

Supporting Information

Surface reconstruction induced in-situ phosphorus doping in nickel oxides for enhanced oxygen evolution reaction

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1. Electrochemical measurements

To prepare the CFP supported Ni₅P₄ (Ni₅P₄@CFP) working electrode, 100 mg of Ni₅P₄ pre-catalyst powders were dispersed in 2 ml ethanol and then ultrasonication for 20 min to get a homogeneous catalyst ink. Subsequently, 10 μL of the prepared catalyst ink was drop-cast onto a tailored CFP (0.5 × 1 cm² in working area) and dried naturally in the air. Thus, the mass loading of Ni₅P₄ pre-catalyst on the CFP was 1 mg cm⁻². In addition, the NiO@NF and P-NiO@NF were directly used as the working electrodes in this work.

The electrochemical measurements were conducted by using a CHI 660E electrochemistry workstation in standard three-electrode system at room temperature. A saturated Ag/AgCl electrode was used as the

reference electrode. To avoid the influence of counter electrode on experimental results, Pt sheet and carbon rod were used as the counter electrode, respectively. OER measurements were performed in 1 M KOH solution (pH = 13.8). The potential values were converted to the potential vs reversible hydrogen electrode (vs RHE) according to the equation: $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.0591 \times \text{pH} + 0.197$. Cyclic voltammetry (CV) scanning for calculating OER overpotential was conducted without iR compensation. Electrochemical impedance spectroscopy was recorded at the corresponding open circuit potential with an amplitude potential of 5 mV and scanning frequencies ranging from 0.01 Hz to 100 kHz.

2. The calculation details of Gibbs free energies

Computational hydrogen electrode (CHE) [1] model was used to calculate the Gibbs free energy change for OER elementary reactions. At electrode potential $U = 0$ V (vs. reversible hydrogen electrode, RHE), the Gibbs free energy change (ΔG) can be calculated by

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S \quad (1)$$

where ΔE is the energy difference between the products and reactants from DFT computations; ΔE_{ZPE} and ΔS are the changes in zero-point energies and entropy, respectively, which are obtained from the vibrational frequency calculations; T is the temperature at 298 K. The energy corrections of gas-phase species in this work, including zero point energies and entropies, are listed in Table S2. The overpotential (η), $\eta = \Delta G_{\text{max}}/e$, where ΔG_{max} is the maximum free energy change among all elementary steps under standard electrode (reduction) potential. Refer to Lee's work in alkaline environment, the oxygen evolution reaction has four elementary steps in alkaline [2]. $\mu e^- - \mu(\text{OH}^-) - eU = 9.65$ eV was obtained by repeated calculations under standard electrode (reduction) potential ($E^0 = 0.402$ V) at $T = 298.15$ K.

The adsorption energy of *OH (ΔE) on the catalyst surface was calculated by

$$\Delta E = E(*\text{OH}) - E(\text{surface}) - E(\text{OH}) \quad (2)$$

in which $E(*\text{OH})$, $E(\text{surface})$ and $E(\text{OH})$ are the total energy of the catalyst surface with adsorbed OH, the catalyst surface and the energy of OH, respectively. Here, $E(\text{OH}) = E(\text{H}_2\text{O}) - 1/2E(\text{H}_2)$.

