

Supplementary Information

Dispersive non-noble metal phosphide embedded in alumina arrays derived from layered double hydroxide precursor toward efficient oxygen evolution reaction and biomass upgrading

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Computational details of the thermodynamic mechanism of OER

The thermodynamic mechanism of OER in alkaline conditions which proposed by Norskov group are extensively used. The scheme of reaction elementary steps is as follows



where ‘*’ means the Ni(111), Ni₂P(111) and clean surface. OH*, O* and OOH* denote the species adsorbed on the surface. To be convenient, the steps (1)-(4) can be converted to the form in the acidic conditions which can be expressed as



The steps (1)-(4) are equivalent to (5)-(8).

The Gibbs free energy changes for reaction (5)-(8) are calculated as

$$\Delta G_1 = \Delta G_{\text{OH}} - eU + kT \ln 10 \text{pH} \quad (9)$$

$$\Delta G_2 = \Delta G_{\text{O}^-} - \Delta G_{\text{OH}} - eU + kT \ln 10 \text{pH} \quad (10)$$

$$\Delta G_3 = \Delta G_{\text{OOH}} - \Delta G_{\text{O}} - eU + kT \ln 10 \text{pH} \quad (11)$$

$$\Delta G_4 = 4.92 [\text{eV}] - \Delta G_{\text{OOH}} - eU + kT \ln 10 \text{pH} \quad (12)$$

G is the Gibbs free energy, and U is the external bias against normal hydrogen electrode (NHE) at standard conditions ($T = 298.15 \text{ K}$, $P = 1 \text{ bar}$, $\text{pH} = 0$). Therefore, here, eU and pH are 0. Due to the Gibbs free energy of formation of two water molecules is $4 \times 1.23 = 4.92 \text{ eV}$, the sum of $\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4$ is fixed to 4.92 eV . The reaction Gibbs free energy is calculated from the adsorption energy of OH*, O* and OOH*, according to $\Delta G_i = \Delta E_i + \Delta \text{ZPE}_i - T \Delta S_i$. The energy differences ΔE_i calculated against H₂O and H₂ are calculated as

$$\Delta E_{\text{OH}} = E(\text{OH}^*) - E(*) - [E(\text{H}_2\text{O}) - 1/2E(\text{H}_2)] \quad (13)$$

$$\Delta E_{\text{O}} = E(\text{O}^*) - E(*) - [E(\text{H}_2\text{O}) - E(\text{H}_2)] \quad (14)$$

$$\Delta E_{\text{OOH}} = E(\text{OOH}^*) - E(*) - [2E(\text{H}_2\text{O}) - 3/2E(\text{H}_2)] \quad (15)$$

The theoretical overpotential is defined as:

$$\eta = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/e - 1.23 \text{ [V]} \quad (16)$$

