Supporting Information

Enhanced electrocatalytic hydrogen evolution reaction, oxygen evolution reaction and biomass oxidation over Ce-doped NiP_x via optimization of electronic modulation

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Experimental section

Materials

All materials had not been further processed unless otherwise specified. Deionized water was produced by an ultra-pure water purification system. Nickel foam (NF) was purchased from Beijing Tianmei Hechuang Technology Corporation Hydrochloric acid [HCl, GR], acetone $[C_3H_6O, AR]$ and Nickel(II) nitrate hexahydrate $[Ni(NO_3)_3 \cdot 6H_2O, AR]$ were purchased from Sinopharm Chemical Reagent Co., Ltd. Cerium nitrate hexahydrate $[Ce(NO_3)_3 \cdot 6H_2O, 99.95\%]$ and Sodium hypophosphite $[NaPH_2O_2, 99.0\%]$ were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 5-hydroxymethylfurfural [HMF, 99.54%], furan-2,5-dicarbaldehyde [DFF, 98%] were purchased from Ark Pharma Scientific Co., Ltd. 5-hydroxymethyl-2-furancarboxylic acid [HMFCA, 98%], 5-formyl-2-furancarboxylic acid [FDCA, 98%] were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

Synthesis

Synthesis of Ce-NiP_x/NF: Firstly, a piece of nickel foam (2 cm × 1 cm) was taken and sonicated in acetone, dilute hydrochloric acid, ethanol and deionised water (DI) for 15 min, then vacuum drying at 60°C for 12 hours. The samples were prepared by one-step electrodeposition method. 43.6 mg Ni(NO₃)₃·6H₂O, 65.1 mg Ce(NO₃)₃·6H₂O and 158.4 mg NaPH₂O₂ were dispersed in 50 mL of DI to get the electrodeposition solution. Electrodeposition was carried out via an electrochemical three-electrode system. Where the treated NF was used as the working electrode, the counter electrode was a platinum sheet electrode and the reference electrode was an Ag/AgCl electrode. Electrochemical deposition was done at room temperature. The deposition potential was -1.0 V vs. Ag/AgCl, and the deposition time was 600 s. After the reaction, the electrodes were stored in a vacuum drying at 60°C for 12 h. The obtained samples were named Ce-NiP_x/NF.

Synthesis of NiP_x/NF and CeP_x/NF: The preparation method was consistent with the above steps. The difference was that NiP_x/NF was obtained by adding no Ce(NO₃)₃·6H₂O to the electrodeposition solution, and CeP_x/NF was obtained by adding no Ni(NO₃)₃·6H₂O to the electrodeposition solution.

Characterization

The morphology and microstructure of the materials were characterised by transmission electron microscopy (TEM, JEM2200FS, Japan) and field emission scanning electron microscopy

(FE-SEM, Hitachi SU8010, Japan). The X-ray diffraction (XRD) patterns were obtained by Bruker D8 ADVANCE with Cu K α radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, USA) was used to obtain the information for elements in materials. High-resolution Raman spectrometer (LabRAM HR Evolution) (532 nm) was used to measure the evolution of surface structure during electrochemical reaction. Electron paramagnetic resonance (EPR) spectra were obtained by Bruker A300–10/12. The XAFS spectra were obtained at room temperature on the BL14W1 baseline in the Shanghai Synchrotron Radiation Facility (SSRF).

Electrochemical test

All electrochemical tests were conducted on a CHI-660D electrochemical workstation (CHI Instrument, Shanghai, China)). Electrochemical testing uses a three-electrode system. This consists of a working electrode (prepared nickel foam), a reference electrode (Hg/HgO electrode) and a counter electrode (graphite rod electrode). The electrolyte solutions used were 1 M KOH (pH = 14, for HER and OER) and 1 M KOH + 50 mM HMF (pH = 14, for HMFOR). The potentials obtained (vs. Hg/HgO) were converted to reversible hydrogen electrode potentials (vs. RHE) according to the Nernst equation: $E(vs. RHE) = E(vs. Hg/HgO) + 0.098 + 0.0591 \times pH$. Electrode activated by cyclic voltammetry (CV) before the electrochemical test, with potentials ranging from 0 - 0.8 V (vs. Hg/HgO) for 80 cycles. Linear scanning voltammetry (LSV) was used to test the potential range 0.8 -0 V (vs. Hg/HgO) with a scanning rate of 5 mV s⁻¹. Tafel slopes were gained via the steady-state timed currents and current densities were tested at 0.05 V intervals in the range of $1.35 - 1.45 V_{RHE}$. The stabilised current density is seen as the steady state current density. The logarithmic plot of the steady-state current density and the corresponding potential is plotted and the Tafel slope is derived by fitting the slope of the straight line. The electrochemical impedance spectra (EIS) were tested in the frequency range of 100000 Hz - 0.01 Hz. Equivalent circuits were fitted to obtain the system resistance (R_s) and charge transfer resistance (R_{ct}). The value of the double layer capacitance (Cdl) was obtained from the CV curves in the non-Ferrati interval at different sweep speeds (100, 120, 140, 160, 180 mV s⁻¹). The difference in current density between the forward and backward sweeps in the CV curve was taken as the vertical coordinate, and the corresponding scanning speed was taken as the horizontal coordinate, and a straight line was fitted to obtain the slope of the corresponding Cdl. Electro chemical surface area (ECSA) is obtained by the formula ECSAs = Cdl / Cs, where Cs is the specific capacitance and Cdl is derived from the CV curve. In Drainage gas collection method, gas collection is texted via using inverted measuring cylinder. Hydrogen collection for HER and oxygen collection for OER are texted at 50 mA cm⁻².