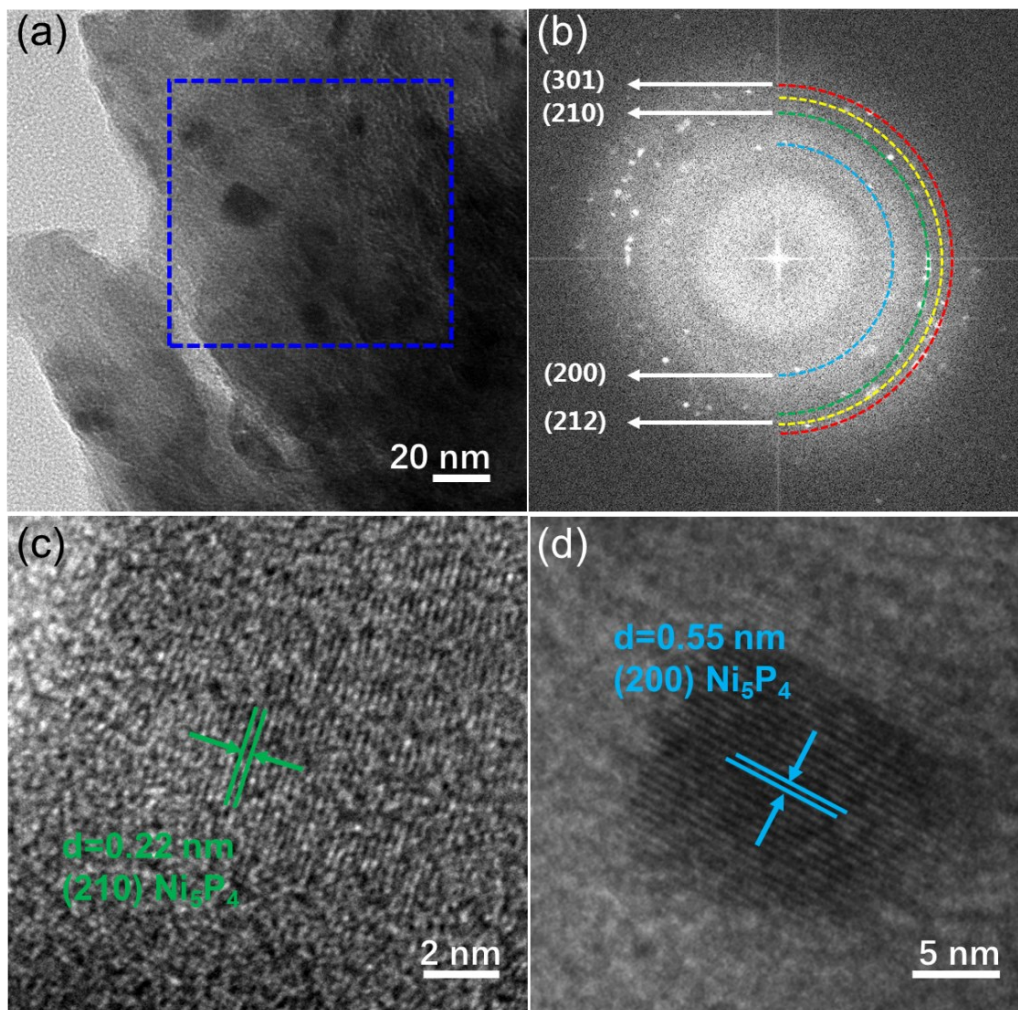


Fig. S1. (a) TEM image of Ni_5P_4 powders synthesized by mechanical alloying. (b) SAED pattern of selected area in Fig. S1a. (c and d) HRTEM images of Ni_5P_4 powders synthesized by mechanical alloying.

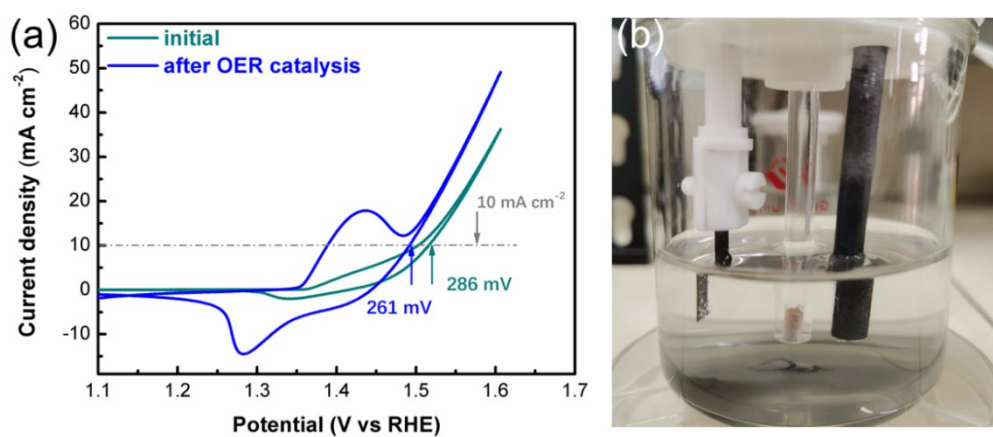


Fig. S2. (a) CV scanning curves of Ni₃P₄@CFP electrode with carbon rod as the counter electrode. (b)

Three-electrode system for OER electrocatalysis with carbon rod as counter electrode.

