Fabrication and Synergistic Effect Studying of Janus Ni_2P/Ni_5P_4 Embedded in N-Doped Carbon as Efficient Electrocatalysts for Hydrogen Evolution Reaction

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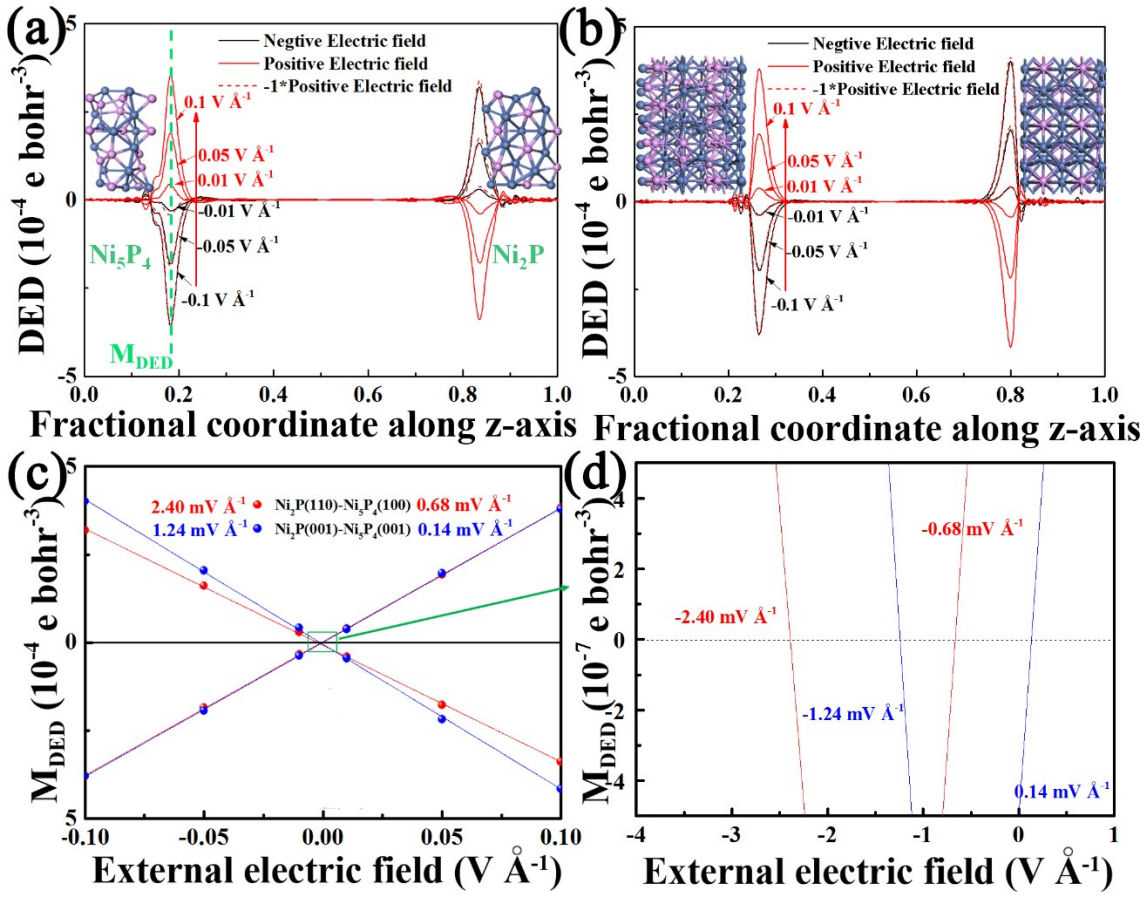

Figure S1. DED (DED = electron density of model with EEF − electron density of model without EEF) along z-axis with different EEF (-0.1, -0.05, -0.01, 0.01, 0.05 and 0.1 V Å^{-1}) (a) Ni_2P (110)-Ni_5P_4 (100) and (b) Ni_2P (001)-Ni_5P_4 (001), (c, d) maximum of DED (M_{DED}) along z-axis of Ni_2P (110)-Ni_5P_4 (100) and Ni_2P (001)-Ni_5P_4 (001).

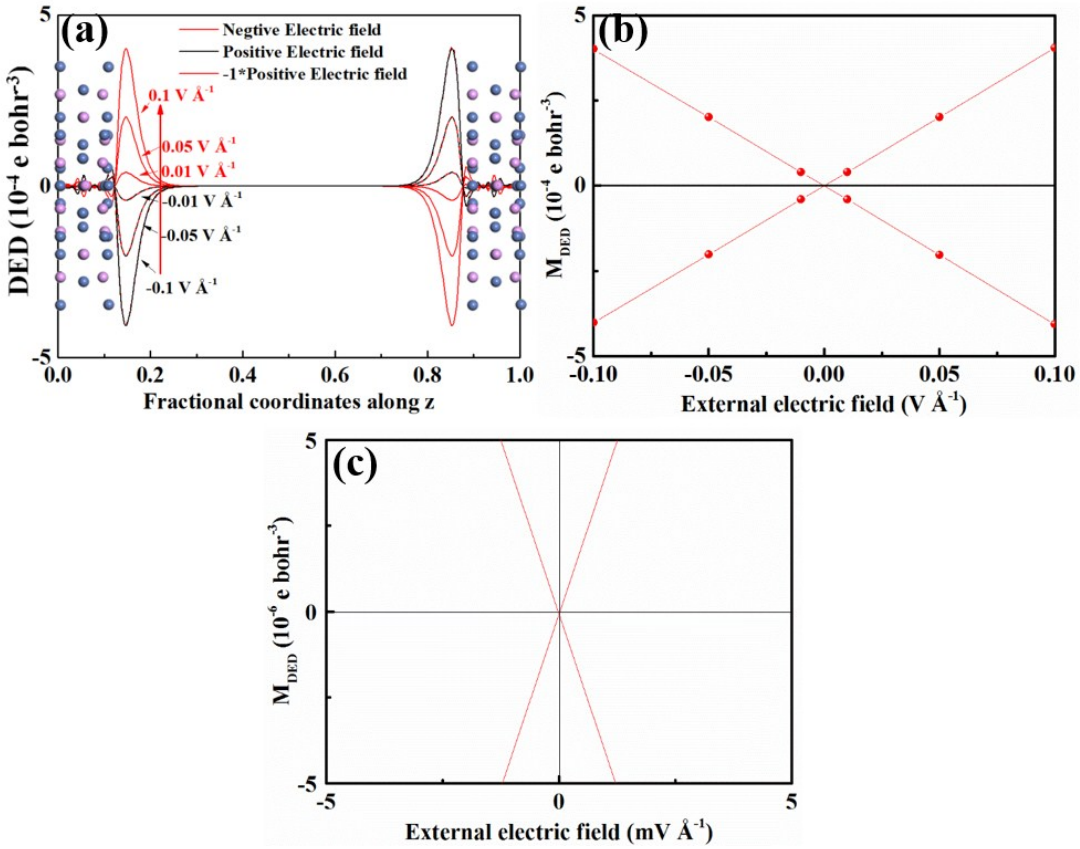

Figure S2. (a) Average DED along z axis of a symmetric slab model of Ni_2P (001) and (b, c) M_{DED} of along z-axis of Ni_2P (001) applied different external electric field.

