₄, and P-terminated NiP₂.

Valence orbitals were described by a plane-wave basis set with the cutoff energy of 400 eV. Electronic energies were calculated with a self-consistent-field (SCF) tolerance of 10⁻⁴ eV on the total energy. Ultrasoft Vanderbilt-type pseudopotentials¹⁴ were used to describe the interactions between ions and electrons. Geometry optimization was performed by minimizing the forces of all atoms to less than 0.02 eV/Å with the total energy of the system converged to within 10-4 eV during self-consistent iterations. In addition, we have calculated total energies for various configurations to determine the energy barrier for HER mechanism on all surface structures. We determined the energy barriers using the climbing-image nudged elastic band (CINEB) method¹⁵ with a force tolerance of 0.02 eV Å. The CINEB method is a more rigorous transition-state search algorithm than the NEB method^{16, 17} since it is designed to make one of the intermediate states near the transition-state climb up along the reaction path to converge on the highest saddle point.¹⁵

In order to further analyze the interaction between the hydrogen and the surfaces, we plotted the charge density difference $\Delta \rho$ for the best adsorption sites as shown in insets of Figure S4. Here $\Delta \rho$ = $\rho(\text{surface} + \text{H}) - \rho(\text{surface}) - \rho(\text{H})$, where $\rho(\text{surface} + \text{H})$ and $\rho(\text{surface})$ are the charge densities

of the surface with and without adsorbed H, respectively, and $\rho(H)$ is the charge density of the isolated H atom. The density of states (DOS) were also plotted in Figure S4 to get insight into the different HER activity of four different structures. As shown in inset figures of Figure S4, both Ni₁₂P₅ and NiP₂, having excellent HER activity, clearly exhibit large amount of charge transfer than other phases. These results are attributed to the P(s)–H(s) direct bonding nature of both phases as clearly shown in Figure S4, meaning that large interaction volume between s-orbitals leads to increase amount of charge transfer between P(s)–H(s) bond. Moreover, both Ni₁₂P₅ and NiP₂ have lower energy barriers than other phases in Heyrovsky reaction maybe because the highly negative charged H on surface is ease to react with the surrounding protons, desorbing as H₂.

Adsorption of H atom on Ni_xP_y surfaces

The differential adsorption energy of hydrogen is chosen to describe the stability of hydrogen according to the literature¹⁸ and the equation is as follows:

$$\Delta E_{\rm H} = E(Ni_{\rm x}P_{\rm y} + n{\rm H}) - E(Ni_{\rm x}P_{\rm y} + (n-1){\rm H}) - 1/2 E({\rm H}_2)$$
(1)

Where $E(Ni_xP_y + nH)$ is the total energy of Ni_xP_y with the n hydrogen atoms adsorbed on

surfaces, $E(Ni_xP_y + (n-1)H)$ is the total energy of Ni_xP_y with (n-1) hydrogen atoms adsorbed on surfaces. $E(H_2)$ is the total energy of hydrogen molecule in gas phase. The equation (1) gives the adsorption energy of single H atom for adsorption when n is equal to 1.

The calculated adsorption energies of single H atom on the selected four Ni_xP_y (001) surfaces are listed in Table S5. The data shows that the site # 1 is the most favorable site for H adsorption among various adsorption sites as shown in Figure S3.

Catalytic activity of Ni_xP_y

To compare the catalytic activity of the selected four Ni_xP_y phases, we calculated the Gibbs free energy of hydrogen adsorption following the equation below:

$$\Delta G^{\circ}_{H} = \Delta E_{H} + \Delta E_{ZPE} - T \Delta S_{H}$$

Where ΔE_{ZPE} is the difference in zero-point energy between the adsorbed state and the gas phase, ΔS_H is the entropy difference between the adsorbed state and the gas phase. The gas phase entropy of H is taken from literature.¹⁹ The calculated ΔG°_H values for H adsorption on the four Ni_xP_y (001) surfaces are listed in Table S5. It will be a good catalyst for hydrogen evolution if the free energy of adsorbed H is close to that of the reactant or product (i.e., $\Delta G^{\circ}_H \sim 0$).



Figure S3. Top views of the surface structures for the Ni₄P₅-terminated Ni₁₂P₅ (001), Ni₃P₂-terminated Ni₂P (001), Ni₄P₃-terminated Ni₅P₄ (001), and P-terminated NiP₂ (001). The dotted rectangular boxes at top views represent 1 x 1 unit cells. The yellow balls represent Ni atoms, blue for P.

