Supporting Information

Construction of 2D C,N-co doped ZnO/Co_3O_4 over $Ni(OH)_2$ mesoporous ultrathin nanosheets on Ni foam as high-performance electrocatalysts for benzyl-alcohol oxidation and accelerating hydrogen evolution

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Experimental section

Reagents and materials: All reagents used in this study were purchased and directly used without further purification: $Co(NO_3)_2 \cdot 6H_2O$(AR), $Zn(NO_3)_2 \cdot 6H_2O$(AR), $Ni(NO_3)_2 \cdot 6H_2O$ (AR), 2-Methylimidazole (AR) and urea (AR) were purchased from Shanghai Titan Scientific Co., Ltd.. Nickel foam (NF) was purchased from Suzhou Cheng Er Nuo Technology Co. Ltd. .

Physical characterizations: The structure of $ZnO/Co_3O_4@Ni(OH)_2$/NF is determined by PXRD (Bruker D8, Cu-Kα). the spectra were recorded in the 2θ range of 15° to 70°. The morphology of $ZnO/Co_3O_4@Ni(OH)_2$/NF were investigated by scanning electron microscopy (SEM, Hitach S-4800) and transmission electron microscope (TEM, JEOL 2100F). X-ray electron spectroscopy (XPS) was performed on AXIS Supra by Kratos Analytical Inc. Using monochromatized Al Ka radiation as X-ray source. All spectra were calibrated by C 1s (284.8 eV).

Product analysis: Benzyl alcohol and its products were examined by a high performance liquid chromatography (HPLC) system (Waters 1525) equipped with a

C18 column (4.6 × 250 mm) and an ultraviolet-visible detector. Specifically, 1 mL of electrolyte was sampled during the electrolysis and diluted to 100 mL with ultrapure water and analysed by HPLC. The detection wavelength and temperature were set to 245 nm. A mixed solution containing acetonitrile and 0.02M formic acid (the volume ratio is 3 : 7) was used as the mobile phase with a flow rate of 1 mL min^{-1}.

The conversion of benzyl alcohol can be calculated by the following eqn

$$Conversion = \frac{n(reacted\ benzylalcohol)}{n(initial\ benzylalcohol)} \times 100\%$$

The selectivity and yield of the benzoic acid were determined by the following eqn respectively :

$$Selectivity = \frac{n(benzoicacid\ production)}{n(reacted\ benzylalcohol)} \times 100\%$$

$$Yield = \frac{n(benzoicacid\ production)}{n(initial\ benzylalcohol)} \times 100\%$$

The faradaic efficiency of the product was calculated using eqn

$$FE = \frac{4 \times n \times 96485}{Qtotal} \times 100\%$$

Electrochemical measurements: All electrochemical tests were carried out in a three-electrode system using a CHI760E electrochemical workstation (Shanghai Chenhua, China) without iR correction. BOR and OER were carried out in a typical three-electrode system with a H-type cell separated by an anion exchange membrane (N117 DuPont). Pt wire and Hg/HgO were used as counter electrode and reference electrode, the as-prepared ZnO/Co_3O_4@$Ni(OH)_2$/NF (1cm ×1cm) material was used as the working electrode. The measured voltage value is converted into the electrode potential *vs* the reversible hydrogen electrode (RHE) by the equation $E_{RHE}=E_{Hg/HgO}$ + 0.059×pH + 0.098 V. The electrochemical OER and BOR experiments were conducted in 15 mL

of 1.0 M KOH solution with and without 0.1 M benzyl alcohol. Electrochemical impedance spectroscopy (EIS) measurements were recorded in the frequency range of 10^5–0.1 Hz with an amplitude of 5 mV. The electric double layer capacitance of the prepared catalyst was determined by the CV of different scanning speeds (10, 20, 40, 60, 80 and 100 mV s^{-1}).

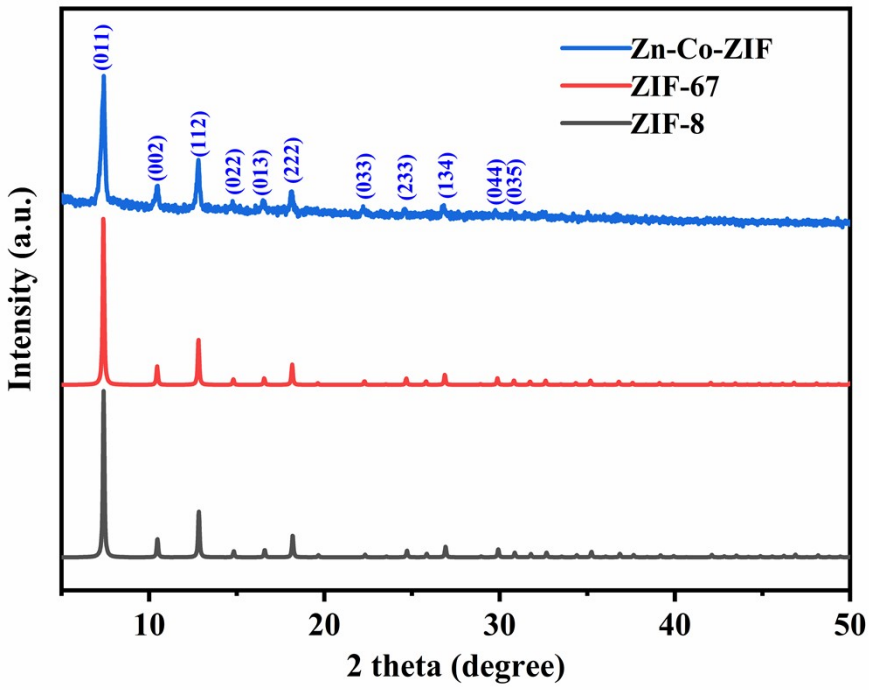


Fig. S1. XRD of powder scraped from Zn-Co-ZIF/NF.