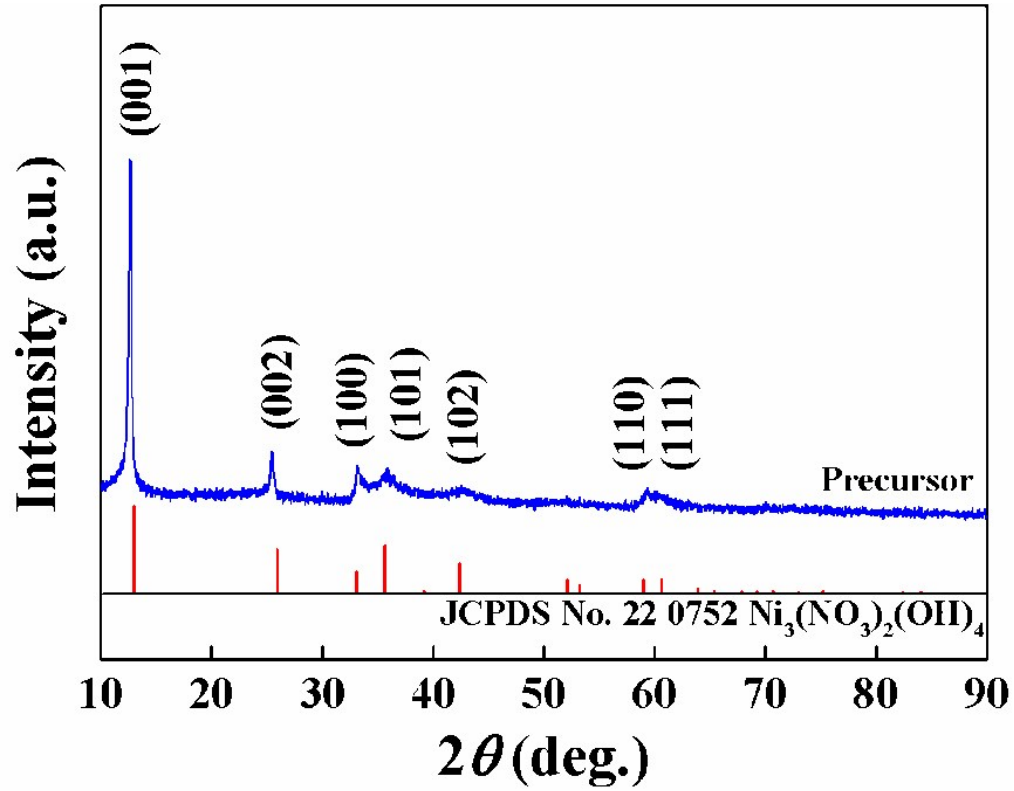

Figure S3. XRD pattern of precursor.

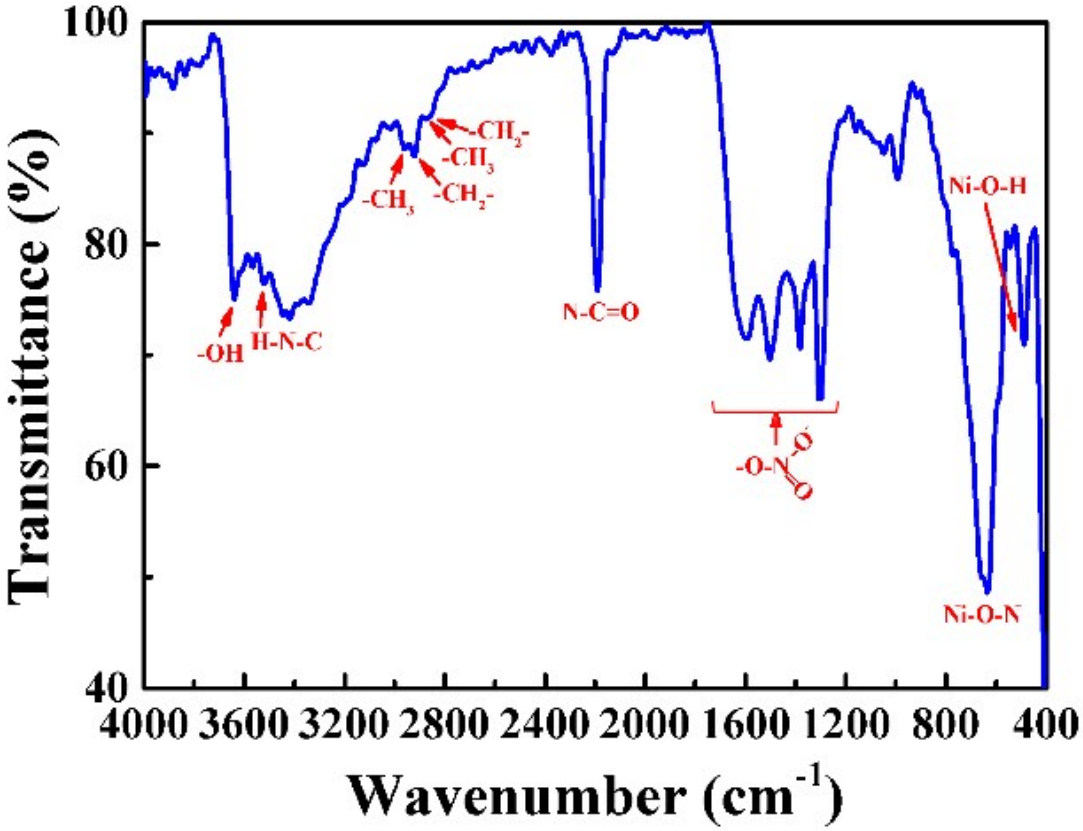

Figure S4. FTIR spectrum of precursor.