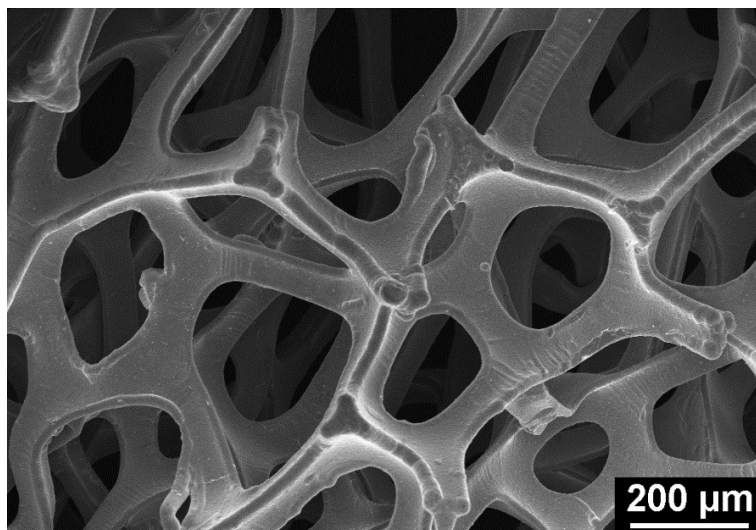


Fig. S1 SEM image of NF

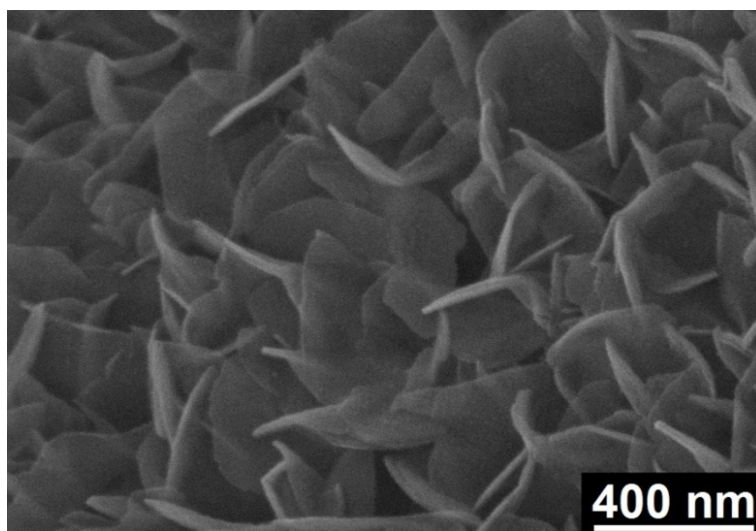


Fig. S2 SEM image of NiAl-HPO₄-LDH/NF intermediate.

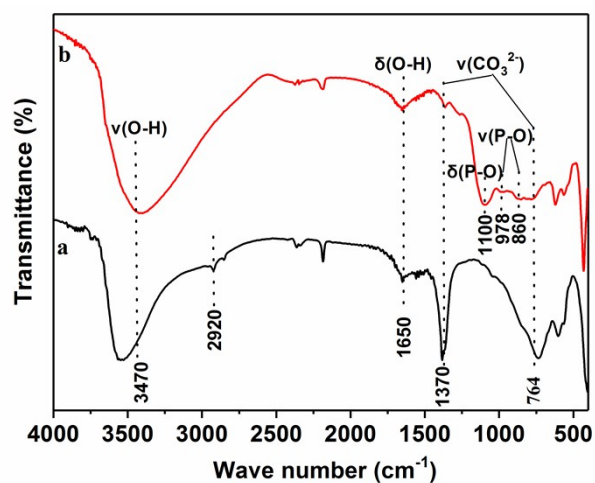


Fig. S3 FT-IR spectrum of NiAl-PO₄-LDH/NF intermediate.

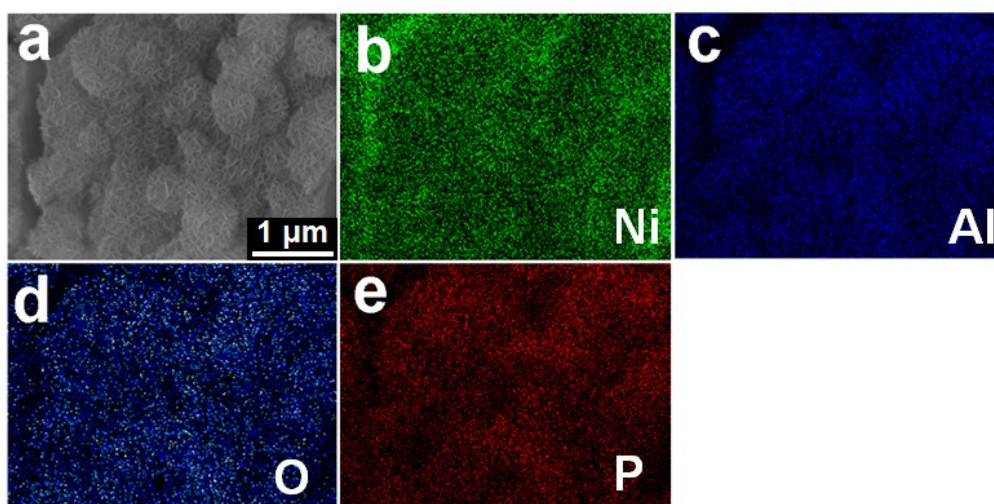


Fig. S4 a) SEM image a) and b-d) elemental mapping images of Ni, Al, O, and P of NiAl-HPO₄-LDH/NF intermediate