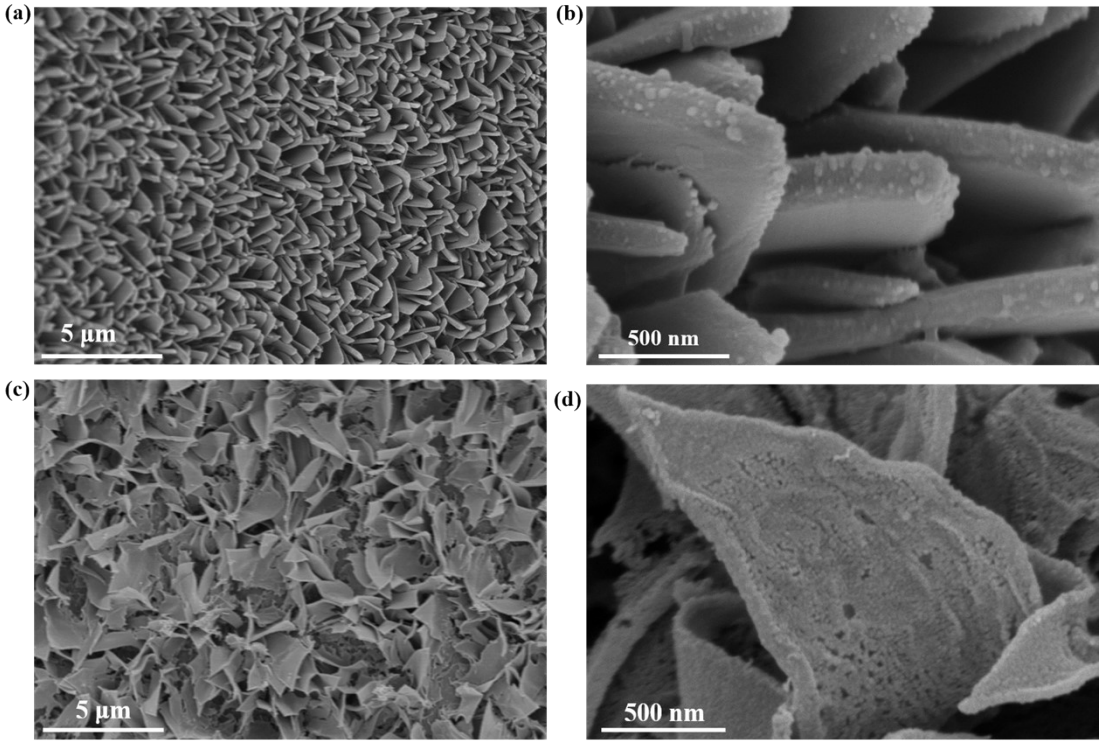
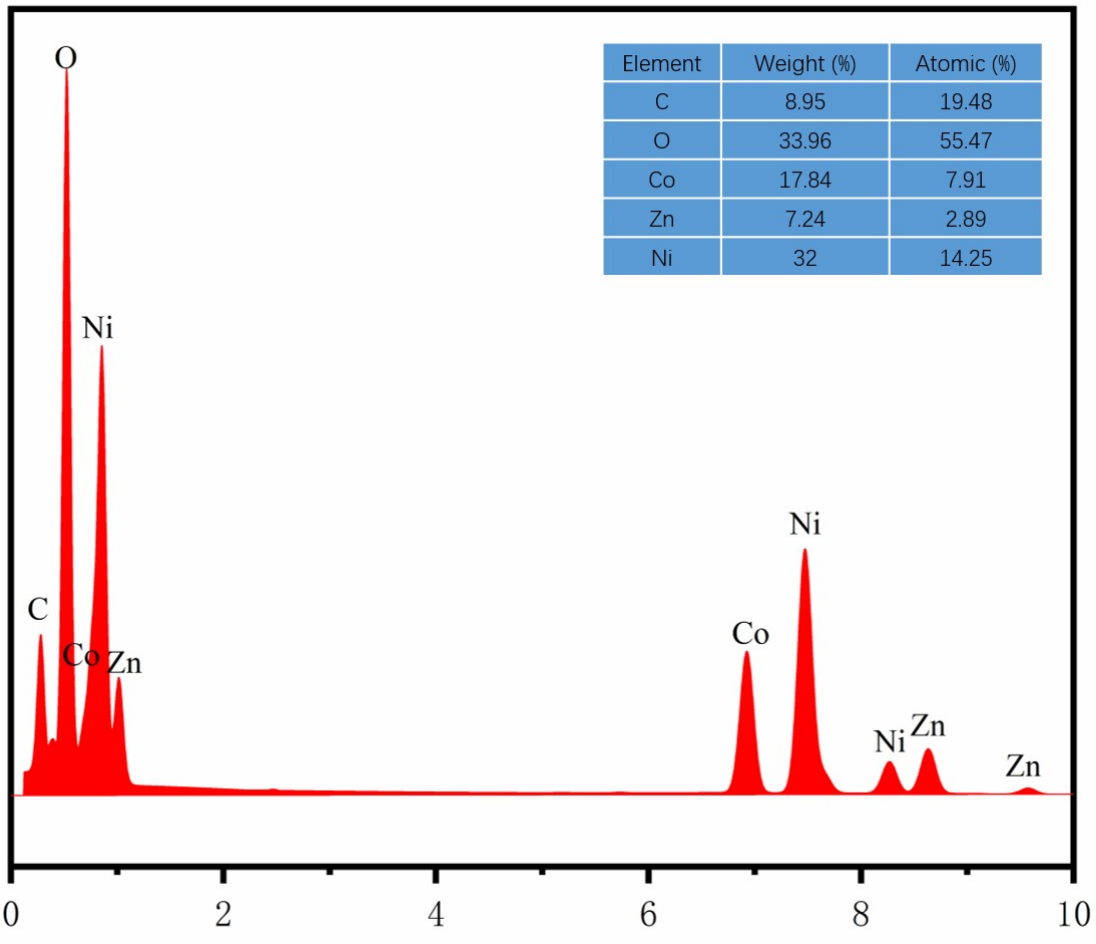


Fig. S2. (a, b) SEM images of Zn–Co-ZIF/NF and (c, d) ZnO/Co_3O_4/NF



Element	Weight (%)	Atomic (%)
C	8.95	19.48
O	33.96	55.47
Co	17.84	7.91
Zn	7.24	2.89
Ni	32	14.25

Fig. S3. EDX of ZnO/Co_3O_4@$Ni(OH)_2$/NF

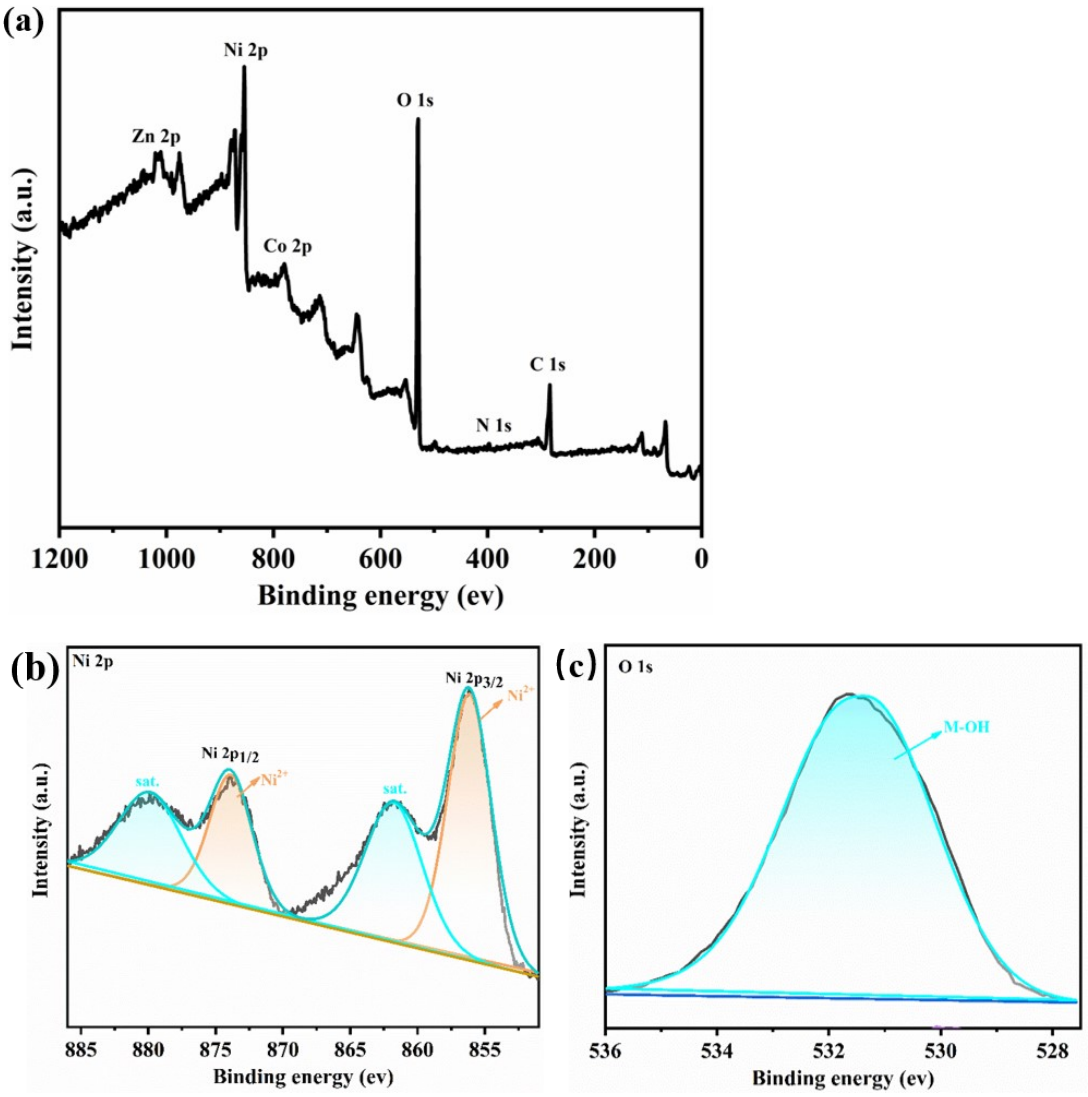


Fig. S4. (a) XPS survey spectrum of $ZnO/Co_3O_4@Ni(OH)_2/NF$, XPS spectra of the $Ni(OH)_2/NF$ (a) Ni 2p and (b) O 1s