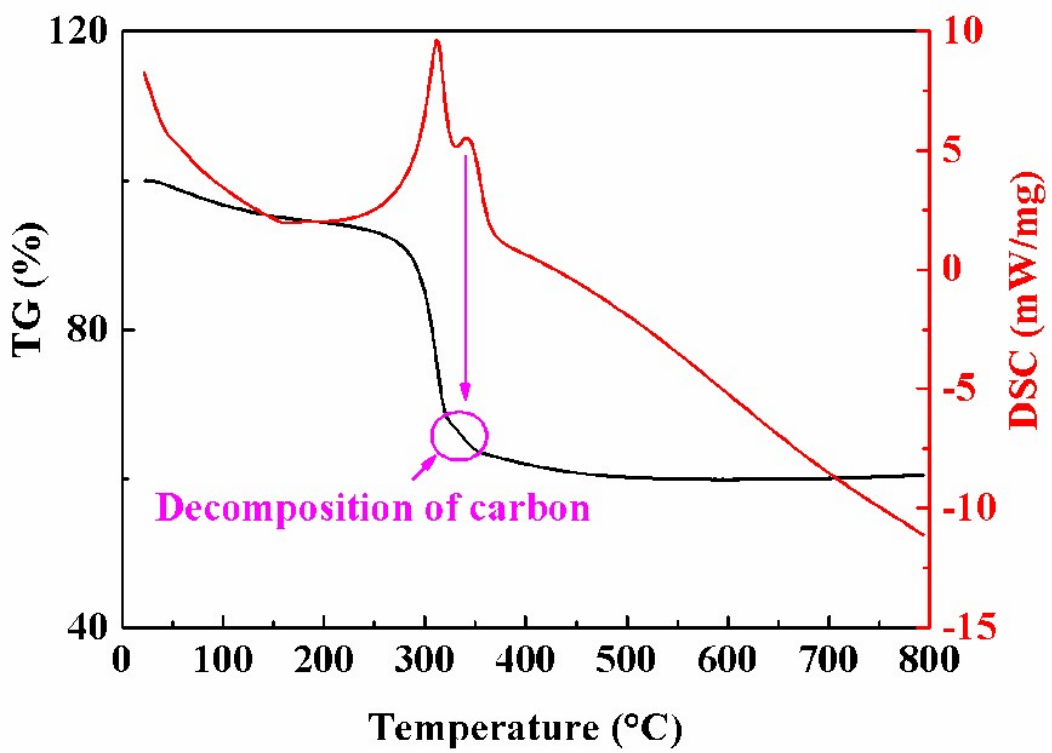

Figure S5. Thermogravimetry and differential thermal curves of precursor

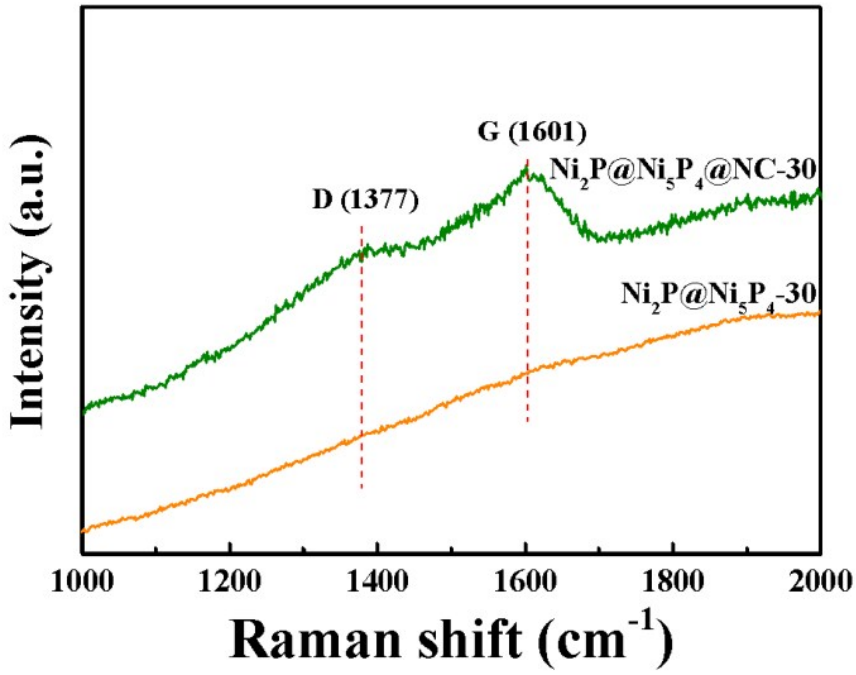

Figure S6. Raman spectra of Ni_2P/Ni_5P_4@NC-30 and Ni_2P/Ni_5P_4-30.