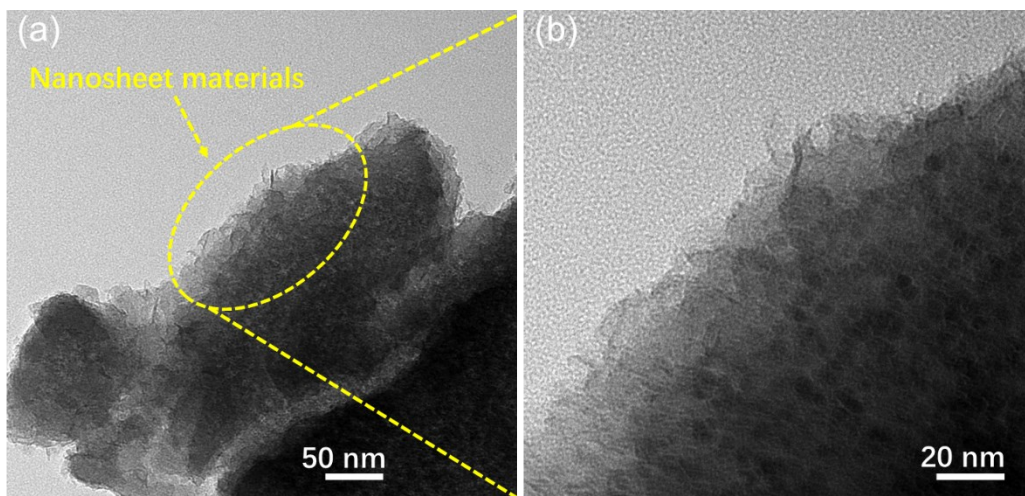


Fig. S3. (a and b) TEM images of derived NiO nanosheets after OER electrocatalysis.

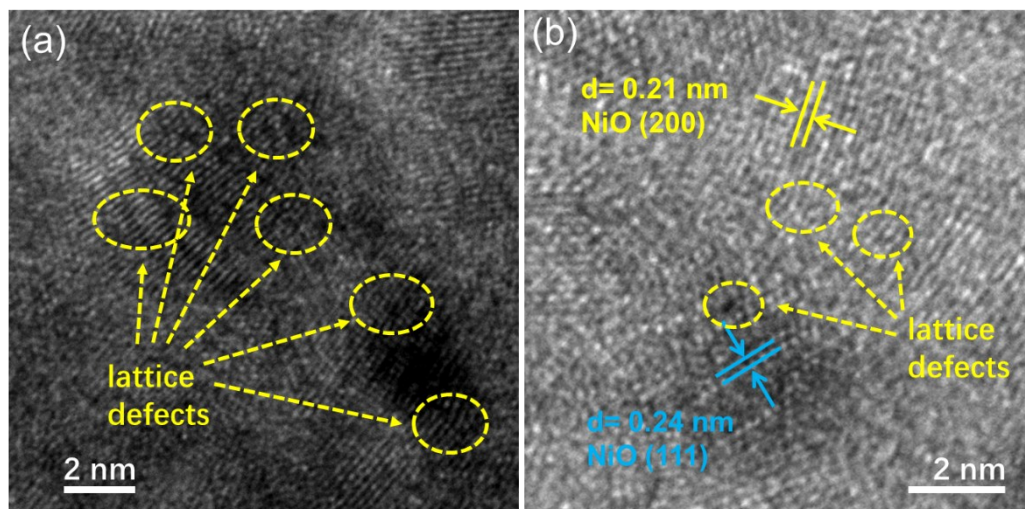


Fig. S4. (a and b) HRTEM images of derived NiO nanosheets after OER electrocatalysis.