Adsorption energies and coverage table

Phase	Numbe r of site	E _{ad} (eV)	G _{ad} (eV)	Number of H atoms/unit cell	Area/unit cell (Å ²)	Coverage (mmol/m ²)
	1	-0.50	-0.24			
Ni12P5	2	-0.35	-0.09	4	74,4551	8 92 X 10 ⁻³
11121 5	3	-0.35	-0.09			0.921110
	4	-0.35	-0.09			
Ni ₂ P	1	-0.58	-0.39	1	29.7873	5.57 X 10 ⁻³
Ni ₅ P ₄	1	-0.76	-0.52	2	39.7934	8 34 X 10 ⁻³
	2	-0.39	-0.20			0.5 12210
	1	-0.42	-0.16		2 0 7 22 1	
N1P ₂	2	-0.41	-0.15	2	29./334	1.12 X 10 ⁻²

Table S5. Adsorption energies (E_{ad} , eV) and free energies (G_{ad} , eV) depending on various H adsorbed sites including the number of adsorbed H atoms per unit cell, surface area per unit cell (Å²), and coverage (mmol/m²) for Ni₁₂P₅ (001), Ni₂P (001), Ni₅P₄ (001) and NiP₂ (001).



Figure S4. Partial density of states (PDOS) for H(1s) and its bonded Ni(3d), P(2p), P(1s) when H is adsorbed on the surfaces of Ni₁₂P₅, Ni₂P, Ni₄P₅, and NiP₂. Inset figures: differential charge density of H adsorbed on various Ni phosphide phases. The yellow area means that electron gain and the blue area means that electrons lose. Inset boxes: amount of charge transfers for H, Ni, and P atoms confirmed by Bader charge analysis.



Figure S5. Top views of the surface structures for the $Ni_{12}P_5$ (111), Ni_2P (111), Ni_5P_4 (111), and NiP_2 (111). The dotted rectangular boxes at top views represent 1 x 1 unit cells. The yellow balls represent Ni atoms, blue for P.

Adsorption energies and coverage table

Phase	Numbe r of site	E _{ad} (eV)	G _{ad} (eV)	Number of H atoms/unit cell	Area/unit cell (Å ²)	Coverage (mmol/m ²)
Ni ₁₂ P ₅	1	-0.79	-0.52		96.5444	6.88 X 10 ⁻³
	2	-0.67	-0.41	4		
	3	-0.65	-0.38			
	4	-0.30	-0.03			
NiaP	1	-0.46	-0.27	2	45 2986	7 22 X 10-3
1121	2	-0.21	-0.02		43.2900	7.33 A 10*
	1	-0.45	-0.22		134.892	7.39 X 10 ⁻³
	2	-0.23	-0.01			
Ni-P.	3	-0.43	-0.20	6		
11151 4	4	-0.39	-0.16	0		
	5	-0.36	-0.13			
	6	-0.13	0.01			
NiP ₂	1	-0.24	-0.02	2	51.4998	3.22 X 10 ⁻³

Table S6. Adsorption energies (E_{ad} , eV) and free energies (G_{ad} , eV) depending on various H adsorbed sites including the number of adsorbed H atoms per unit cell, surface area per unit cell (Å²), and coverage (mmol/m²) for Ni₁₂P₅ (111), Ni₂P (111), Ni5P₄ (111), and NiP₂ (111).



Figure S6. (a) The optimized surface structures for $Ni_{12}P_5$ (111), Ni_2P (111), Ni_5P_4 (111), and NiP_2 (111). (b) Energetics of the HER process on different catalysis, which corresponds to (a).



Figure S7. Overall reaction mechanism for HER on the surface of (001) faceted NiP₂. Relative free energy (G) values and activation energies (for the Volmer and Heyrovsky routes) are also shown. The yellow balls represent Ni atoms, blue for P, red for O and pink for H.

Physical characterization

The morphology of Ni/CNFs were characterized using a field emission scanning electron microscopy. (FE-SEM, MERLIN Compact, ZEISS) Transition electron microscopy (TEM, Tecnai F20, FEI / JEM-2100F, JEOL Ltd.) was also used to investigate the structure and fringe of nanoparticles with a 200kV accelerating voltage. To analyze the phase of Ni and Ni phosphide, X-ray diffraction (XRD, New D8 Advance, Bruker) was used in theta-2theta scan mode with Cu K_a radiation. The accelerating voltage and current were set to 40kV and 40mA. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 500 VersaProbeTM model (ULVAC-PHI) with the Al K_a (1486.6eV) X-ray source. To eliminate the effect of surface oxide due to air oxidation, 5~10 nm of the surface was etched out using Ar plasma before XPS analysis.

TEM Analysis on Ni/CNFs

a

b



Figure S8. (a) Diffraction pattern and (b) HRTEM image of Ni nanoparticle. D-spacing well corresponds to the reference of (111) faceted Ni.



Figure S9. XPS spectra of Ni/CNFs which undergo different pO_2 controlled carbonization. (a) Ar 1.0 Torr, (b) $O_2 0.5$ Torr, (c) $O_2 1.0$ Torr, (d) $O_2 1.5$ Torr, (e) $O_2 2.0$ Torr.