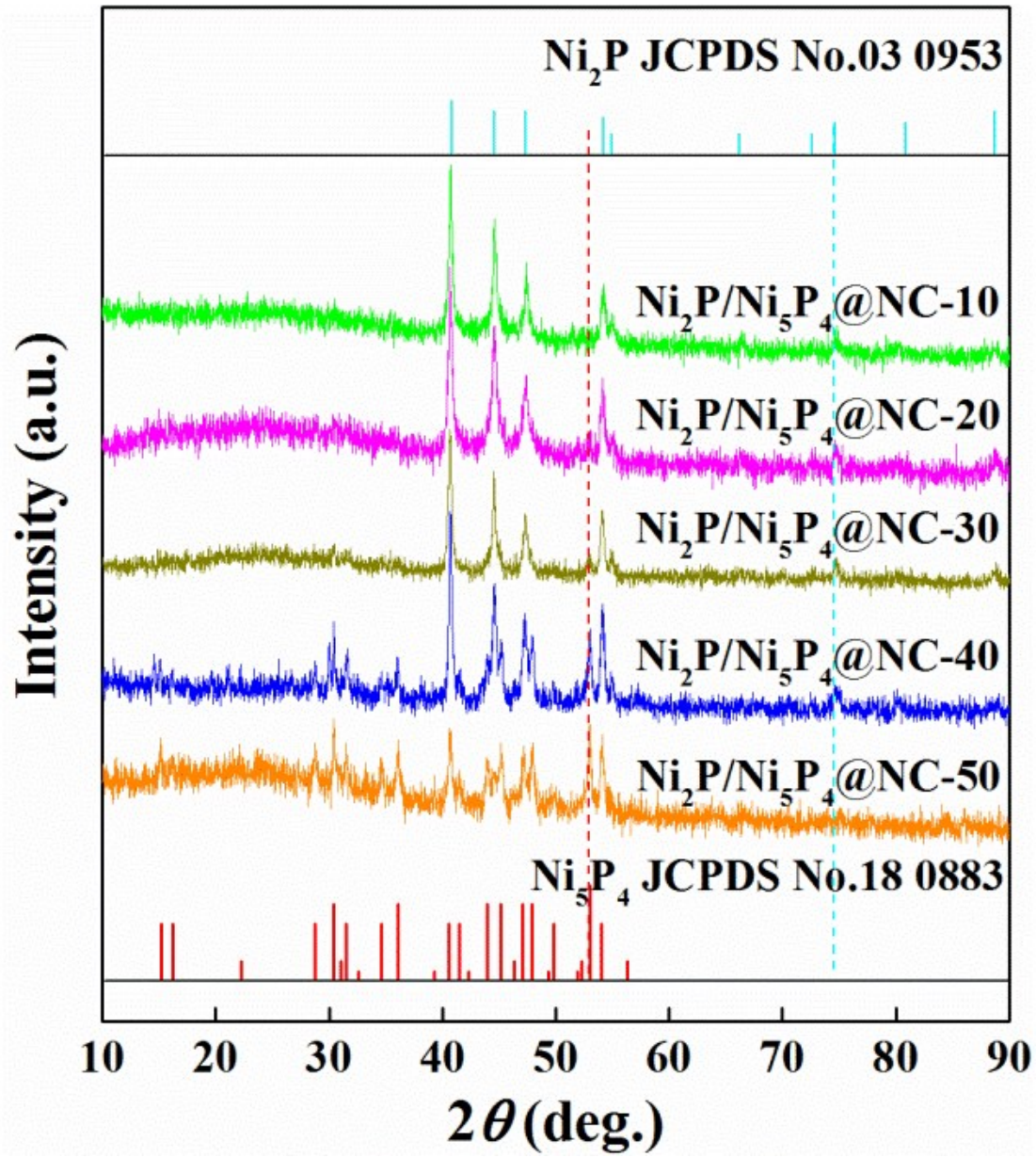

Figure S7. XRD patterns of Ni_2P/Ni_5P_4@NC-x (x=10, 20, 30, 40, 50).

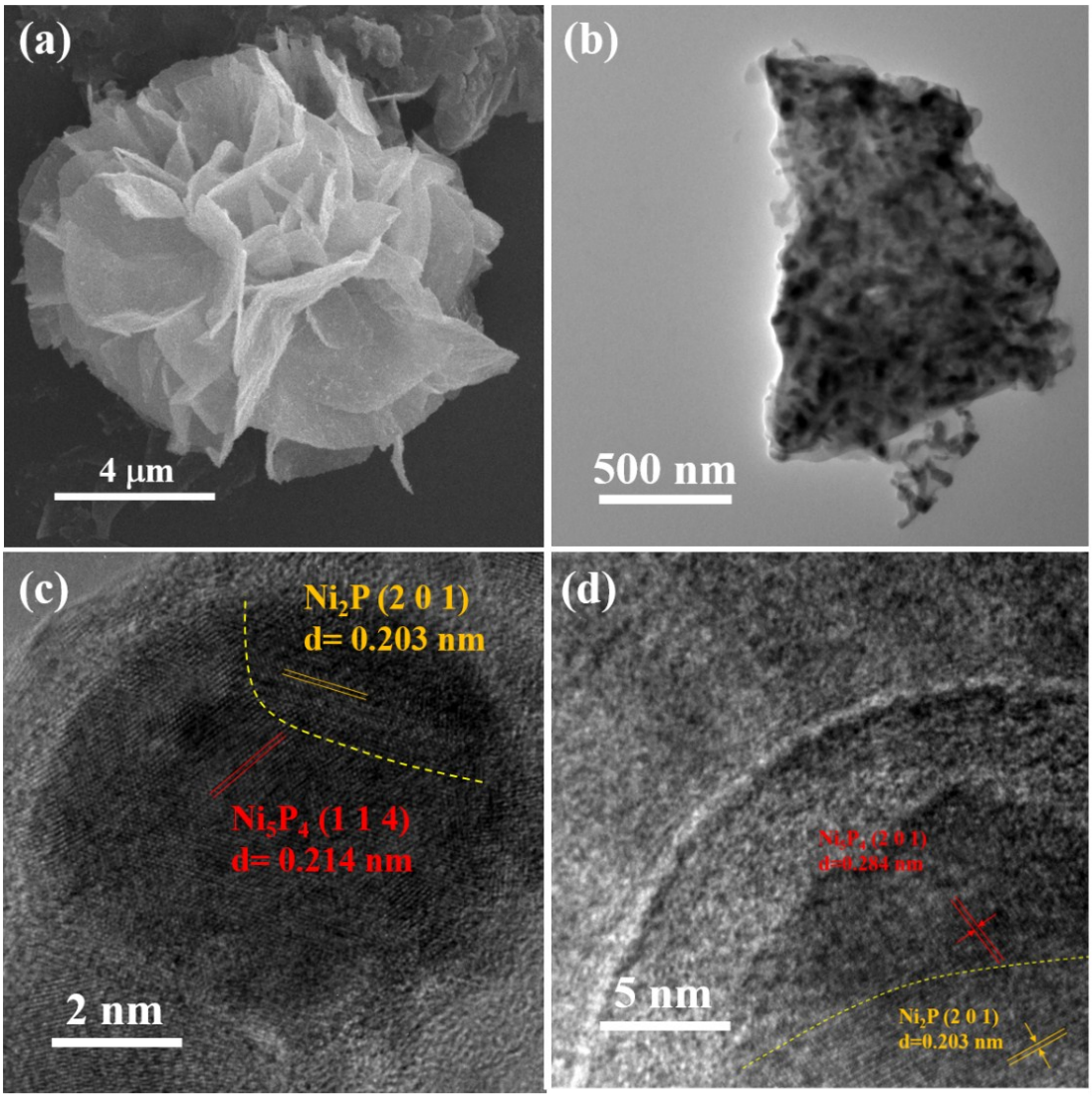

Figure S8. (a) SEM image, (b) TEM images and (c-d) HRTEM images of Ni_2P/Ni_5P_4@NC-30.

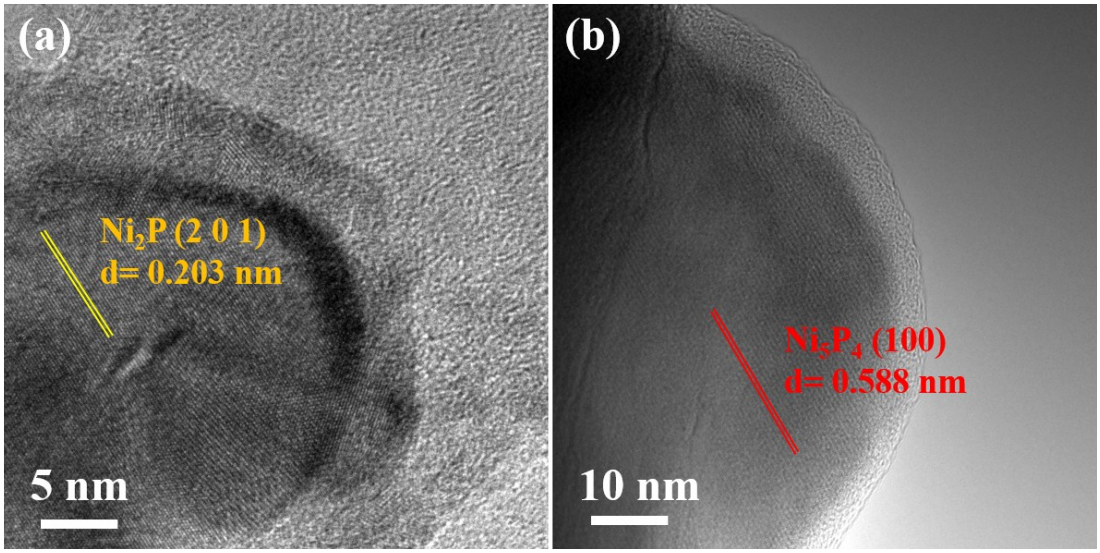

Figure S9. HRTEM images of (a) Ni_2P/Ni_5P_4@NC-10 and (b) Ni_2P/Ni_5P_4@NC-50.