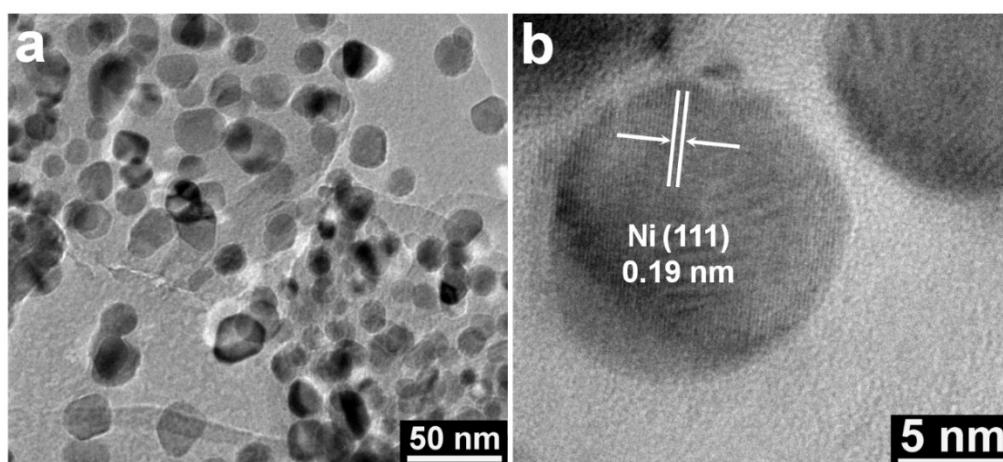


Fig. S5 a) TEM and b) HRTEM images of Ni-Al₂O₃/NF sample

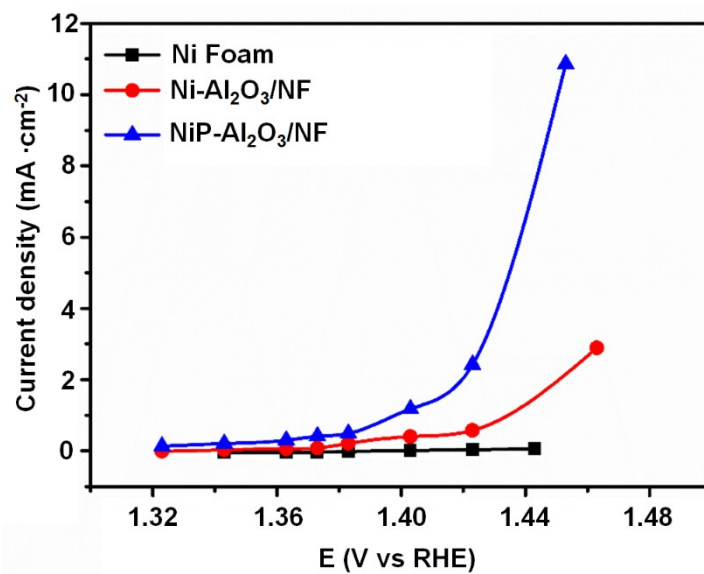


Fig. S6 Partial LSV curves separated of NF, Ni-Al₂O₃/NF, NiP-Al₂O₃/NF in 1.0 mol L⁻¹ KOH from oxidation peaks by i-t tests.