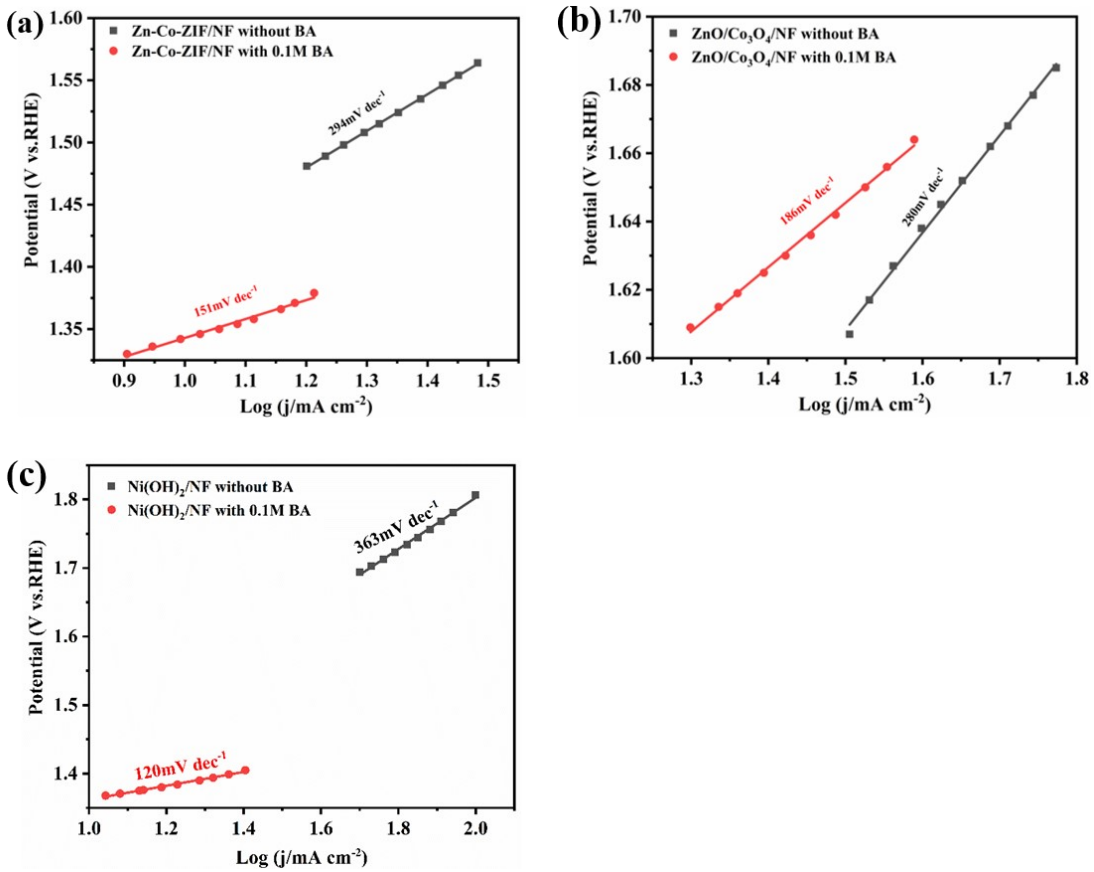


Fig. S5. Tafel plots of Zn-Co-ZIF/NF (a), ZnO/Co_3O_4/NF (b) and (c) $Ni(OH)_2$/NF electrocatalysts in 1.0 M KOH with and without 0.1 M benzyl alcohol

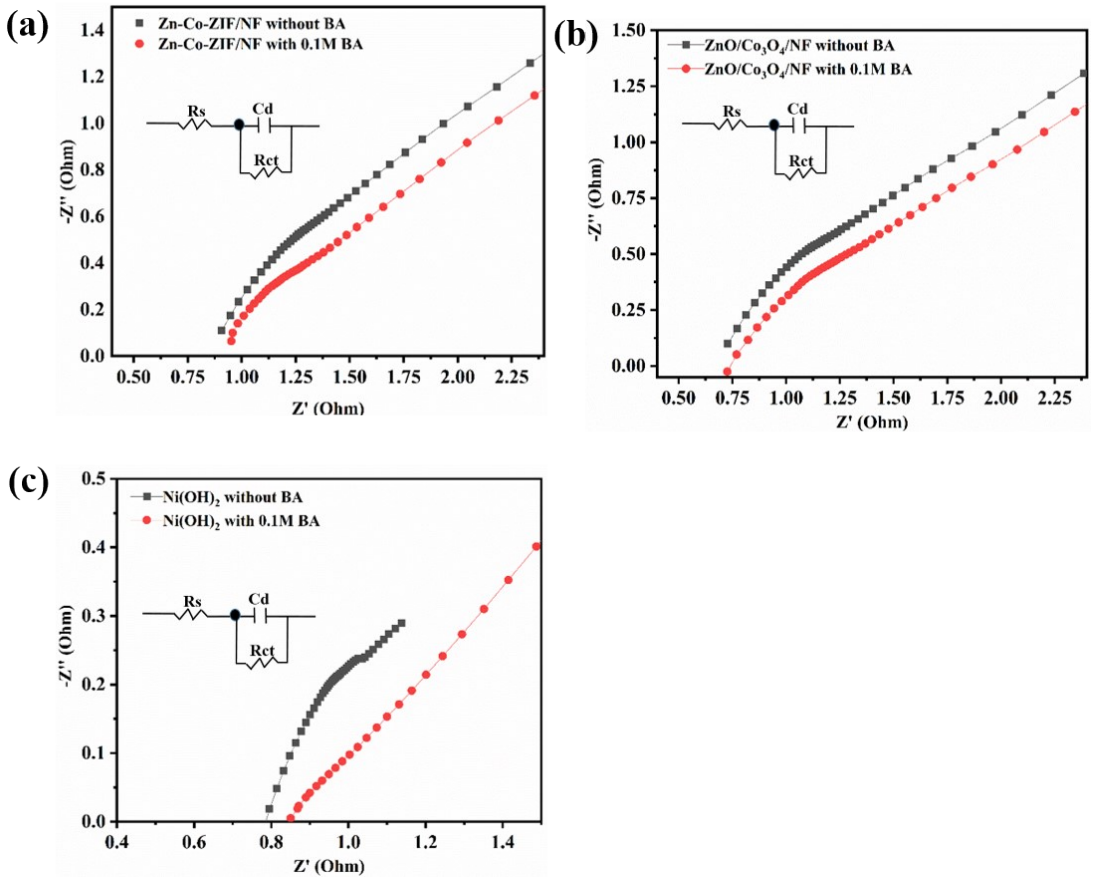


Fig. S6. The Nyquist plots over the Zn-Co-ZIF (a), the ZnO/Co_3O_4/NF (b) and (c) $Ni(OH)_2$/NF electrocatalysts in 1.0 M KOH with and without 0.1 M benzyl alcohol.