Figure S10. Ni 2p_{3/2} XPS spectra of Ni/CNFs.

Ni $2p_{3/2}$ XPS spectra from Ni/CNFs shows peak near 853eV which is consistent with the Ni⁰ peak reported in previous research. The peak shoulder found in higher energies corresponds to Ni²⁺, which is known to occur when Ni nanoparticles are slowly oxidized in air. ^{20, 21}

Characterization of electrochemically active surface area (ECSA) of Ni/CNFs



Figure S11. Analysis of ECSA of Ni/CNFs by measuring the slope of current density versus scan rate (10, 20, 30, 40, 50mV/s) in the potential range of $-0.18 \sim 0.22$ V vs RHE.



X-ray diffraction analysis on Ni phosphide/CNFs

Figure S12. XRD pattern for Ni phosphide/CNFs after pP4 controlled phosphidation at (a) 300°C, (b) 400°C, (c) 450°C, (d) 500°C, and (e) 550°C.

Although the temperatures were above the boiling point, phosphidation was not fully performed due to slow kinetics at 300 and 400°C.

Electrochemical characterization

Analysis of catalytic performance was carried out in a three-electrode electrochemical cell configuration using $0.5M H_2SO_4$ (Sigma Aldrich, 95~98%) solution as electrolyte. Saturated calomel electrode (SCE) as reference electrode and Pt wire as counter electrode were used. The potential relation between SCE and reversible hydrogen electrode (RHE) is described in the equation below.

$$E(RHE) = E(SCE) + 0.242 + 0.059 \times pH$$

4mg of sample was dispersed in the mixture of 200µl of ethanol, 800µl of deionized water and 80µl of Nafion^R perfluorinated resin solution. (5wt % in mixture of lower aliphatic alcohols and water, Sigma Aldrich) To make ink dispersed evenly, ink was sonicated for 30 minutes. Working electrode was prepared using glassy carbon electrode (CHI 104, CH Instrument, Inc.) by simple drop-casting method and dried at 60°C for 24 hours. For catalytic performance measurement, the potential was sweeped between 0 V ~ -0.5 V (vs RHE.) at a rate of 2mV/s.

HER catalytic performance depending on structure



Figure S13. HER catalytic performance of (a) Ni₂P/CNFs (b) NiP₂/CNFs depending on structure modifications. Commercial Pt electrode was also investigated as reference.

Catalyst	Current density (j, mA/cm ²)	η at the corresponding j (mV)	Stability test	Reference
Ni ₂ P/CNFs	10	108	~ 120 hours	This work
NiP ₂ /CNFs	10	71	~ 110 hours	This work
MoS ₂ /RGO	10	150	$\sim 1000^{\text{th}} \text{ cycles}$	22
Double-gyroid MoS ₂ /FTO	2	190	-	23
1T MoS ₂ nanosheets	10	195	$\sim 1000^{th}$ cycles	24
Defect-rich MoS ₂	13	200	$\sim 3000^{th}$ cycles	25
Mo ₂ C/CNT	10	152	$\sim 3000^{th}$ cycles	26
Co _{0.6} Mo _{1.4} N ₂	10	200	$\sim 3000^{\text{th}}$ cycles	27
CoSe ₂ NPs/CP	10	139	$\sim 5000^{\text{th}}$ cycles	28
Exfoliated WS ₂ nanosheets	10	~220	~ 10000 th cycles / ~ 100 hours	29
Ni ₂ P nanoparticles	20	130	$\sim 500^{\text{th}} \text{ cycles}$	30
FeP nanosheets	10	~240	-	31
CoP/CNT	10	122	$\sim 2000^{th}$ cycles /	32

Summary of HER catalytic performance of various transition metal compounds

			~ 18 hours	
CoP/CC	10	67	~ 80000 s	33
CoP/Ti	10	90	$\sim 1000^{\text{th}} \text{ cycles}$	34
Ni-P/CP	10	117	~ 1000 th cycles / ~ 150 hours	35
Ni ₁₂ P ₅ nanoparticles	20	143	~1000 th cycles / ~ 10000 s	36
Ni ₅ P ₄ pellet	10	23	~ 16 hours	37
NiP ₂ /NS/CC	10	75	~ 3000 th cycles / ~ 60 hours	38
Ni ₂ P-G/NF	10	50	$\sim 500^{\text{th}} \text{ cycles } /$ $\sim 15 \text{ hours}$	39
Ni ₂ P/Ni/NF	10	98	~ 20 hours	40
NiCoP/NF	10	32	~ 24 hours	41

Table S7. Comparison of HER catalytic performance for our Ni₂P/CNFs and NiP₂/CNFs with other catalysts.

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