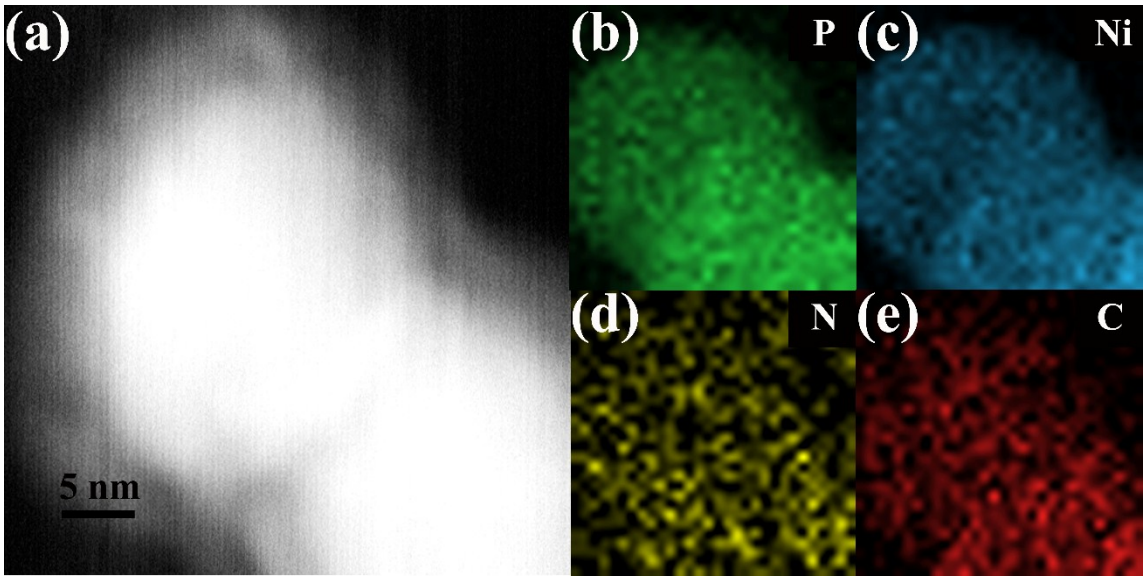

Figure S10. (a) HAADF image of Ni_2P/Ni_5P_4@NC-30 and energy-dispersive X-ray (EDX) mapping analysis of Ni (b), P (c), C (d) and N (e).

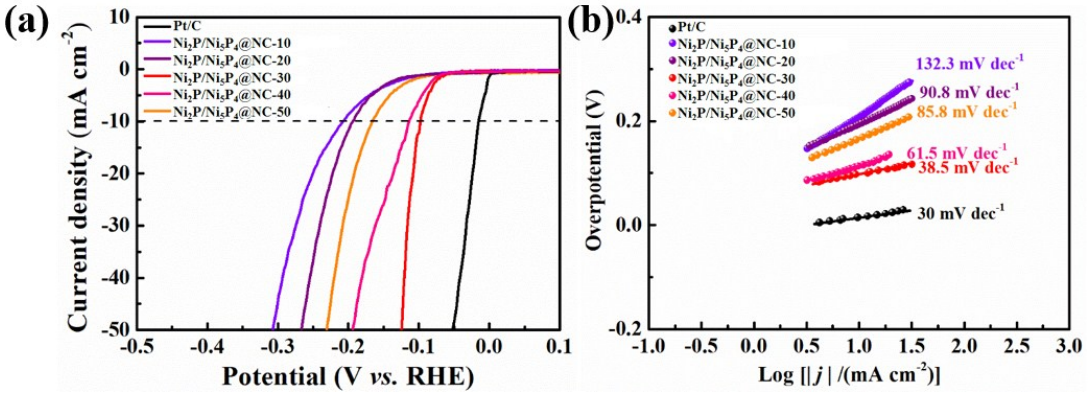

Figure S11. LSV and Tafel curves of Ni_2P/Ni_5P_4@NC-x (x=10, 20, 30, 40, 50) and Pt/C in 0.5 M H_2SO_4 with a scanning rate of 5 mV s^{-1}.

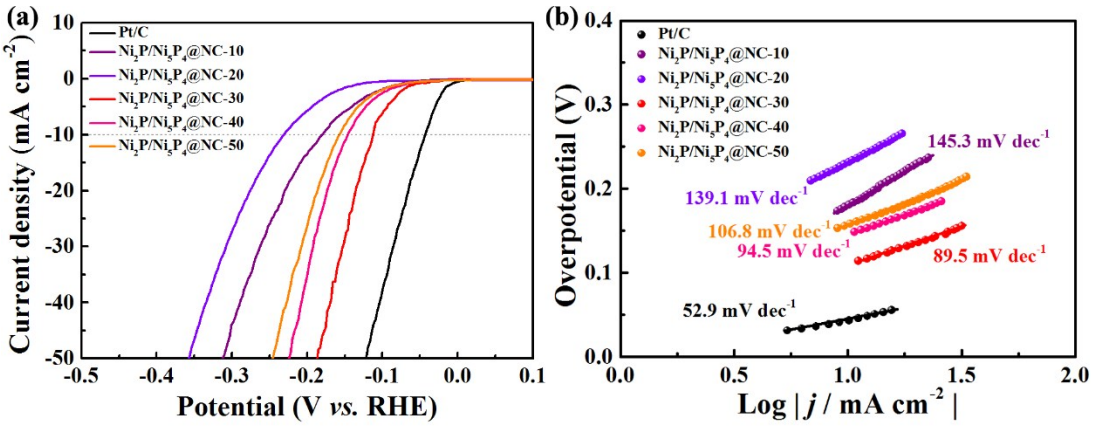

Figure S12. LSV and Tafel curves of Ni_2P/Ni_5P_4@NC-x (x=10, 20, 30, 40, 50) and Pt/C in 1 M KOH with a scanning rate of 5 mV s^{-1}.