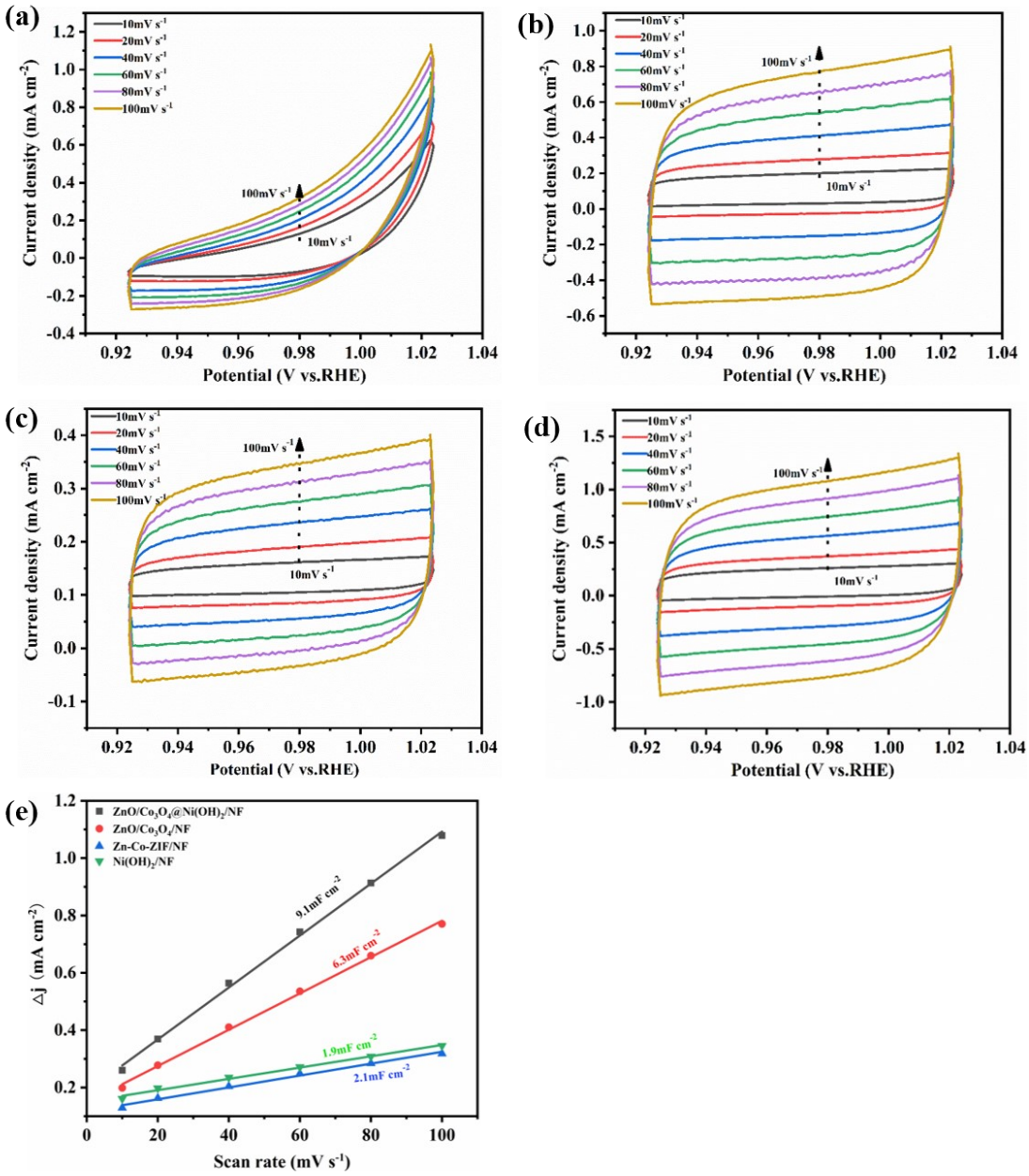


Fig. S7. The CVs for (a) Zn-Co-ZIF, (b) ZnO/Co_3O_4/NF, (c) $Ni(OH)_2$/NF, (d) ZnO/Co_3O_4@$Ni(OH)_2$/NF and (e) corresponding capacitive current as a function of scan rate in 1 M KOH with 0.1 M benzyl alcohol.

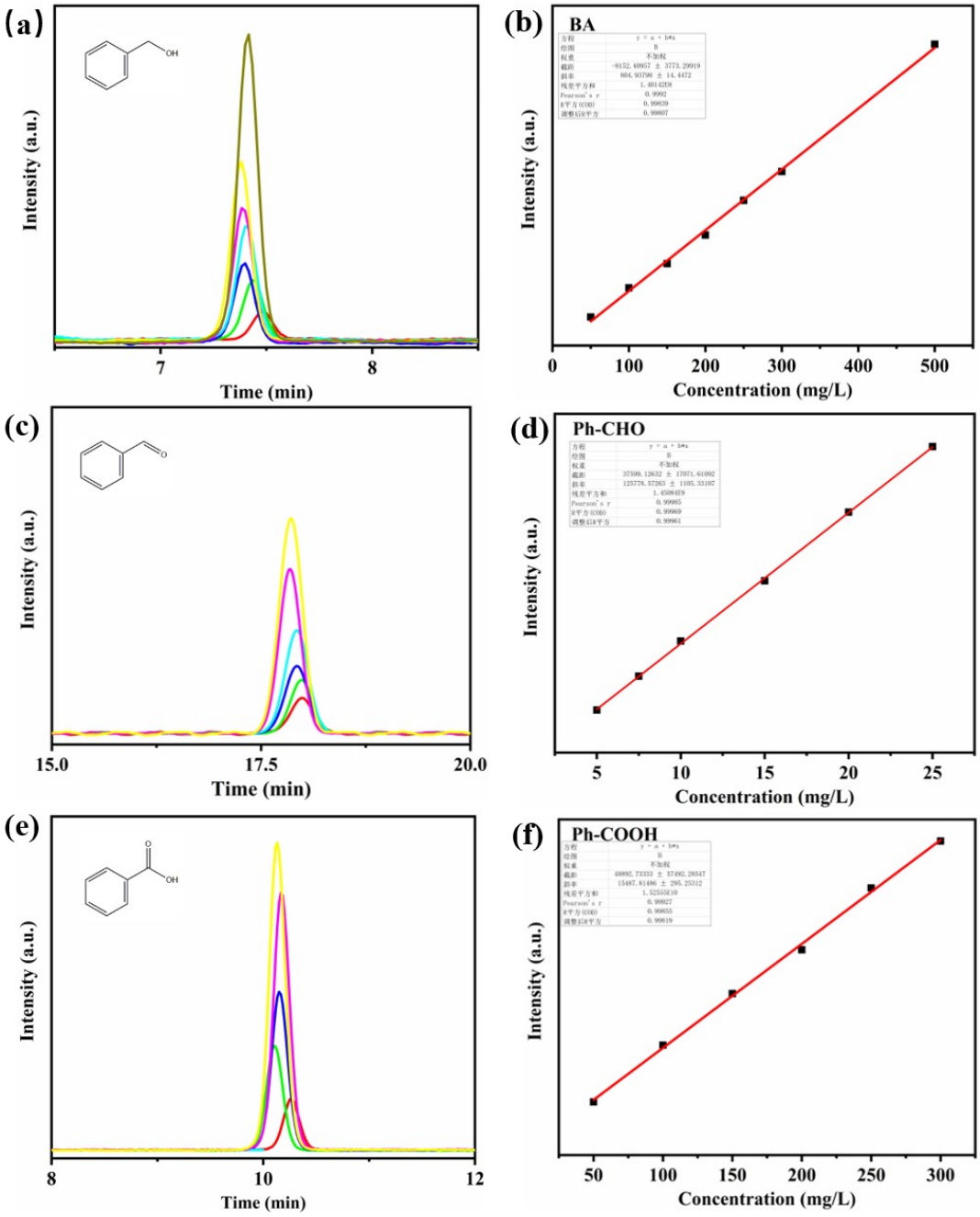


Fig. S8. HPLC chromatogram of standard samples at different concentrations: (a) benzyl alcohol, (c) benzaldehyde, (e) benzoic acid. Calibration of the HPLC for (b) benzyl alcohol, (d) benzaldehyde, (f) benzoic acid.