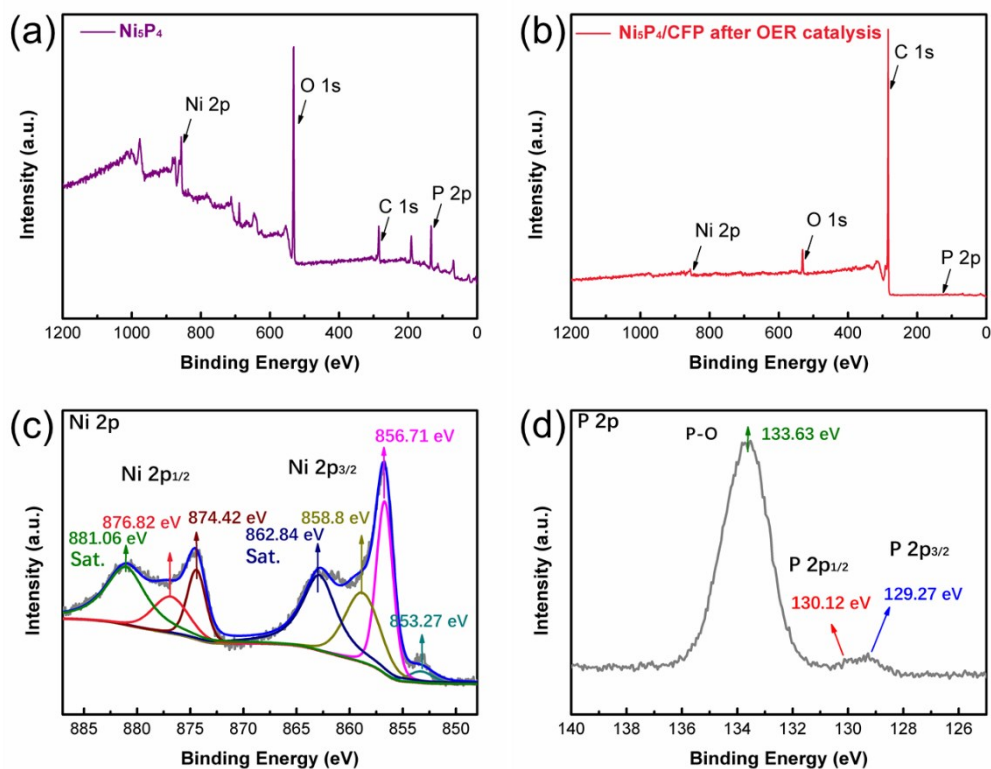


Fig. S5. XPS survey spectra of (a) Ni_5P_4 powders synthesized by ball-milling reaction, (b) Ni_5P_4 powders after the continuous OER electrocatalysis. (c) High resolution XPS spectra of (c) Ni 2p and (d) P 2p for the Ni_5P_4 powders synthesized by ball-milling reaction.

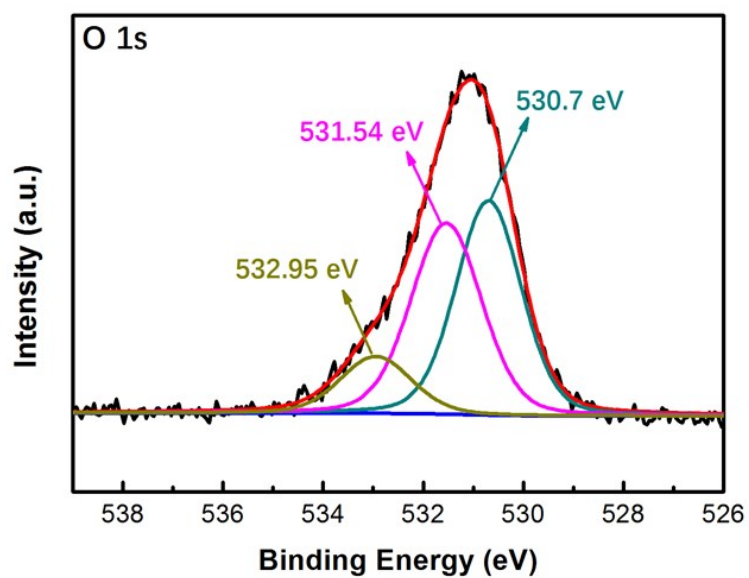


Fig. S6. High-resolution XPS spectra of O 1s for the Ni_5P_4 powders after OER electrocatalysis.

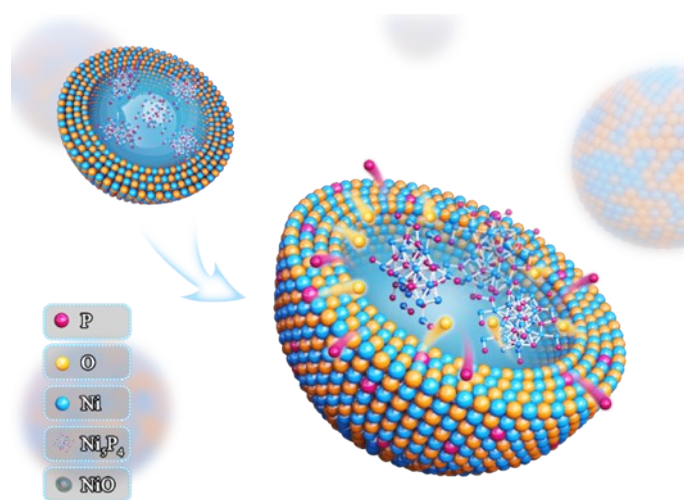


Fig. S7. Illustration of the surface reconstruction induces in-situ P doping into NiO crystal.