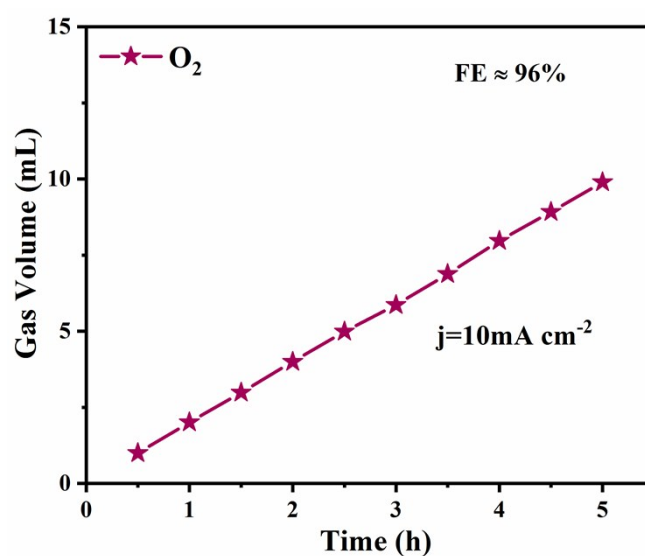


Fig. S7 The amount of O₂ versus time at a constant current density of 10 mA cm⁻² in 1 M KOH.

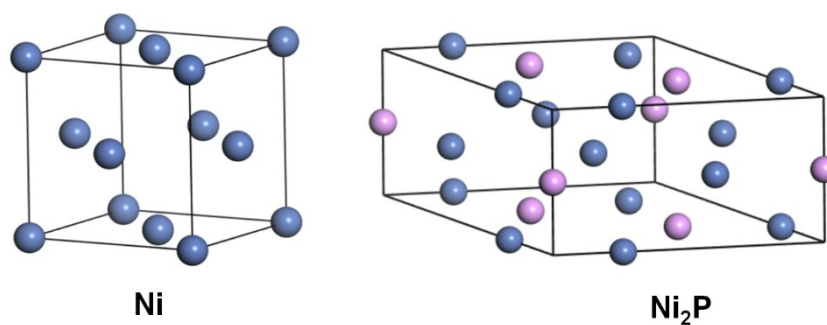


Fig. S8 The optimized primitive cell of Ni and Ni₂P.

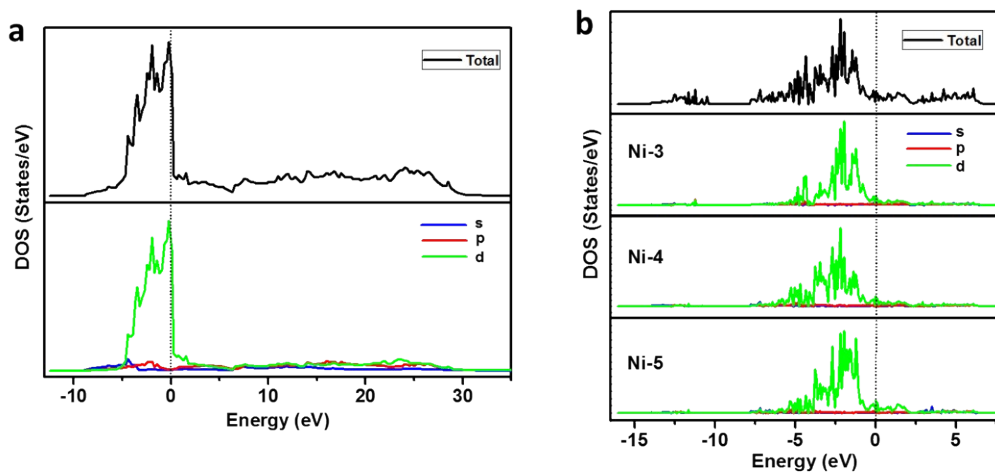


Fig. S9 The total and projected density of states of a) Ni and b) Ni₂P. Ni-n (n=3, 4, 5), and n means the different coordination number of Ni in Ni₂P (111).