Table S1. Comparison of HER performance in acidic electrolyte for Ni_5P_4/Ni_2P@NC with other HER catalysts

Catalyst	Potential (mV, j = 10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Journal	Reference
CoP NTs	129	60	J. Mater. Chem. A	**2014,** *2* (36), 14812
Ni_5P_4-Ni_2P-NS	130	79	Angew. Chem. Int. Edit.	**2015,** *54* (28), 8188
Ni_2P/CNT	124	53	J. Mater. Chem. A	**2015,** *3* (24), 13087
Se-enriched $NiSe_2$ NS	117	32	Angew. Chem. Int. Edit.	**2016,** *55* (24), 6919
Mo doped Ni_2P	67	77	Nanoscale	**2017,** *9* (43), 16674
CoP-CNT	139	52	Small	**2017,** *13* (15), e1400268
FeP/C	71	52	J. Am. Chem. Soc.	**2017,** *139* (19), 6669
CoP_3/Ni_2P	115	49	J. Mater. Chem. A	**2018,** *6* (14), 5560
Au@CoP	160	52	Nano Energy	**2018,** *50*, 273
Ni_2P/Ni_5P_4@NC	104	38.5	-	- This work

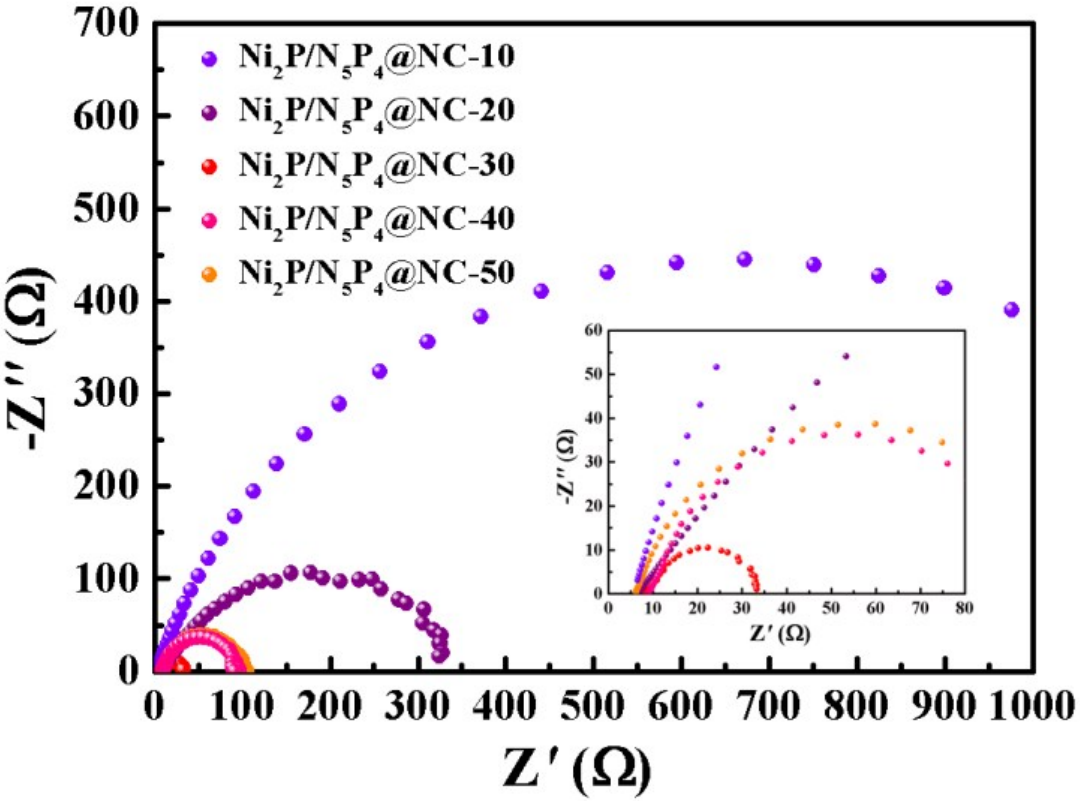

Figure S13. Nyquist plots of Ni_2P/Ni_5P_4@NC-x (x=10, 20, 30, 40, 50) at the potential of -104 mV *vs.* RHE.