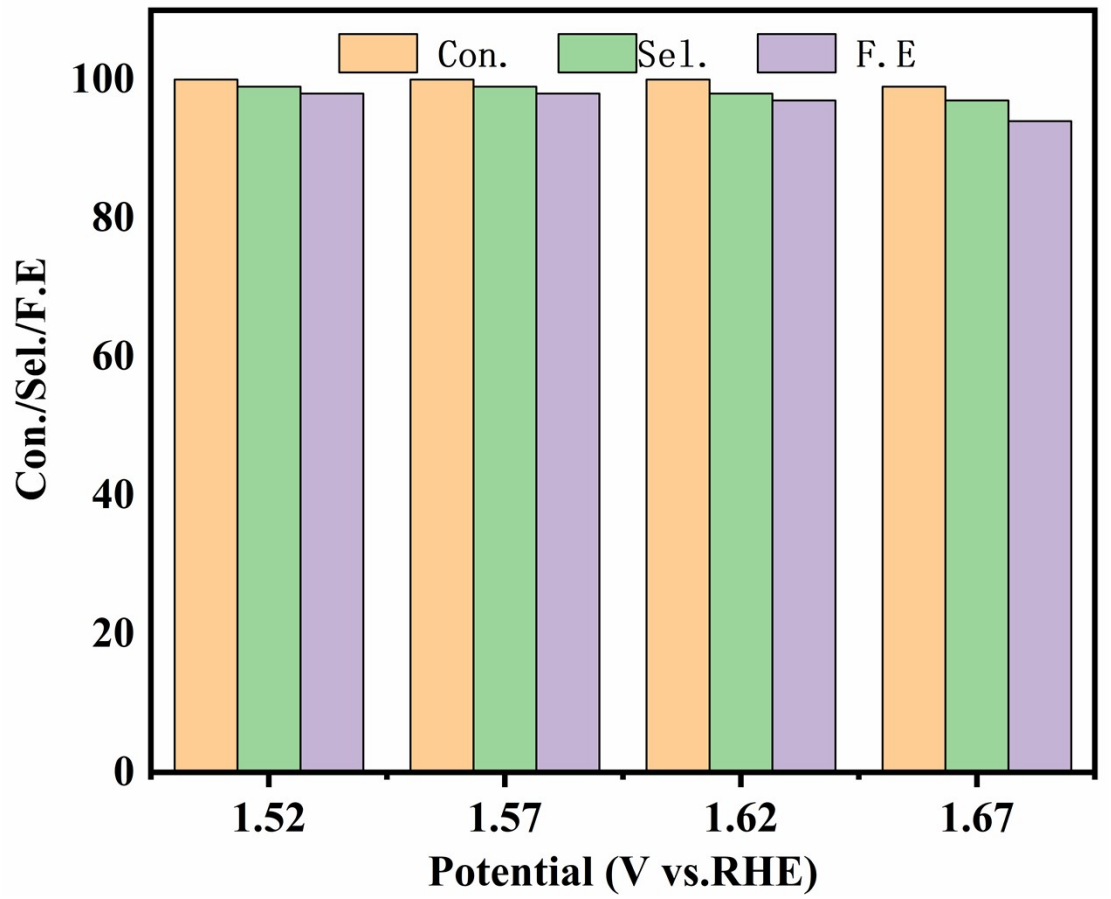


Fig. S9. The conversion, selectivity, and Faradic efficiency for oxidation of benzyl alcohol at different applied potentials using $ZnO/Co_3O_4@Ni(OH)_2$/NF electrode.

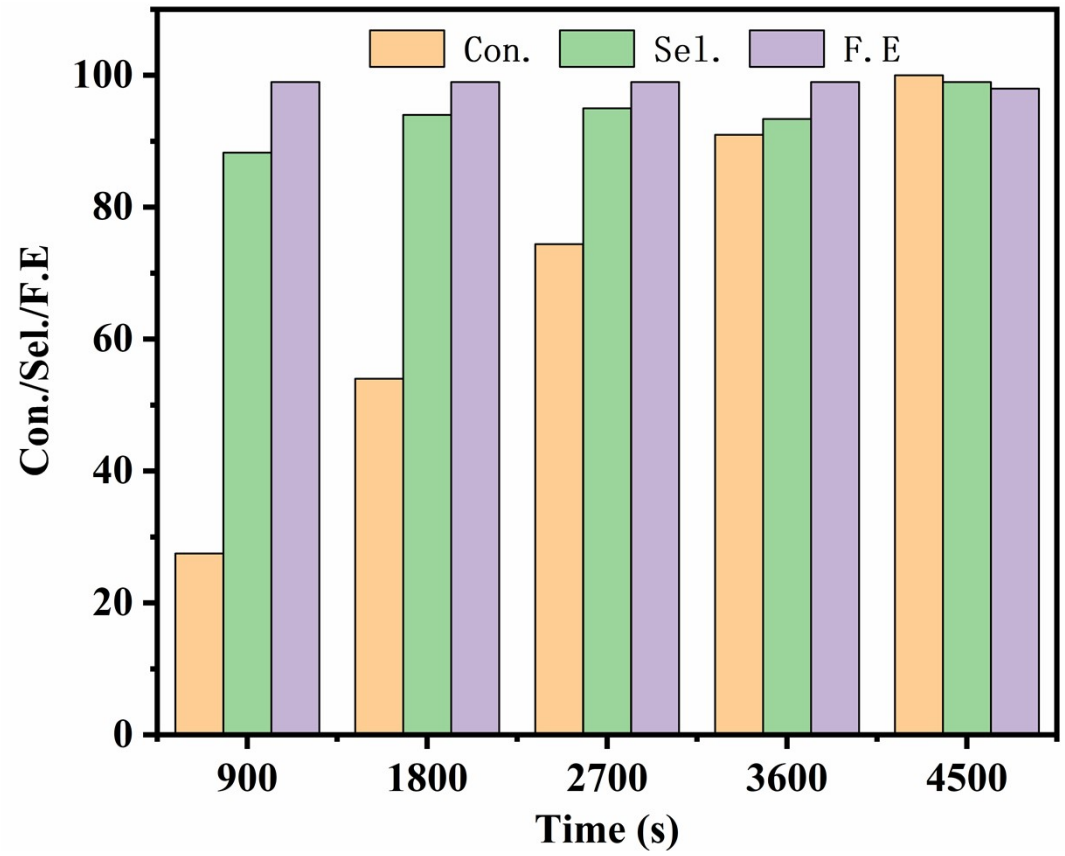


Fig. S10. The conversion of benzyl alcohol, and the selectivity and yield of benzoic acid for $ZnO/Co_3O_4@Ni(OH)_2/NF$ at the different successive electrolysis time.

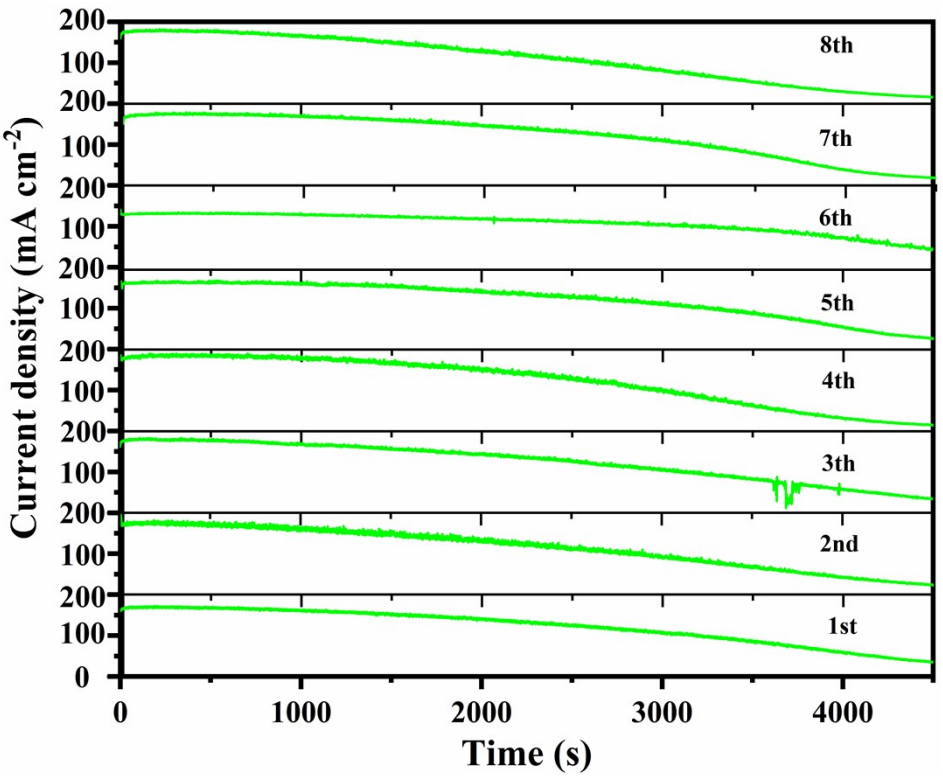


Fig. S11. The i-t curves of BA oxidation for $ZnO/Co_3O_4@Ni(OH)_2/NF$ at a constant potential of 1.52 V (vs. RHE) for the eight successive cycles.

