Supporting Information

Amorphous nickel boride facilitates active site generation

for HMF electrooxidation

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Methods

Material and chemicals

All chemicals were purchased from commercial sources and used without additional purification. Deionized water (DI water) purified to >18.2 M Ω cm by Millipore system was used in all experiments. 5-Hydroxymethylfurfural (HMF, 99%), 2,5-furandicarboxylic acid (FDCA, 98%), 2-formyl-5-furancarboxylic acid (FFCA, >98%), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA, 98%), 2,5diformylfuran (DFF, >98%) and sodium hydroxide (NaOH, 97%) were purchased from Aladdin Biochemical Technology Co., Ltd. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98%) and ammonium fluoride (NH₄F, 96%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Sodium borohydride (NaBH4, 97%) and potassium hydroxide (KOH, 85%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Urea (CH4N2O, >99%) was purchased from Shanghai Titan Scientific Co., Ltd. Ni foam (thickness: 1.6 mm, bulk density: 0.23 g cm⁻³) was purchased from Heze Tianyu Technology Development Co., Ltd.

Synthesis of NiB(O)/NF, B-NiO/NF and NiO/NF

Before the synthesis, Ni foam (NF) with a size of $2\times 2 \text{ cm}^2$ was repeatedly and sequentially washed with ultrasonic cleaner in acetone, 3 M hydrochloric acid, DI water and ethanol, until the light green color of Ni²⁺ ions no longer appeared in the final ethanol solution, and then dried in an oven as a substrate. NiB(O)/NF electrodes were synthesized by a facile electroless plating method through alternately dipping. Firstly, 1.454 g Ni(NO₃)₂·6H₂O was dissolved in 10 mL water as solution A of nickel source solution. 0.757 g NaBH₄ and 0.04 g NaOH were dissolved in 10 mL DI water as solution B of alkaline reducing solution. Then, the washed Ni foam was dipped into solution A for 10 s, and dipped into solution B for 10 s. Subsequently, the Ni foam was dipped alternately between solution A and B 10 s by turns, until the reaction was over (about 20 turns). Finally, the electrode was washed with DI water. The synthesizing method of NiB(O)/NF is scalable, where different sizes of NiB(O)/NF can be synthesized by proportionally scaling up the substrate area and solution volume.

B-NiO/NF was prepared by calcining NiB(O)/NF in furnace at 500 °C for 3 h. NiO/NF was prepared by calcining Ni foam in furnace at 500 °C for 3 h.

Synthesis of CoB(O)/NF and NiCoB(O)/NF

CoB(O)/NF and NiCoB(O)/NF were synthesized using a similar method of NiB(O). Synthesis of CoB(O)/NF simply replaced the Ni(NO₃)₂·6H₂O with 1.454 g Co(NO₃)₂·6H₂O. Synthesis of NiCoB(O)/NF simply replaced the Ni(NO₃)₂·6H₂O with 0.7276 g Co(NO₃)₂·6H₂O and 0.727 g Ni(NO₃)₂·6H₂O.

Synthesis of Ni(OH)₂/NF, Co(OH)₂/NF and NiCo-LDH/NF

Ni(OH)₂/NF was synthesized by a typical hydrothermal method. Briefly, 0.727 g Ni(NO₃)₂· $6H_2O$, 0.148 g NH₄F and 0.6 g urea were dissolved in 30 mL DI water. After stirring for 30 min, the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave where a piece of NF (2×3 cm²) was vertically placed into it. The autoclave was sealed and maintained at 120°C for 12 h to obtain Ni(OH)₂/NF.

 $Co(OH)_2/NF$ and NiCo-LDH/NF were synthesized using a similar method of Ni(OH)_2/NF. Synthesis of Co(OH)_2/NF simply replaced the Ni(NO₃)_2·6H₂O with 0.7276 g Co(NO₃)_2·6H₂O. Synthesis of NiCo-LDH/NF simply replaced the Ni(NO₃)_2·6H₂O with 0.3638 g Co(NO₃)_2·6H₂O and 0.3635 g Ni(NO₃)_2·6H₂O.

Collection of the electrode after reaction and the powder sample

Samples after 5-hydroxymethylfurfural oxidation reaction (HMFOR) were obtained after five cycles of 1 hour testing in 1 M KOH with 50 mM HMF at a reaction potential of 1.5 V *vs.* reversible hydrogen electrode (RHE). Samples after oxygen evolution reaction (OER) were obtained after 5 hours of testing in 1 M KOH at a reaction potential of 1.5 V *vs.* RHE. The powder sample was obtained by scraping the

catalyst from the corresponding electrode. The powder sample was used to the characterization of X-ray diffraction (XRD), transmission electron microscopy (TEM) and inductively coupled plasma optical emission spectroscopy (ICP-OES).