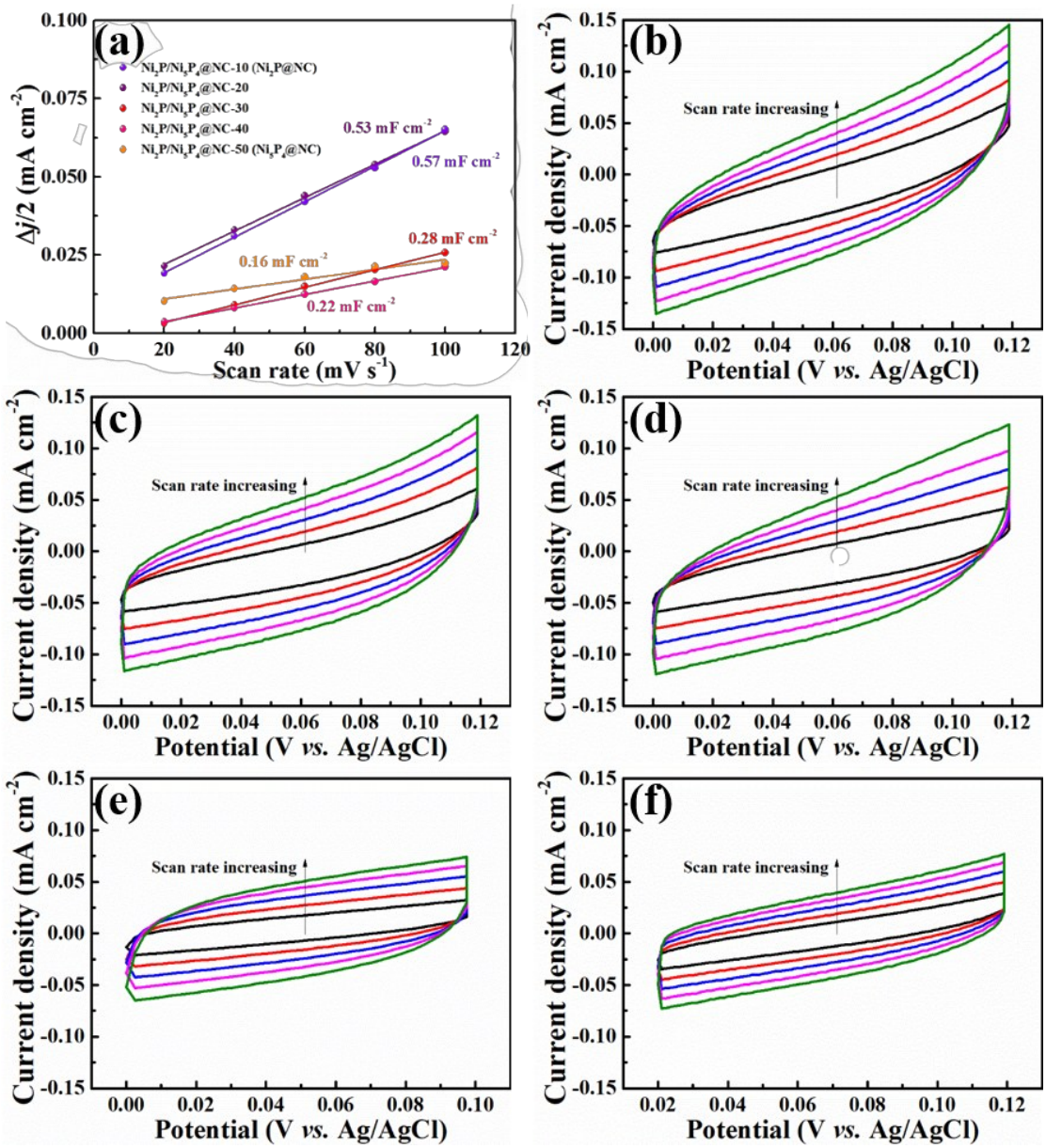

Figure S14. (a) Electrochemically doubl-layer capacitance (C_{dl}) and cyclic voltammetry curves of (b) Ni_2P/Ni_5P_4@NC-10, (c) Ni_2P/Ni_5P_4@NC-20, (d) Ni_2P/Ni_5P_4@NC-30, (e) Ni_2P/Ni_5P_4@NC-40, (f) Ni_2P/Ni_5P_4@NC-50. The sample was scanned five cycles at different scan rates (20, 40, 60, 80, and 100 mV/s).

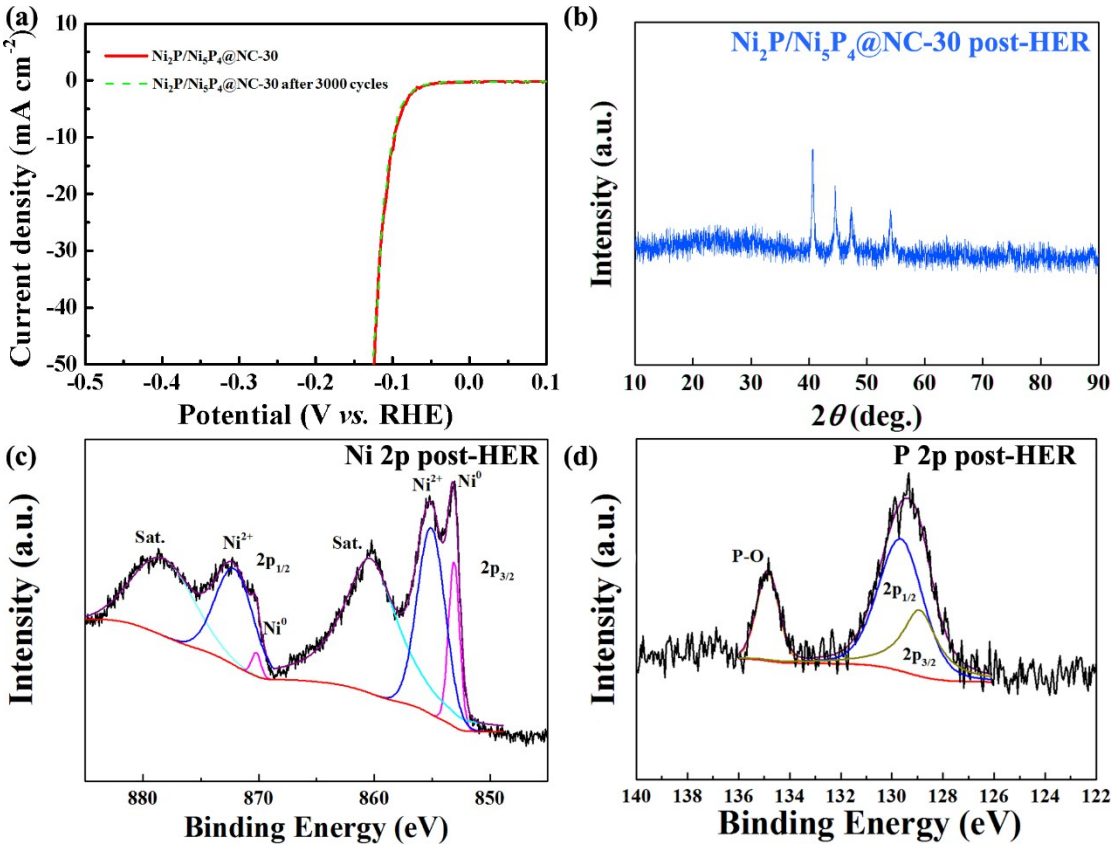

Figure S15. (a) Polarization curve before and after 3000 cycles of a durability test in 0.5 M H_2SO_4, (b) XRD pattern, XPS spectra of (c) Ni 2p and (d) P 2p regions of Ni_2P/Ni_5P_4@NC-30.

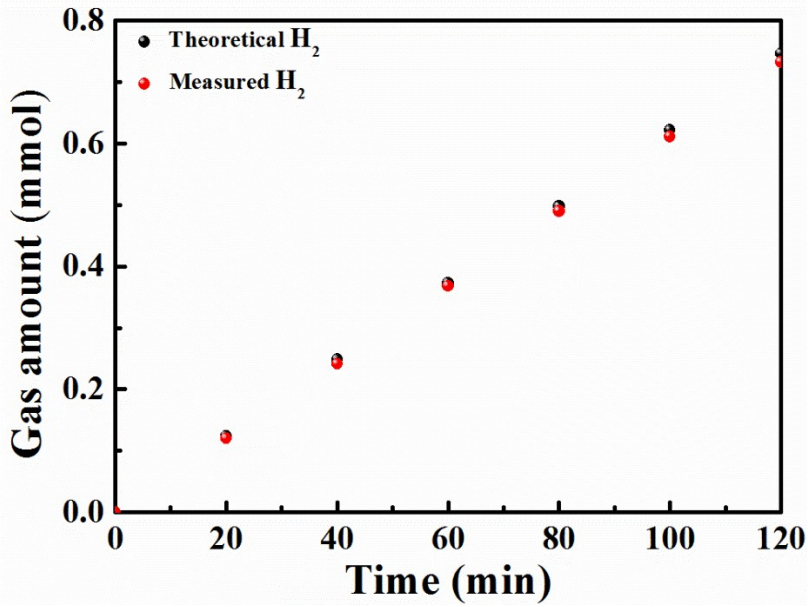

Figure S16. The amount of H_2 theoretically calculated and experimentally measured versus time in 0.5 H_2SO_4.