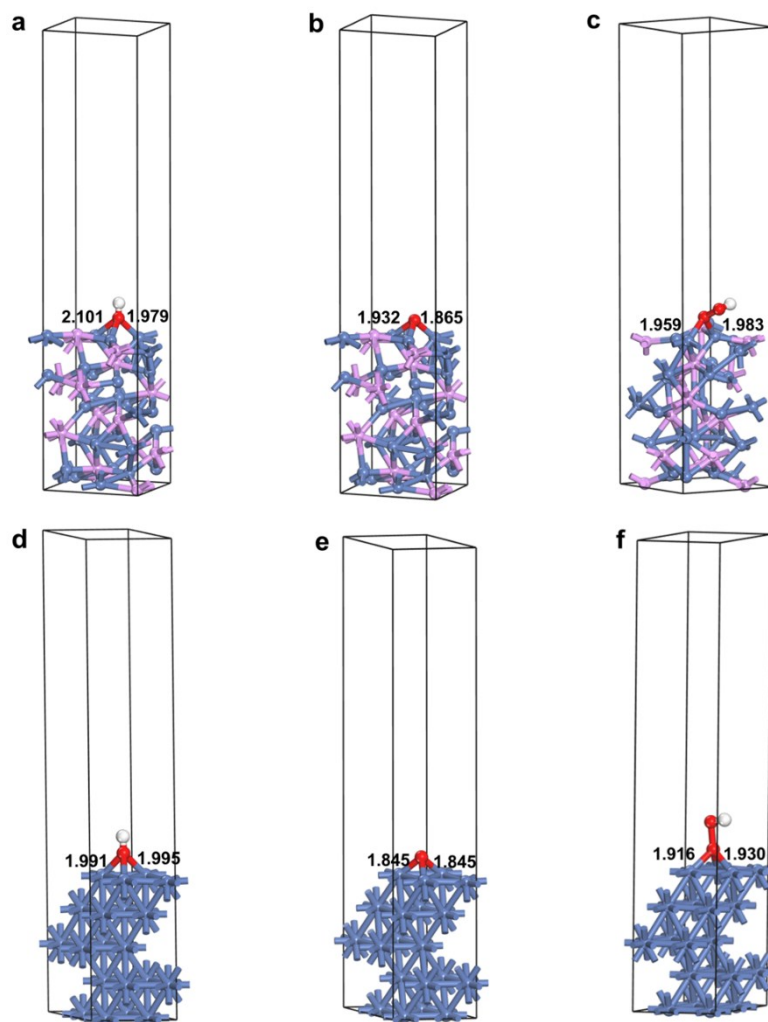


Fig. S10 Different species (*OH, *O, *OOH) combined with (a-c) Ni₂P and (d-e) Ni. The Ni-O bond lengths (unit: Å) are labeled in Fig., respectively.

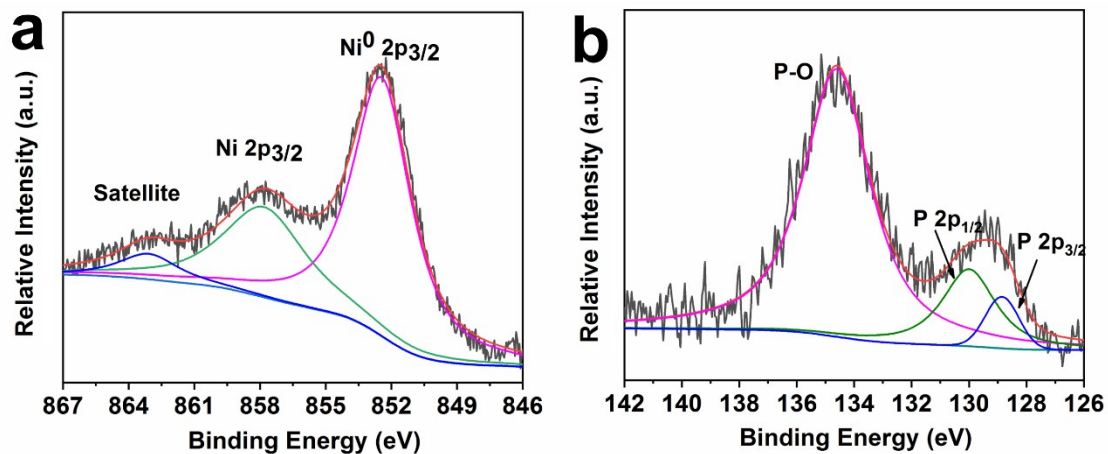


Fig. S11 a) Ni 2p and b) P 2p XPS of NiP-Al₂O₃/NF after chronopotentiometry test.