Characterization of materials

The crystal structure of samples was characterized by X-ray diffraction (XRD, D/max2550V). The morphology of the samples was characterized by Scanning electron microscopy (SEM, Hitachi S4800), and transmission electron microscopy (TEM, Thermo Fisher Talos F200X). High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were recorded with a convergence semi angle of 11 mrad, and inner and outer collection angles of 59 and 200 mrad, respectively. Energy dispersive X-ray spectroscopy (EDS) was performed using four in-column Super-X detectors. The chemical states of the elements on the sample surface were examined by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) with Al Ka X-ray beam (1,486.6 eV), with all binding energies calibrated against the C 1s peak at 284.8 eV as the reference. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5800 VDV) was employed to determine the element content of Ni and B. Inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7800) was employed to determine the content of element Ni and B in electrolyte. In situ Raman spectroscopy (Thermo Fisher Scientific DXR3) was performed, utilizing an excitation laser with a wavelength of 532 nm. NiB(O)/NF and B-NiO/NF were used as the working electrode, with Ag/AgCl and platinum wire serving as the counter electrode and reference electrode, respectively.

Electrochemical measurements

All electrochemical measurements were carried in a three-electrode system with an electrochemical station (CHI 760E) in a 10 mL H-type cell separated by FAB-PK-130 membrane. The obtained catalysts were used as the working electrode with a geometric surface area of 1 cm² (1 cm×1 cm) for electrocatalytic tests. Hg/HgO was used as reference electrode, and a Pt mesh was used as the counter electrode. The Hg/HgO reference electrode was calibrated with RHE. The calibration was performed in the high-purity H_2 saturated 1 M KOH electrolyte with Pt mesh as the working electrode and counter electrode. All potentials were referenced to RHE using the following calculation:

$$E_{RHE} = E_{Hg/Hg0} + 0.059 \times pH + 0.098 V$$

The scanning rate of linear sweep voltammetry (LSV) was set to 5 mV s⁻¹. All LSV curves were corrected with *i*R compensation (85%). The electrochemical OER tests was conducted in 1 M KOH solution. The electrochemical HMFOR tests were conducted in 1 M KOH with 50 mM HMF solution. The HMF conversion tests of catalysts were evaluated by chronoamperometry at 1.5 V *vs*. RHE without *i*R compensation. The EIS measurements were carried on with frequency from 0.01 Hz to 100 kHz with an amplitude of 5 mV. All experiments were carried out at RT.

Product quantification

The 300 μ L electrolyte was neutralized and diluted 50 times with 100 μ L HCl (3 M) and 14,600 μ L deionized water and then analyzed using high-performance liquid chromatography (HPLC, HITACHI L-2000) with Agilent 5- μ m C18 column for testing the concentration of HMF and its products. The flow phase consisted of methanol and 5 mM ammonium formate aqueous solution with a volume ratio of 3:7, and the flow rate was 0.6 mL min⁻¹. The used wavelength in UV-vis is 220 nm. Each separation lasted 10 min. The quantification of HMF and its oxidation product was calculated based on the calibration curves of standard compounds with known concentrations (Fig. S2). The conversion, yield and Faradaic efficiency (FE) were calculated based on the following equations:

$$HMF \ conversion \ (\%) = \frac{mol \ of \ HMF \ consumed}{mol \ of \ HMF \ initial} \times 100\%$$
$$FDCA \ yield \ (\%) = \frac{mol \ of \ FDCA \ formed}{mol \ of \ HMF \ initial} \times 100\%$$

Faradaic efficiency (%) =
$$\frac{mol \ of \ FDCA \ formed}{Q/nF} \times 100\%$$

Where Q is the passed charge during reaction. F is the Faraday constant (96,485 C mol⁻¹), n=6 is the electron transfer number for the formation of a mole of FDCA, n=4 is the electron transfer number for the formation of a mole of FFCA and n=2 is the electron transfer number for the formation of a mole of HMFCA or DFF.





Fig. S2. Digital image of blank Ni foam, synthesized NiB(O)/NF, B-NiO/NF and NiO/NF.



Fig. S3. SEM images of (a) NiB(O), (b) and (c) B-NiO, (d) and (e) NiO, respectively. SEM images of NiB(O) after (f) HMFOR and (g) OER, respectively. SEM images of B-NiO (h) after HMFOR and (i) OER, respectively.



Fig. S4. (a) TEM image of B-NiO. (b) HADDF-STEM and the corresponding elemental maps of Ni, B and O in B-NiO.



Fig. S5. Raman spectra for powder samples of NiB(O) and B-NiO.



Fig. S6. CV curves of (a) NiB(O)/NF, (b) B-NiO/NF, and (c) NiO/NF with different scan rates from 20 to 100 mV s⁻¹ in 1 M KOH with 50 mM HMF.