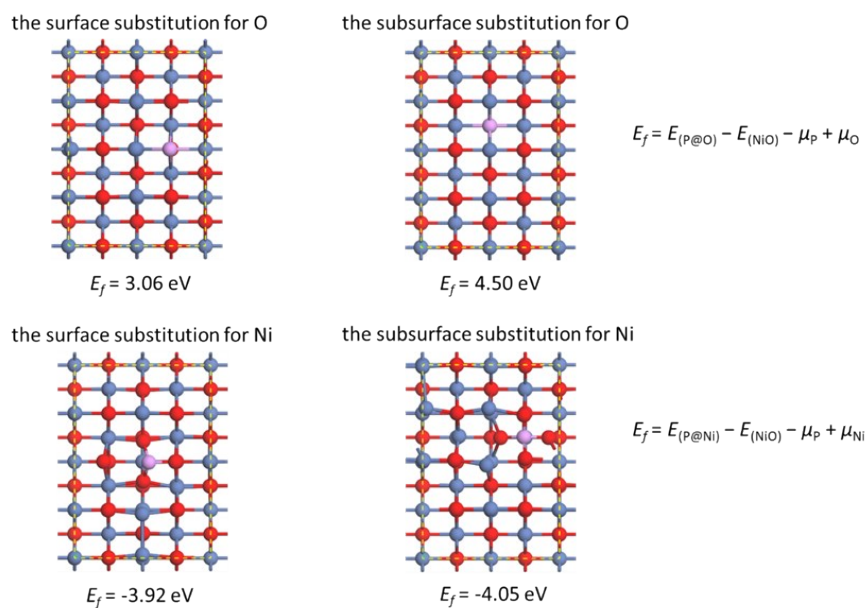


Fig. S8. The configurations and formation energies of different P substitution sites on the NiO(110) surface and subsurface. In this calculation, $E_{(P@O/Ni)}$ is the total energy of NiO containing the dopant P and $E_{(NiO)}$ is the total energy of the pure 64-atom NiO. μ_P , μ_O and μ_{Ni} is the chemical potential for black phosphorus, O_2 and metal Ni, respectively.

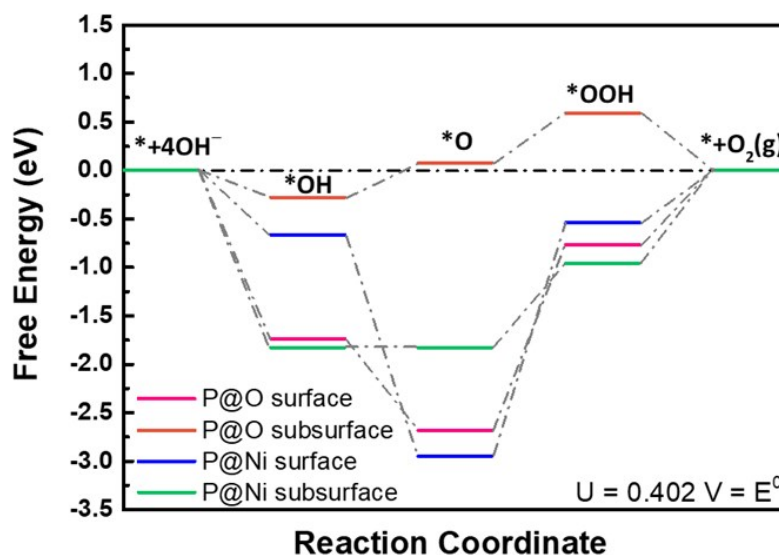


Fig. S9. The free energy diagram of different P substitution sites on the NiO(110) surface and subsurface at the equilibrium potential $E^0 = 0.402$ V vs NHE.

Table S1. Bader charge in e for P-NiO(110) and NiO(110) without and with OH adsorption.

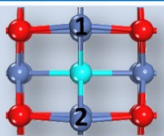
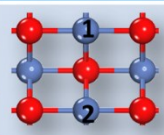
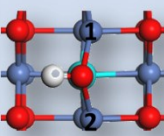
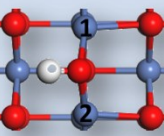
P-NiO(110)	N_e (e)	Structure	NiO(110)	N_e (e)	Structure
Ni1	-0.68		Ni1	-1.14	
Ni2	-0.67		Ni2	-1.14	
P	0.03		O	1.19	
P-NiO(110) with OH adsorption	N_e	Structure	NiO(110) with OH adsorption	N_e	Structure
OH	0.48		OH	0.57	
Ni1	-0.96		Ni1	-1.21	
Ni2	-0.77		Ni2	-1.21	
P	-0.02		O	1.22	

Table S2. Total energies (E, eV), zero point energy (ZPE) corrections and entropic contributions (TS) ofH₂O, H₂ and adsorbates to the free energies.