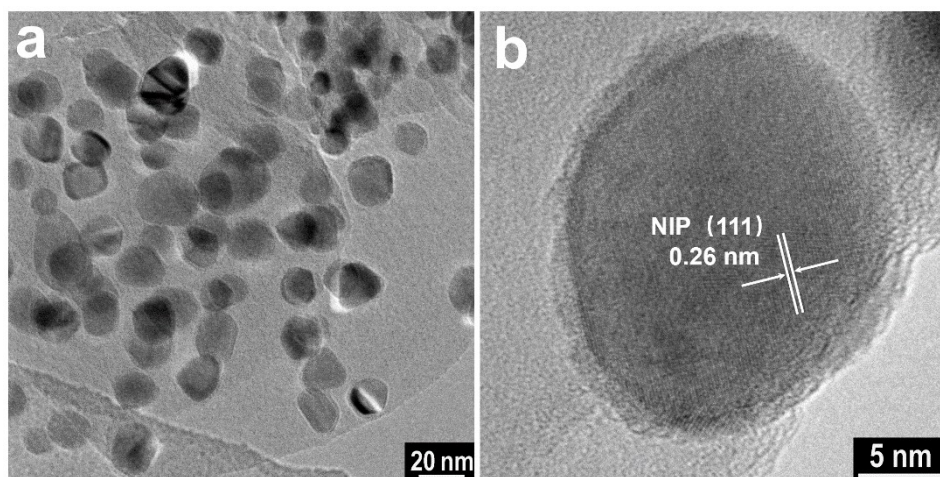


Fig. S12 a) TEM and b) HRTEM images of NiP-Al₂O₃/NF after chronopotentiometry test.

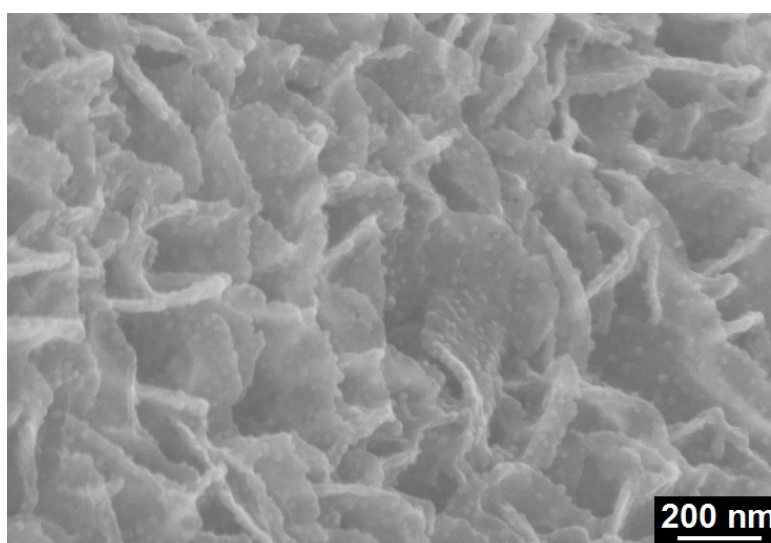


Fig. S13 SEM image of NiP-Al₂O₃/NF after five successive cycles of electrocatalytic oxidation of HMF.