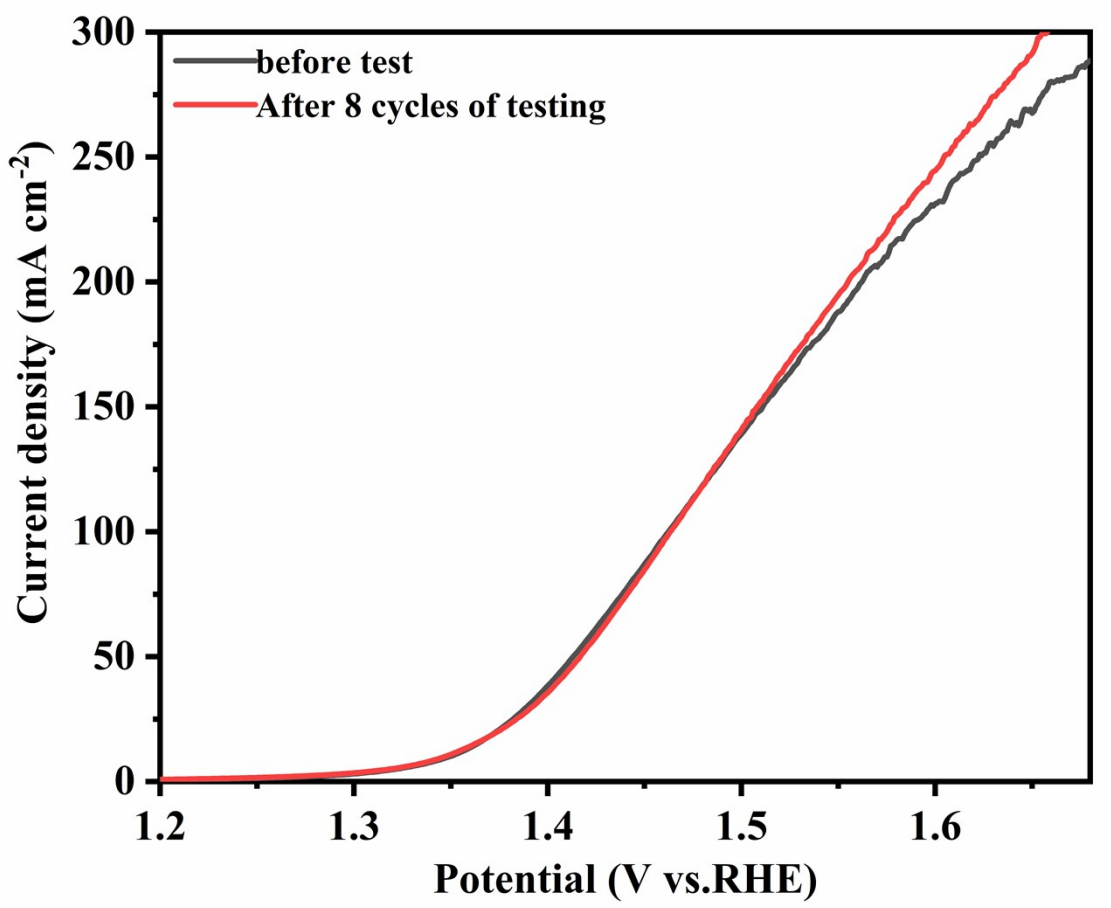


Fig. S12. The LSV curves of $ZnO/Co_3O_4@Ni(OH)_2/NF$

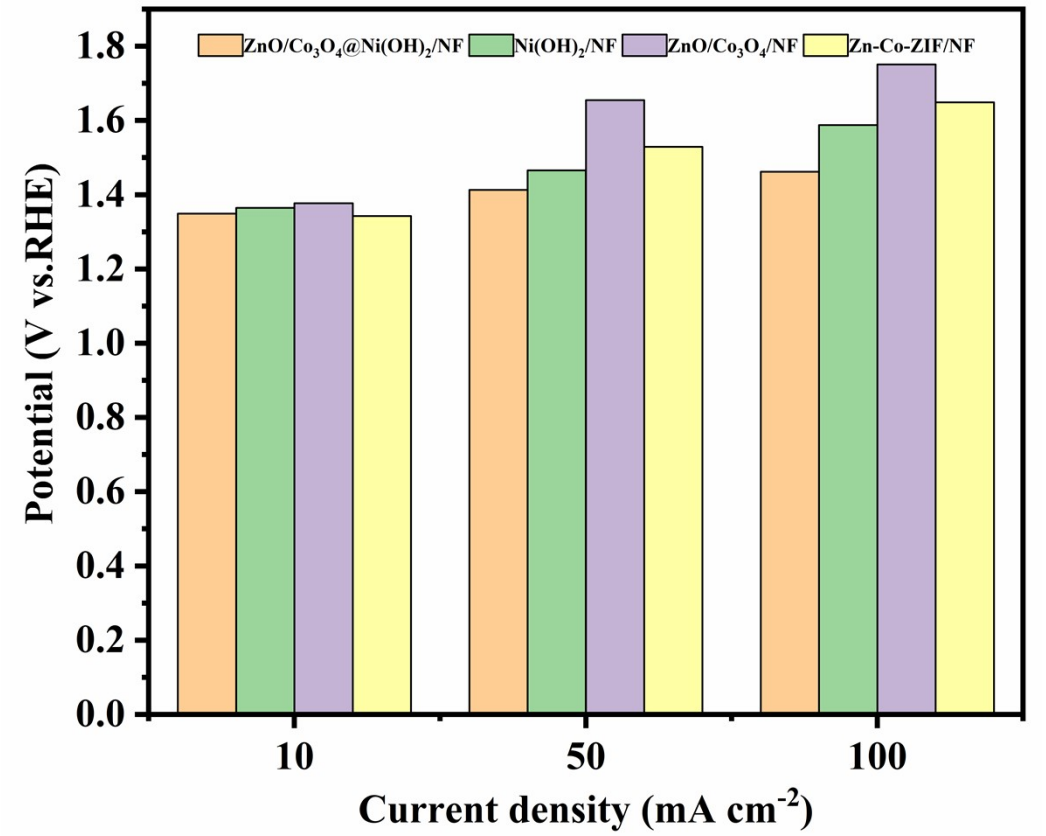


Fig. S13. The required voltages of Zn–Co-ZIF, ZnO/Co_3O_4/NF, $Ni(OH)_2$/NF and ZnO/Co_3O_4@$Ni(OH)_2$/NF at different reference currents.

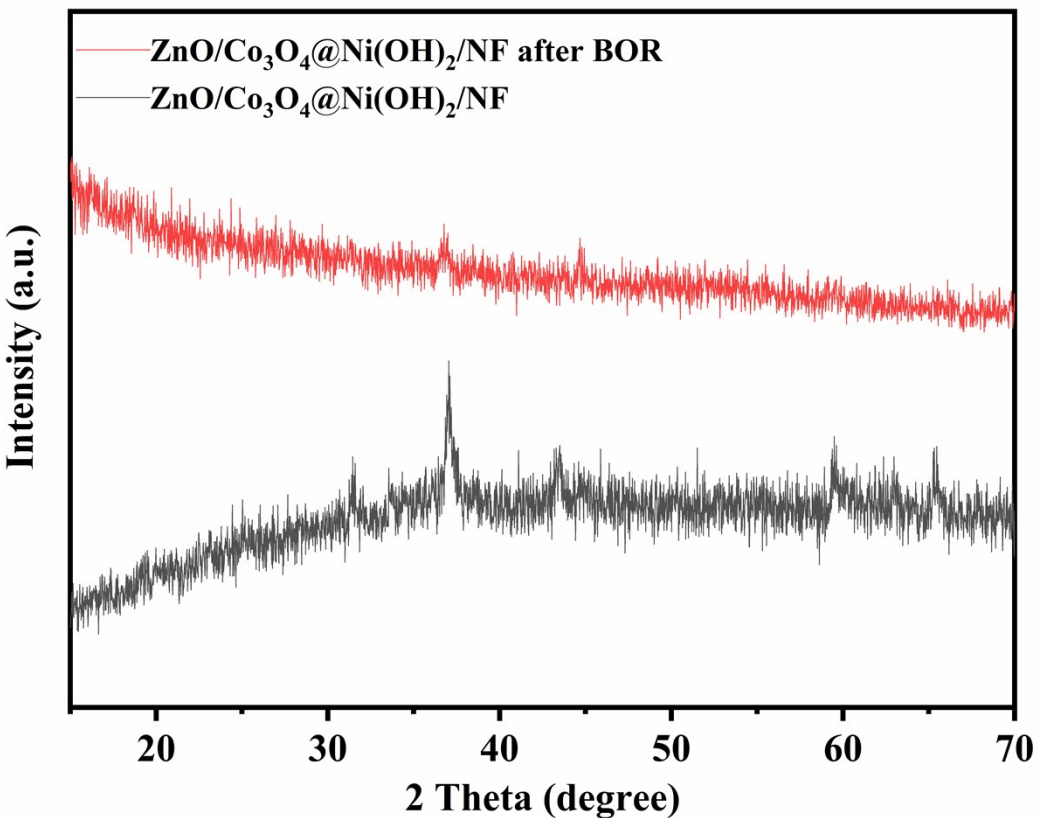


Fig. S14. XRD of the comparison of before and after eight times chronoamperometric tests for $ZnO/Co_3O_4@Ni(OH)_2/NF$.