HPLC analysis:

The contents of HMF, HMFCA, DFF, FFCA and FDCA involved in the work were determined by high-performance liquid chromatography (HPLC, Agilent 1260 Infinity Series, USA) with an Agilent Zorbax SB-C18 (150 mm × 6 mm, 5 μ m) column and an ultraviolet-visible (UV-vis) detector. In this case, the mobile phase A was methanol and the mobile phase B was ammonium formate (5 mM), and the mixing ratio A / B = 3 / 7, and the flow rate was 0.6 mL min⁻¹. The column temperature was 30°C, and each separation time lasted for 10 min. In the constant potential electrolysis experiments, the voltage was set to 1.40 V_{RHE}, and the electrolyte was 8 mL of 1 M KOH + 10 mM HMF. When different charges (0, 10 C, 20 C, 30 C, 40 C and 46.3 C) were reached, take 50 μ L from the electrolyte solution and added into 5 mL DI. And then take 1 mL from the mixed solution for HPLC analysis. A standard curve was plotted and fitted by the HPLC results of different concentrations of substrates (1 mM, 2 mM, 4 mM, 8 mM and 16 mM). The standard curve was used to quantitatively monitor the reaction products.

The number of charges transferred in HMFOR was calculated by the following equation (where 6 was the number of charges transferred when a single HMF molecule was converted to FDCA):

$$6 \times 10 \text{ mM} \times 8 \text{ mL} \times 96485 \text{ C mol}^{-1} = 46.3 \text{ C}$$
 (1)

The conversion of HMF, the yield of FDCA and the Faraday efficiency (F.E.) were obtained by the following equations:

$$HMF_{conversion} (\%) = (mole of HMF_{consume} / mole of HMF_{initial}) \times 100$$
(2)

Yield (%) = (mole of formed product / mole of HMF_{initial}) × 100 (3)

where F was the Faraday constant (96485 C mol⁻¹) and n was the number of charges transferred.



Fig. S1. SEM image of NiP_x/NF.



Fig. S2. SEM image of CeP_x/NF.



Fig. S3. HRTEM image of Ce-Ni P_x /NF.

	3-						Element	Atom (%)
	-	1					0	75.54
>	2-						Р	15.81
cps/e	-						Ni	4. <mark>6</mark> 1
	1-	0					Ce	4.04
	- - 0	Ni Çe P		li Ni				
	0		5	1	0	.,	15	keV

Fig. S4. The EDX spectrum of Ce-Ni P_x /NF and the relative content of four elements.



Fig. S5. a) TEM image and SAED of NiP_x/NF. b) The EDX spectrum of NiP_x/NF and the relative content of four elements. c) EDX mapping of NiP_x/NF.



Fig. S6. a) TEM image and SAED of CeP_x/NF. b) The EDX spectrum of CeP_x/NF and the relative content of four elements. c) EDX mapping of CeP_x/NF.



Fig. S7. CV curves at 100, 120, 140, 160 and 180 mV $\rm s^{-1}$ for a) $\rm NiP_x/\rm NF,$ b) CeP_x/\rm NF and c) Ce-

NiP_x/NF for HER.



Fig. S8. Operando Nyquist plots of a) NiP_x/NF and b) CeP_x/NF at various potentials for HER.



Fig. S9. Bode plots of a) NiP_x/NF , b) CeP_x/NF and c) Ce- NiP_x/NF at various potentials for HER.



Fig. S10. Current density-time curve of Ce-NiP_x/NF for HER.



Fig. S11. a) Voltage-time curve for HER. b) Device for the drainage gas collection method for HER. c-k) Photos taken at (c) 0 s, (d) 300 s, (e) 600 s, (f) 900 s, (g) 1200 s, (h) 1500 s, (i) 1800 s (j) 2100 s and (k) 2400 s. Ce-NiP_x/NF was directly used as a cathode and hydrogen was collected in a cylinder. The current was constant as -50 mA and the ambient temperature was about 20°C.



Fig. S12. Over-potential of NiP_x/NF, CeP_x/NF and Ce-NiP_x/NF at 10 mA cm⁻² and 50 mA cm⁻² for



Fig. S13. CV curves at 100, 120, 140, 160 and 180 mV s⁻¹ of a) NiP_x/NF, b) CeP_x/NF and c) Ce-

NiP_x/NF for OER.



Fig. S14. Operando Nyquist plots of a) NiP_x/NF , b) CeP_x/NF at various potentials for OER.