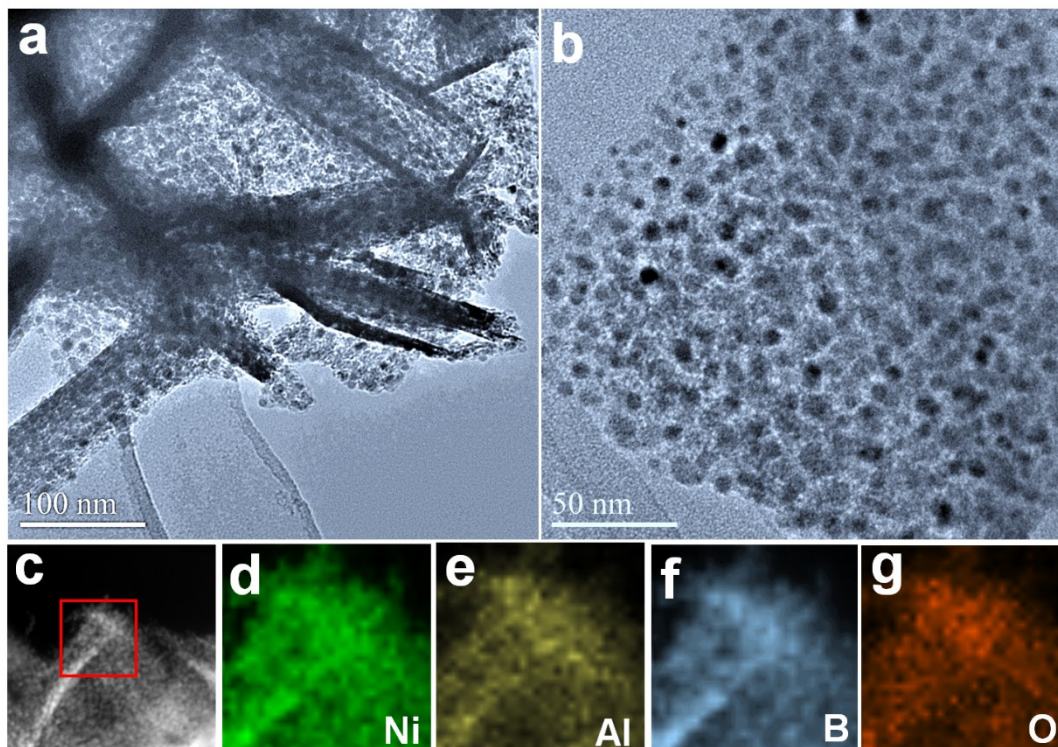


Fig. S14 a, b) TEM images of NiB-Al₂O₃/NF. c-g) HAADF-STEM image and elemental mapping images of Ni, Al, B, and O of NiB-Al₂O₃/NF, respectively.