Fig. S7. Standard curves of (a) HMF, (b) FDCA, (c) HMFCA, (d) DFF and (e) FFCA gained by HPLC data.



Fig. S8. The HPLC spectra exhibited the concentration changes of substrates, intermediates and products in NiB(O)/NF during the HMFOR process.



Fig. S9. Current density and charge-time plots for five cycles of electrolysis experiments on B-NiO/NF.



Fig. S10. Current density-time plots for 20 cycles of HMFOR on NiB(O)/NF.



Fig. S11. The XRD patterns of the NiB(O) powder before and after reconstruction.



Fig. S12. TEM images of (a) NiB(O) after HMFOR and (c) B-NiO after HMFOR. HADDF-STEM and the corresponding elemental maps of Ni, B and O in (b) NiB(O) after HMFOR and (d) B-NiO after HMFOR.



Fig. S13. HRTEM images of (a) NiB(O) and (b) B-NiO after HMFOR. The insets show the FFT pattern for corresponding regions.



Fig. S14. The ratio of Ni^{3+}/Ni^{2+} of the NiB(O) before and after reconstruction.



Fig. S15. (a) Ni 2p XPS spectra of NiO. (b) O 1s XPS spectra of NiO. B 1s XPS spectra of (c) NiB(O), (d) B-NiO and (e) NiO.



Fig. S16. LSV curves of NiB(O), CoB(O), NiCoB(O), Ni(OH)₂, Co(OH)₂ and NiCo-LDH in the electrolyte containing 1 M KOH with 50 mM HMF.



Fig. S17. Bode phase plots of *in situ* EIS on NiO in 1 M KOH with 50 mM HMF.



Fig. S18. The optimal equivalent circuit was used for modeling the measured electrochemical response for the HMFOR.¹ In figure of equivalent circuit, R_s stands for the solution resistance, CPE₁ represents double layer capacitance, R_{ct} has contact with the interfacial charge transfer reaction, CPE₂ and R_p are related to the dielectric properties and the resistance of the electrode inner film.



Fig. S19. In situ Raman spectra for NiB(O) and B-NiO at low wavenumber.



Fig. S20. In situ Raman spectra for NiB(O) and B-NiO at high wavenumber.



Fig. S21. Comparison of current density and potential required in HMFOR for NiB(O) with previous reported electrocatalysts.

Sample	Ni (mg/L)	B (mg/L)	atomic ratio (Ni:B)
NiB(O)	20	3.7	1:1.004
B-NiO	21	3.9	1:1.008

Table S1. Ni and B contents of the samples obtained from ICP-OES measurements.

Sample	Ni (mg/L)	B (mg/L)	Atomic ratio (Ni:B)
NiB(O) before reaction	20	3.7	1:1.004
NiB(O) after HMFOR	28.9	1.6	1:0.3

Table S2. Ni and B contents of NiB(O) before and after HMFOR obtained from ICP-OES measurements.

Sample	Ni (mg/L)	B (mg/L)
Electrolyte after the first cycle of HMFOR	4.476	12.026
Electrolyte after the fifth cycle of HMFOR	0.010	0.243

Table S3. Ni and B contents of electrolyte after the first and the fifth cycles of HMFOR

 obtained from ICP-MS measurements.

Samples	HMF Concentration (mM)	Potential (V vs. RHE)	Current density (mA cm ⁻²)	Reference
NiB(O)/NF	50	1.44	300	This Work
NiB(O)/NF	50	1.38	200	This Work
NiB(O)/NF	50	1.33	100	This Work
W-NiS _x ²	50	1.35	50	<i>Appl. Catal., B</i> , 2025, 361 , 124692
Ni ₃ Fe@NC ³	300	1.467	100	Chem. Eng. J., 2024, 499 , 156320
CeO ₂ /NiCoOOH ⁴	50	1.5	92.7	J. Mater. Chem. A, 2024, 12 , 29550-29561
av-Ni(OH) ₂ /CP ⁵	50	1.455	50	Chem. Eng. J., 2023, 477 , 146917
Pd/NiCo ⁶	50	1.38	50	Angew. Chem. Int. Ed., 2023, 62 , e202311696
Rh-SA/NiFe NMLDH ⁷	50	1.48	100	J. Am. Chem. Soc., 2023, 145 , 17577-17587
Mn _{0.2} NiS/GF ⁸	100	1.35	100	<i>Adv. Funct. Mater.</i> , 2023, 33 , 2214488
CuCo ₂ O ₄ ⁹	50	1.37	150	Angew. Chem. Int. Ed., 2020, 59 , 19215-19221
Co-P ¹⁰	50	1.41	50	ACS Energy Lett., 2016, 1, 386-390

Table S4. Comparison of current densities and corresponding potential required inHMFOR for NiB(O) with reported electrocatalysts.

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