OER.



Fig. S15. Bode plots of a) NiP_x/NF and b) CeP_x/NF at various potentials for OER.



Fig. S16. LSV curves of Ce-Ni P_x /NF before and after the 100000 s OER stability test.



Fig. S17. a) Voltage-time curve for OER. b) Device for the drainage gas collection method for OER. c-g) Photos taken at (c) 0 s, (d) 600 s, (e) 1200 s, (f) 1800 s and (g) 2400 s. Ce-NiP_x/NF was directly used as an anode and oxygen was collected in a cylinder. The current was constant as 50 mA and the ambient temperature was about 20°C.



Fig. S18. CV for 60 cycles of (a) NF, (b) NiP_x/NF , (c) CeP_x/NF and (d) $Ce-NiP_x/NF$, (e) Comparison of CV at the cycle 60th of NF, NiP_x/NF and $Ce-NiP_x/NF$, (f) Comparison of CV at the cycle 60th of NF and CeP_x/NF .



Fig. S19. Tafel slopes of NiP_x/NF , CeP_x/NF and $Ce-NiP_x/NF$ for HMFOR.



Fig. S20. CV curves at 100, 120, 140, 160 and 180 mV s⁻¹ for a) NiP_x/NF, b) CeP_x/NF and c) Ce-



Fig. S21. ECSA-normalized LSV curves of NiP_x/NF, CeP_x/NF and Ce-NiP_x/NF for HMFOR.



Fig. S22. Operando Nyquist plots of a) NiP_x/NF and b) CeP_x/NF at various potentials for HMFOR.



Fig. S23. Bode plots of a) NiP_x/NF and b) CeP_x/NF at various potentials for HMFOR.



Fig. S24. The peak phase angles of NiP_x/NF, CeP_x/NF and Ce-NiP_x/NF at various potentials for HMFOR.



Fig. S25. Standard peak area-concentration curves for a) HMF, b) HMFCA, c) DFF, d) FFCA, and e)

FDCA.



Fig. S26. Current densities, charges versus time curves.



Fig. S27. Device for a) HER + OER and b) HER + HMFOR.



Fig. S28. a) Ni 2p XPS spectra of NiP_x/NF and NiP_x/NF after HMFOR, b) Ce 3d XPS spectra of CeP_x/NF and CeP_x/NF after HMFOR.



Fig. S29. XRD pattern of Ce-NiP_x/NF after HMFOR.



Fig. S30. a) TEM image of Ce-NiP_x/NF after HMFOR. b) The EDX spectrum of Ce-NiP_x/NF after HMFOR and the relative content of four elements. c) EDX mapping of Ce-NiP_x/NF after HMFOR.



Fig. S31. The k³-weighted Fourier transform (FT) EXAFS spectra of a) k-space of Ni K-edge and b) R-space of Ni K-edge in Ce-NiP_x/NF.

Table S1. ECSA value of NiP_x/NF, CeP_x/NF and Ce-NiP_x/NF for HER, OER and HMFOR, when $C_s = 0.49 \text{ mF cm}^{-2.1}$

ECSA (cm ² _{ECSA})	NiP _x /NF	CeP _x /NF	Ce-NiP _x /NF
HER	7.67	8.06	11.22
OER	2.90	2.90	3.06
HMFOR	2.61	2.71	3.27

Table S2. Comparison of activity for Ce-NiP_x/NF and other reported catalysts.

Electrode Materials	Potential	HMF conversion (%)	FDCA yield (%)	Faradaic efficiency (%)	Ref.
Ce-NiP _x /NF	1.40 V _{RHE}	100	98.69	98.38	This work
CoO _x H _y -MA	$1.52 \ V_{RHE}$	100	98	83	2
Ni _{0.5} Co _{2.5} O ₄	$1.50 \ V_{RHE}$	None	92.42	90.35	3
NiOOH/MoS ₂	1.393 V _{RHE}	99.2	96.7	96.5	4
Ni ₁ Mn ₅ -LDH	$1.40 \ V_{RHE}$	None	94.72	97	5
NiCo ₂ O ₄	$1.55 V_{RHE}$	None	90	92	6
Cu-Co ₃ O ₄ /CuO/NF	$1.45 \ V_{RHE}$	None	93	96	7
Ce-Co ₃ O ₄	$1.45 V_{\text{RHE}}$	98.0	95.48	97	8
Mo-Co ₃ O ₄	$1.40 \ V_{RHE}$	None	95	92	9
FeCoNi-S@NF	$1.45 V_{\text{RHE}}$	95.68	94.83	94.71	10
Co ₂ NiS	$1.45 \ V_{RHE}$	84.5	54	None	11
CuNi	$1.45 \ V_{RHE}$	98.8	93.4	94.4	12
NiFe LDH	$1.44 \ V_{RHE}$	99.9	94.2	90.4	13
d-NiFe LDH/CP	$1.48 \ V_{RHE}$	97.35	96.8	84.47	14
Ce-NiFe	$1.42 \ V_{RHE}$	88.5	83.1	91	15

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