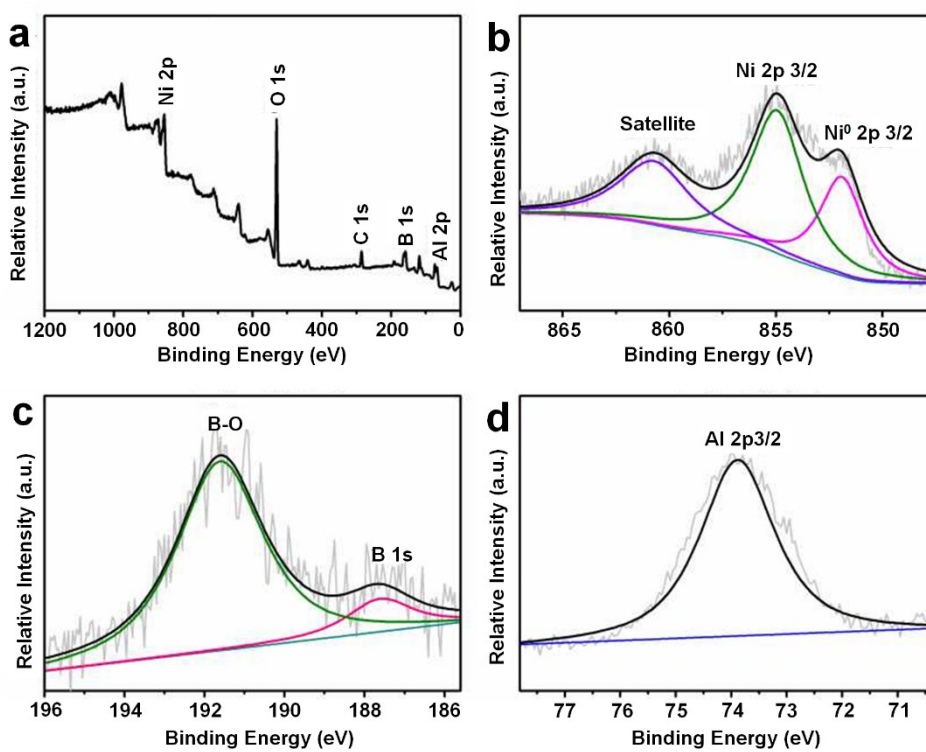


Fig. 15 XPS spectra of NiB-Al₂O₃/NF sample: a) survey, b) Ni 2p, c) B 1s, and d) Al 2p

Table 1. Comparison of OER activities over various electrocatalysts.

Material	Electrolyte	Current density [mA cm ⁻²]	Over-potential [mV]	Refs.
Ni-P/CF	1.0 M KOH	10	325	1
Ni-P NA/NF	1.0 M KOH	20	311	2
f-CoP/CoP ₂ /Al ₂ O ₃	1.0 M KOH	10	300	3
Ni(OH) ₂ /NF	1.0 M KOH	50	330	4
NiSe-NiO _x /NF	1.0 M KOH	10	243	5
Ni _{1.5} Fe _{0.5} P	1.0 M KOH	10	264	6
NiP ₂ /CC	1.0 M KOH	20	310	7
CF@NiP _x	1.0 M KOH	10	200	8
NiSe/NF	1.0 M KOH	20	270	9
NiP _{0.62} S _{0.38}	1.0 M KOH	10	240	10
Ni ₂ P-Al ₂ O ₃ /NF	1.0 M KOH	10	193	This work
Ni ₂ P-Al ₂ O ₃ /NF	1.0 M KOH	20	224	This work
Ni ₂ P-Al ₂ O ₃ /NF	1.0 M KOH	50	258	This work

References for SI

- 1 Q. Liu, S. Gu and C. M. Li, *J. Power Sources*, 2015, **299**, 342-346.
- 2 J. Xiao, Q. Y. Lv, Y. Zhang, Z.Y. Zhang and S. Wang, *RSC Adv.*, 2016, **6**, 107859-107864.
- 3 W. Li, S. L. Zhang, Q. Fan, F. Z. Zhang and S. L. Xu, *Nanoscale* 2017, **9**, 5677-5658.
- 4 J. S. Luo, J. H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N. G. Park, S. D. Tilley, H. J. Fan and M. Grätzel, *Science*, 2014, **345**, 1593-1596.
- 5 R. Q. Gao, G. D. Li, J. B. Hu, Y. Y. Wu, X. R. Lian, D. J. Wang and X. X. Zou, *Catal. Sci. Technol.*, 2016, **6**, 8268-8275.
- 6 H. W. Huang, C. Yu, C. T. Zhao, X. T. Han, J. Yang, Z. B. Liu, S. F. Li, M. D. Zhang and J. H. Qiu, *Nano Energy*, 2017, **3**, 2211-2855.
- 7 Z. H. Pu, Y. Xue, W. Q. Li, I. S. Amiin and S. C. Mu, *New J. Chem.*, 2017, **41**, 2154-2159.
- 8 Z. Y. Zhang, S. S. Liu, J. Xiao and S. Wang, *J. Mater. Chem. A*, 2016, **4**, 9691-9716.

- 9 C. Tang, N. Y. Cheng, Z. H. Pu, W. Xing and X. P. Sun, *Angew. Chem., Int. Ed.*, 2015, **54**, 9351-9355.
- 10 J. Luo, H. Y. Wang, G. Su, Y. L. Tang, H. Q. Liu, F. Y. Tian and D. L. Li, *J. Mater. Chem. A*, 2017, **5**, 14865-14872.