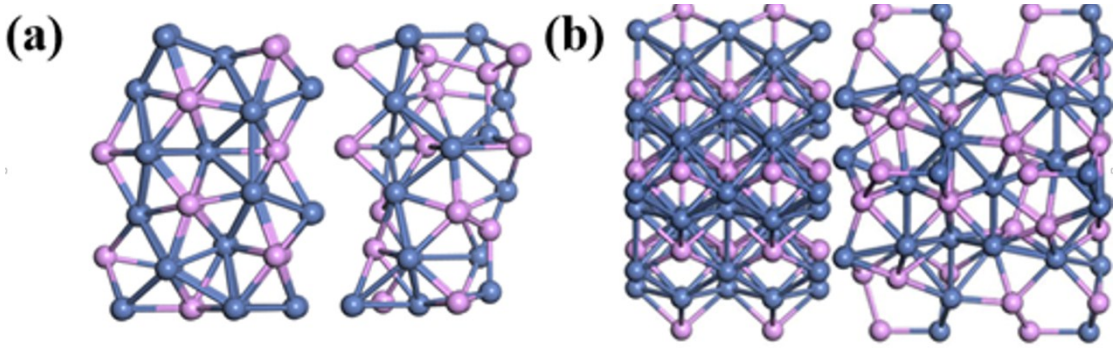

Figure S17. Ni_2P/Ni_5P_4 slab models of (a) Ni_2P (110)-Ni_5P_4 (100) and (b) Ni_2P (001)-Ni_5P_4 (001).

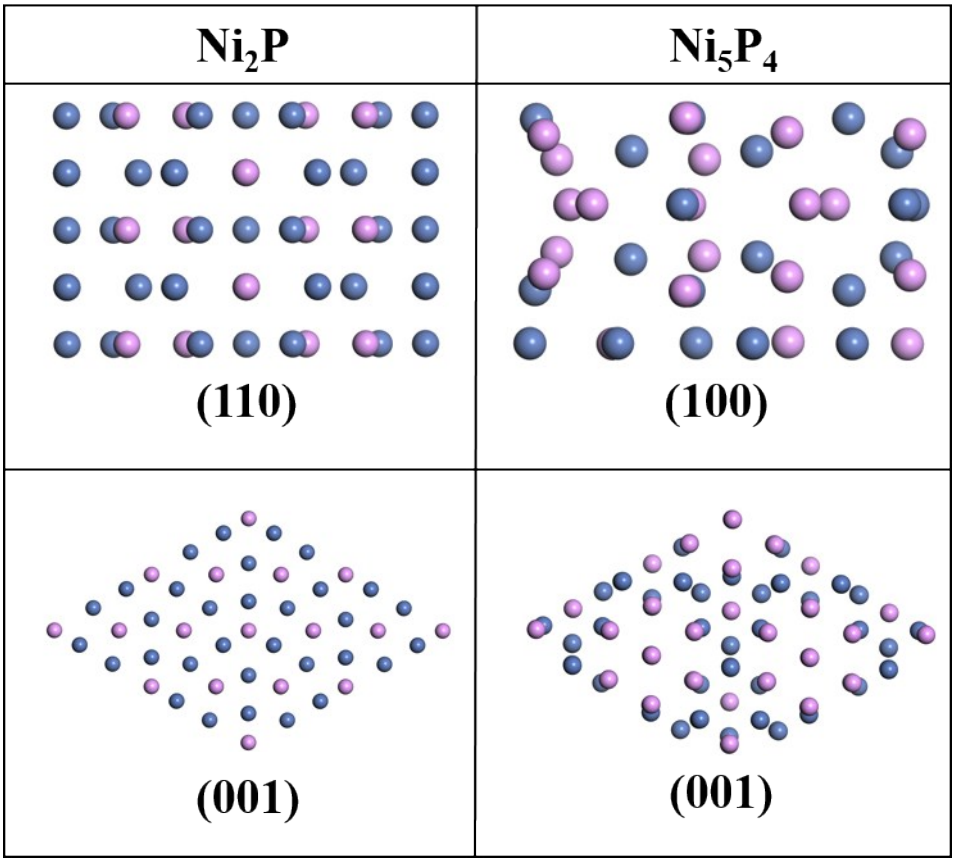

Figure S18. Separation views of Ni_2P (110)-Ni_5P_4 (100) and Ni_2P (001)-Ni_5P_4 (001) slab models.

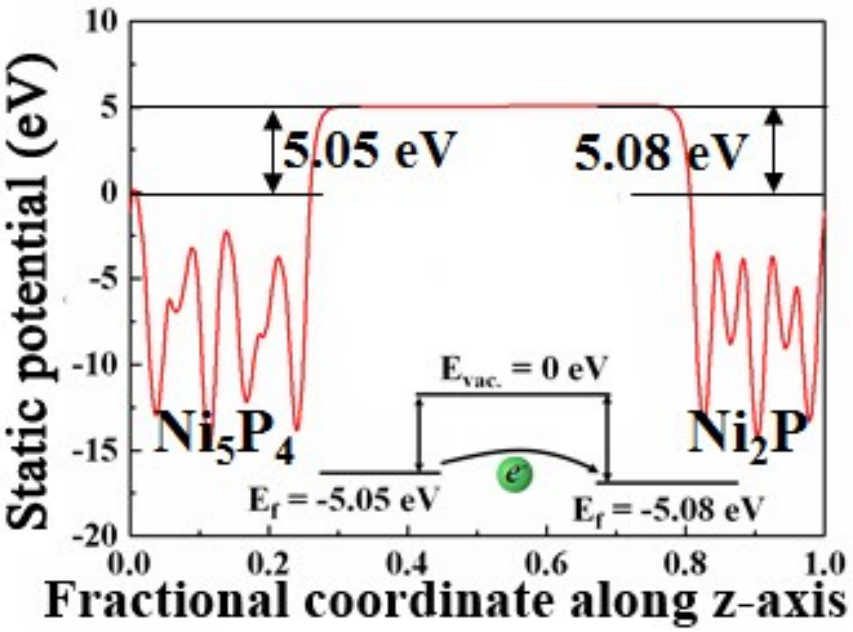

Figure S19. Static potential along z axis of Ni_2P (001)-Ni_5P_4 (001).

Table S2. The calculation results of interfaces

Interface		Ni_2P (110)-Ni_5P_4 (100)	Ni_2P (001)-Ni_5P_4 (001)
B.E. (eV $Å^{-2}$) [a]		11.04	14.27
S_{IEF} ($mV\ Å^{-1}$)	Ni_2P	2.40	1.24
	Ni_5P_4	0.68	-0.14
ΔE_f (eV) [b]		0.15	-0.03
$\Delta G_{H^*\ Ni5P4+Ni2P}$-$\Delta G_{H^*,\ Ni5P4}$ (meV)	P1	-12	17
	P2	-5	19

a) B.E. = Binding Energy

b) $\Delta E_f = E_{f,\ Ni2P} - E_{f,\ Ni5P4}$