Species	E (eV)	ZPE (eV)	TS (eV)
H ₂ O (0.035 bar)	-14.22	0.56	0.67
H ₂	-6.76	0.27	0.41
P-NiO(110)			
*O		0.05	0.06
*OH		0.38	0.06
*OOH		0.43	0.25
NiO(110)			
*O		0.06	0.06
*OH		0.38	0.06
*OOH		0.45	0.17

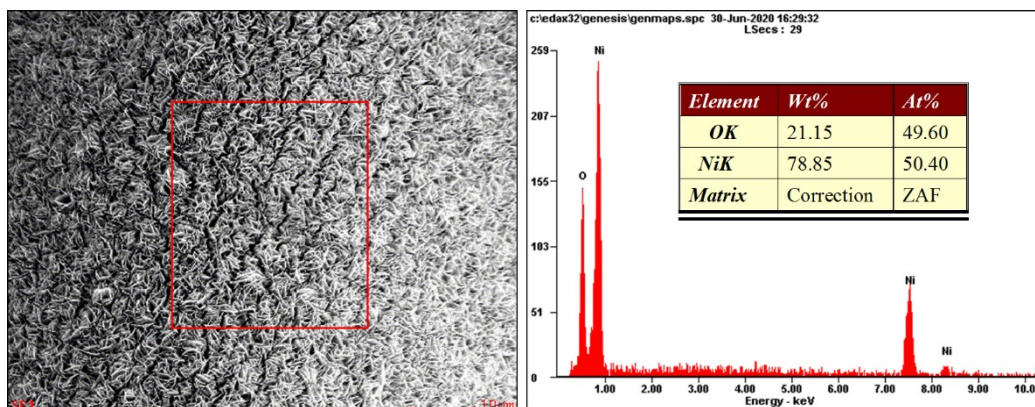


Fig. S10. EDS pattern of NiO@NF working electrode.

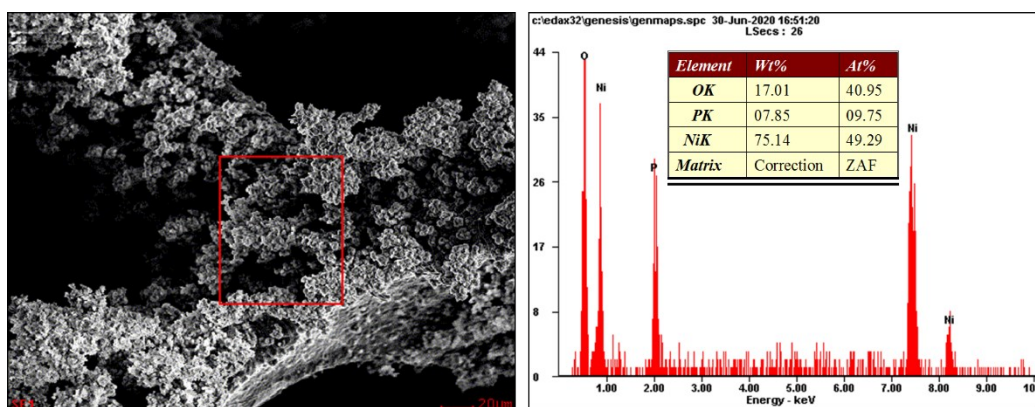


Fig. S11. EDS pattern of P-NiO@NF working electrode.