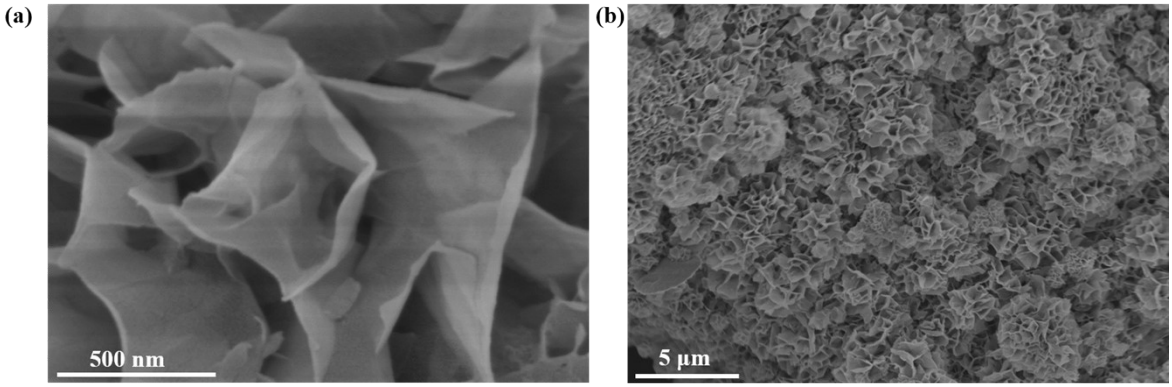


Fig. S15. SEM images of $ZnO/Co_3O_4@Ni(OH)_2/NF$ after eight times chronoamperometric tests.

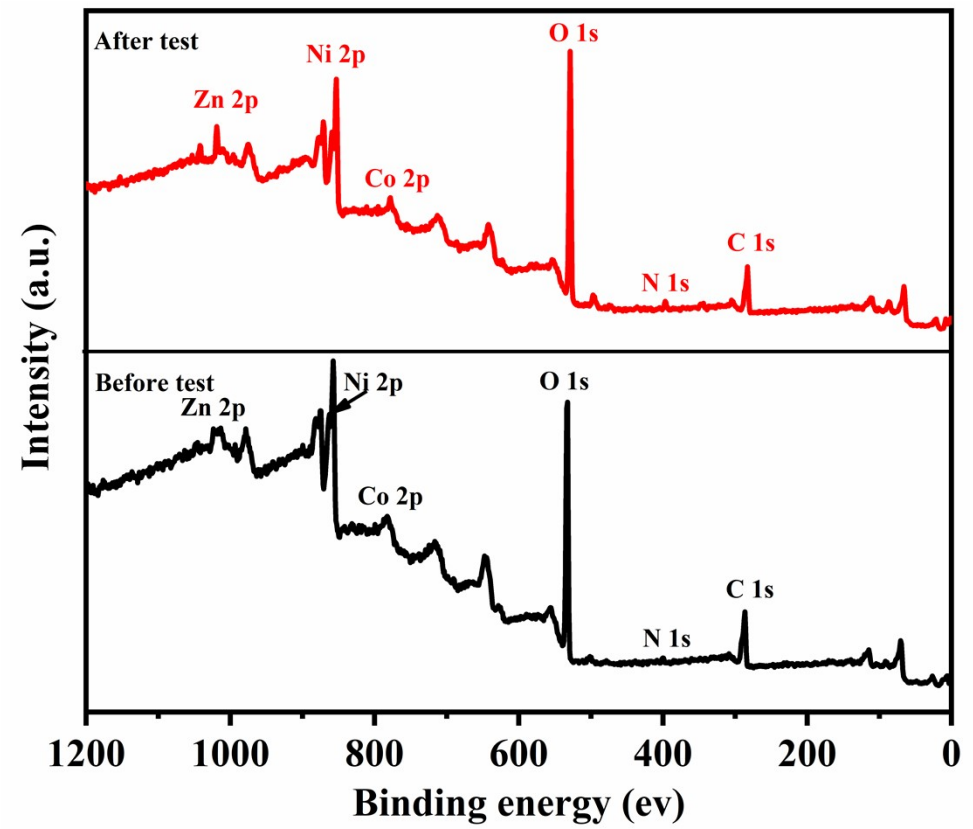


Fig. S16. XPS survey spectrum of $ZnO/Co_3O_4@Ni(OH)_2/NF$ before and after 8 times benzyl alcohol oxidation.

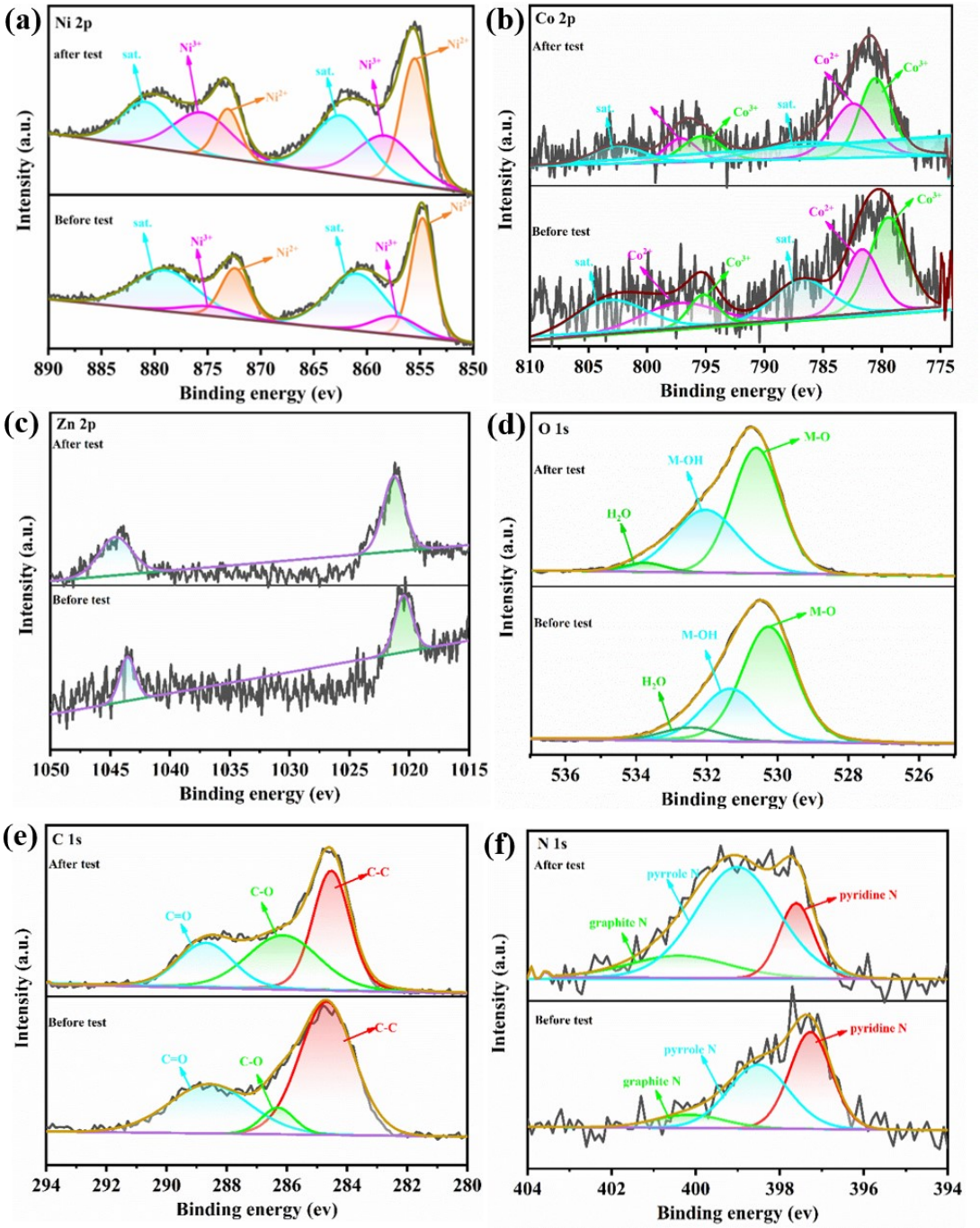


Fig. S17. XPS spectra of Ni 2p (a), Co 2p (b), Zn 2p (c), O 1s (d), C 1s (e) and N 1s (f) before and after 8 times benzyl alcohol oxidation.