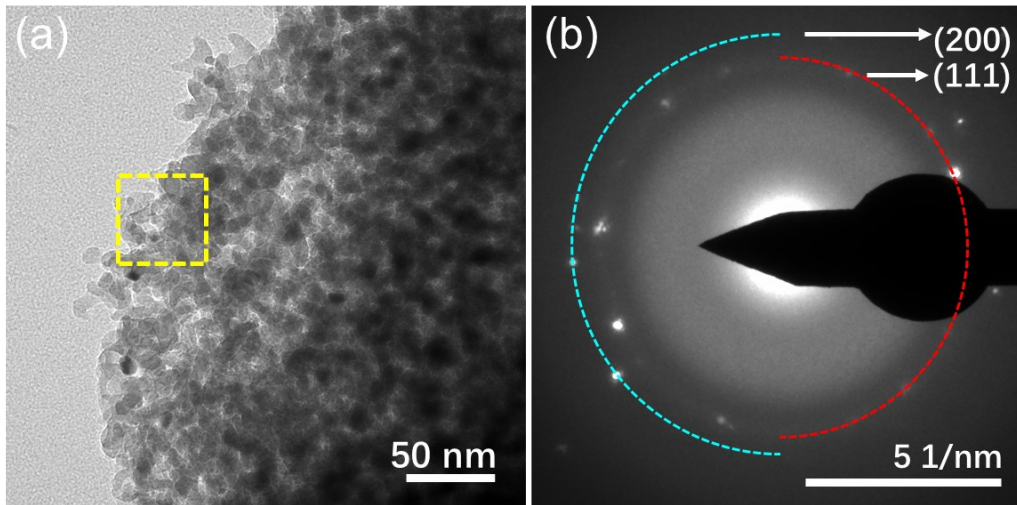


Fig. S12. TEM pattern. (a) TEM image of the coral-like materials on P-NiO@NF electrode, (b) SAED pattern of the coral-like materials on P-NiO@NF electrode as marked in (a).

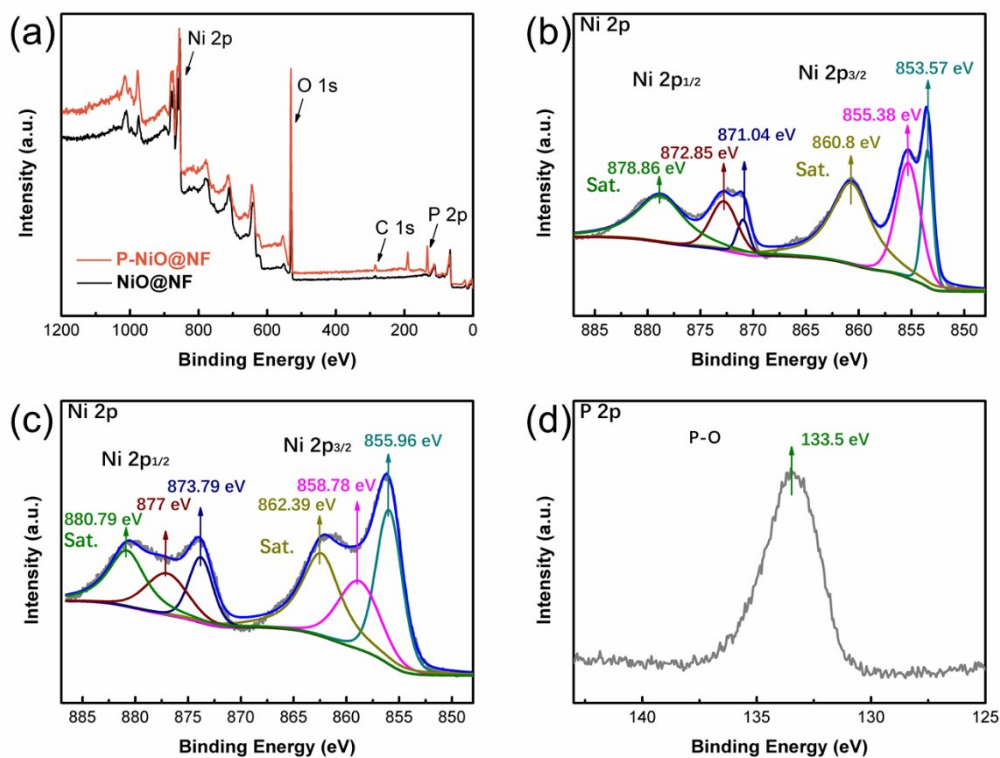


Fig. S13. (a) XPS survey spectra of NiO@NF and P-NiO@NF working electrodes. (b) High resolution XPS spectra of Ni 2p of NiO@NF electrode. High resolution XPS spectra of (c) Ni 2p and (d) P 2p for P-NiO@NF electrode.

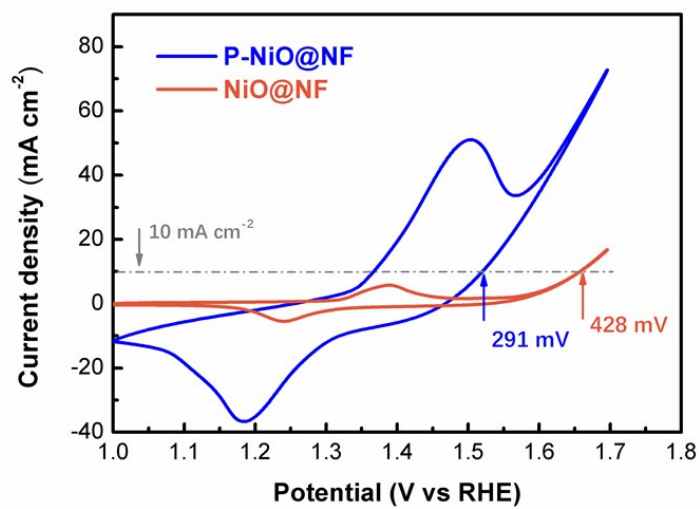


Fig. S14. CV scanning curves of NiO@NF and P-NiO@NF working electrodes with carbon rod as the counter electrode.