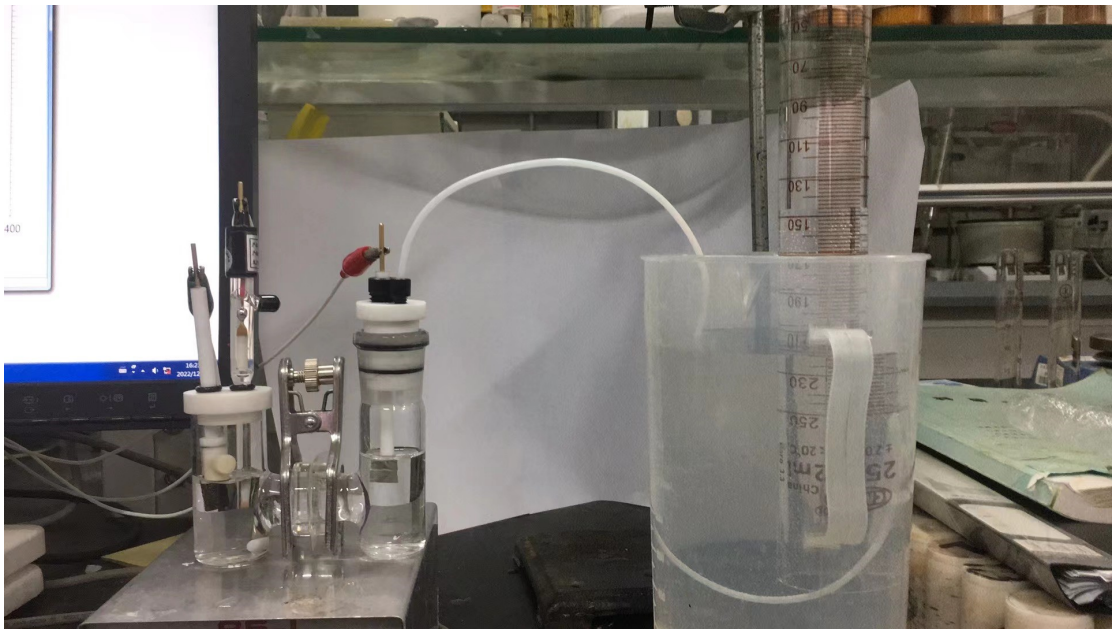


Fig. S18. Diagram of hydrogen collection device in the cathode.

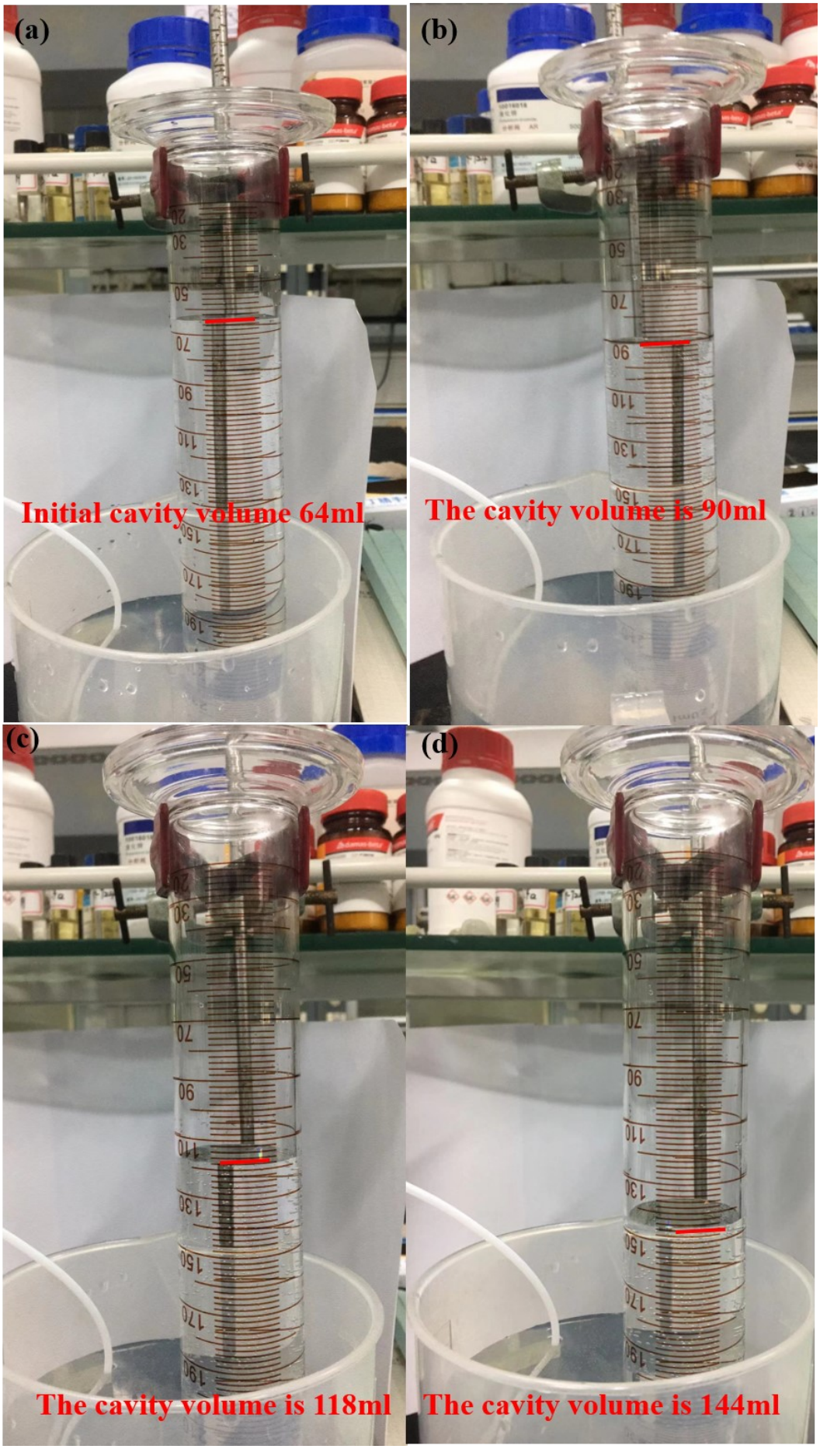

(a)
Initial cavity volume 64ml
(b)
The cavity volume is 90ml
(c)
The cavity volume is 118ml
(d)
The cavity volume is 144ml

Fig. S19. Hydrogen is collected by drainage, Replace the cathode electrolyte with a fresh KOH solution containing 0.1M BA every 20 minutes. (a) The initial volume of the cavity in the cylinder is 64ml.(b) The first 20 minutes (c) The second 20 minutes, total 40 minutes (d) The third 20 minutes, 60 minutes total.

According to the ideal gas equation of state $pV = nRT$ ($p=1.01325\times10^5$Pa, $V=8\times10^{-5}m^3$, R=8.314, T=(273.15+20)K, The temperature of the collected gas is 20℃) . The hydrogen yield was calculated to be 3.32mmol.

Table S1. Impedance fitting results of as-prepared $ZnO/Co_3O_4@Ni(OH)_2$/NF, Zn-Co-ZIF/NF, $Ni(OH)_2$/NF and ZnO/Co_3O_4/ NF

	Rs/Ω cm^{-2}	Rct/Ω cm^{-2}
$ZnO/Co_3O_4@Ni(OH)_2$/NF	1.01	0.25
Zn-Co-ZIF/NF	1.16	0.5
$Ni(OH)_2$/NF	1.05	0.29
ZnO/Co_3O_4/ NF	1.13	0.34

Table S2. Comparison of $ZnO/Co_3O_4@Ni(OH)_2$ with other catalysts for BOR.

Electrocatalyst	substrate	Catalysts loading amount (mg cm^{-2})	Electrolyte	con .(%)	FE (%)	Potential (V vs. RHE)	**Ref.**
Co_3O_4 NWs/Ti	Ti membranes	/	10 mM BA	**99**	**/**	**2.42**	**1**
NC@$CuCo_2$Nx/CF	carbon fiber (CF)	2	15 mM BA	**97.25**	**81.3**	**1.62**	**2**
Co_3O_4/NF	Ni foam (NF)	/	20 mM BA	**99**	**91.4**	**1.52**	**3**
CuO-NR	Copper foam (CF)	/	10 mM BA	**90**	**97**	**1.39**	**4**
h-$Ni(OH)_2$	carbon fiber (CF)	0.625	40 mM BA	**100**	**98.2**	**/**	**5**
N-Mo-Ni/NF	Ni foam (NF)	/	0.1 M BA	**100**	**98.7**	**1.52**	**6**
$ZnO/Co_3O_4@Ni(OH)_2$/NF	Ni foam (NF)	0.6	0.1 M BA	**100**	**97**	**1.52**	**This work**

References:

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