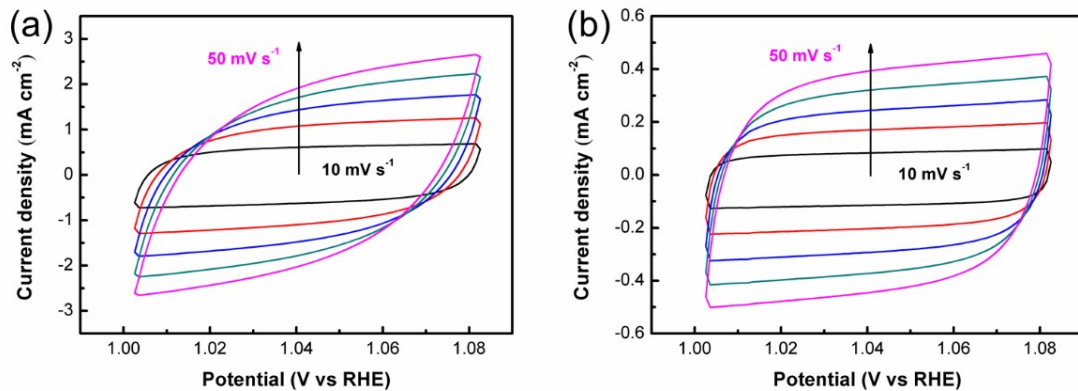


Fig. S15. CV scanning curves with a potential window of 1.00 to 1.08 V (vs RHE) at different scan rates

of 10, 20, 30, 40 and 50 mV s⁻¹. (a) NiO@NF working electrode, (b) P-NiO@NF working electrode.

Table S3. Electrochemical OER performances comparison of Ni₅P₄@CFP, NiO@NF and P-NiO@NF working electrodes with some recently reported catalysts.

Electrocatalysts	Electrolyte	j/mA cm ⁻²	η /mV	References
Ni _{0.75} Mn _{0.25} oxides	1M KOH	10	297	ACS Energy Lett. 2018 , 3, 2150–2158.
N-NiO	1M KOH	10	270	ACS Appl. Mater. Interfaces 2019 , 11, 30865–30871.
Cobalt phosphonate (CoPIII)	1M KOH	10	334	Chemical Engineering Journal 396 (2020) 125245.
P-Co _{0.9} Ni _{0.9} Fe _{1.2} NCs	1M KOH	10	273.1	Sci. China Mater. 2019 , 62(9): 1285–1296.
SrCo _{0.85} Fe _{0.1} P _{0.05} O _{3-δ} nanofilm	1M KOH	10	290	Applied Catalysis B: Environmental 272 (2020) 119046
O-NiSe@Ni/SS	1M KOH	10	290	Electrochimica Acta 353 (2020) 136519
S-CoO _x /NF	1M KOH	10	370	Nano Energy 71 (2020) 104652
3-D PC-G@NiO nanosheets	1M KOH	10	320	Electrochimica Acta 342 (2020) 136118
NiCo/NiCoO _x @FeOOH	1M KOH	10	278	Electrochimica Acta 257 (2017) 1–8
CoO@FeOOH	1M KOH	10	255	Electrochimica Acta 257 (2017) 356–363
Ni(OH) ₂ nanosheet	1M NaOH	10	295	Nanoscale, 2018 , 10, 5054–5059
Ni₅P₄@CFP	1M KOH	10	269	This work
Ni₅P₄@CFP after OER electrocatalysis	1M KOH	10	240	This work
NiO/NF	1M KOH	10	415	This work
P-NiO/NF	1M KOH	10	286	This work

References

- [1]. Peterson, A. A.; Abild-Pedersen, F.; Studt, F.; Rossmeisl, J.; Nørskov, J. K. *Energy Environ. Sci.* **2010**, 3, 1311.
- [2]. Lee, C. H.; Jun, B.; Lee, S. U. *ACS Sustainable Chemistry & Engineering* **2018**, 6, 4973.