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Controllable Evolution of NiOOH/Au^{3+} Active Species for the Oxidation of 5-Hydroxymethylfurfural

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Experimental

Chemicals

HMF, 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA) and furan-2, 5-dicarbaldehyde (DFF) and FDCA were purchased from Aladdin. All other chemicals and reagents were obtained from Sinopharm Chemical Reagent Co., Ltd in China.

Synthesis

Firstly, Ni-BTC MOF was prepared on copper foam (CF) by electrochemical deposition. Under constant stirring, 1.1 g 1, 3, 5-benzenetricarboxylic acid, 1.6 g methyltributylammonium methyl sulfate and 0.65 g $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in 50 mL DMF to obtain electrodeposition solution. Electrodeposition potential: -1.5 V vs. Ag/AgCl, electrodeposition time: 800 s. Finally, the prepared CF-Ni MOF sample was washed with deionized water. Secondly, under vigorous stirring, dilute $NaBH_4$ solution (1 mg/L) was slowly added to 50 mL $HAuCl_4$ solution (0.5 mM) until the solution was burgundy. The prepared CF-Ni MOF was soaked in the above solution for 5 min, washed with deionized water and dried in a vacuum drying oven.

Characterization

The micro-morphology of samples was obtained by scanning electron microscopy (SEM, Apreo S HiVac). The valence-state and contents of samples were measured by X–ray photoelectron spectroscopy (XPS, Physical Electrons Quantum 2000 Scanning Esca Microprobe). The crystalline phases of samples were determined by (XRD, Bruker D8 Advance X–ray diffractometer).

Electrochemical measurements

Electrochemical tests (cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and open-circuit voltage-time (OCPT)

were conducted in an H-shaped electrolytic cell. Activated CF-Ni MOF/Au was used as the working electrode, Ag/AgCl and Pt wire electrodes were used as the reference electrode and counter electrode, respectively. The electrolyte was 1.0 M KOH (pH 14.0), and the scanning rate was 5 mV/s. The frequency range of electrochemical impedance measurement is 0.1–10^6 Hz.

The oxidative activation of the Ni MOF/Au catalyst was mainly accomplished in two steps. First, the catalyst Ni MOF/Au was subjected to three consecutive LSV scans in 1.0 M KOH. Subsequently, another 120 cycles of CV scanning were performed to ensure that the catalyst surface had been completely oxidized to high-valence NiOOH/Au^{3+} species.

HPLC analysis

The quantitative analysis of HMF and products was recorded on high performance liquid chromatography (HPLC, Shim-pack GWS C-18 column: 5.0 μm*4.6 mm*150 mm). Detection wavelength: 265 nm, Column temperature: 40°C. Mobile phase A: 70% ammonium formate (5.0 mM), Mobile phase B: 30% methanol. Flow rate: 0.6 mL/min. 20 μL sample was diluted to 2 mL as HPLC test solution. HMF conversion, FDCA yield and Faradaic efficiency (FE) were calculated using the following equations. *F* (96485 C/mol) represents Faraday's constant.

$$\text{HMF conversion} = \frac{\text{Consumed HMF}}{\text{Initial HMF}} \times 100\%$$

$$\text{FDCA yield} = \frac{\text{Formed FDCA}}{\text{Initial HMF}} \times 100\%$$

$$\text{FE of FDCA} = \frac{\text{Formed FDCA}}{\text{Consumed charge}/(6 \times \text{F})} \times 100\%$$

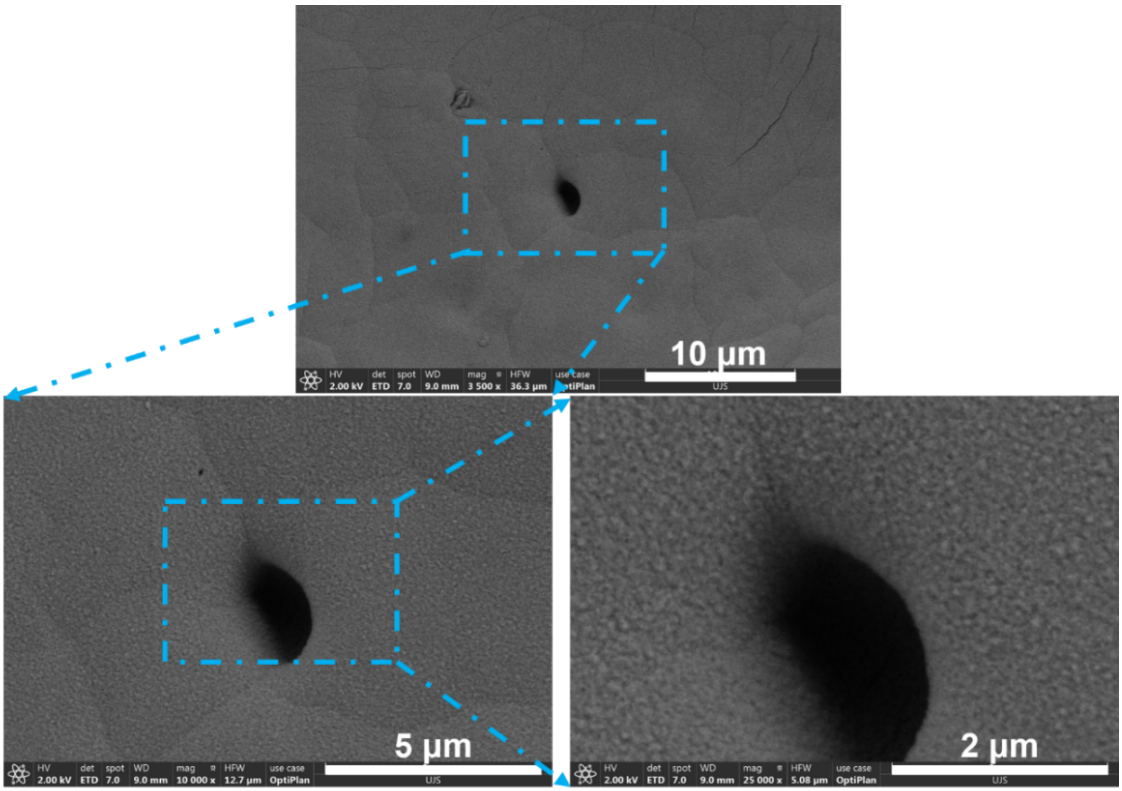


Fig. S1. SEM images of CF-Ni MOF.

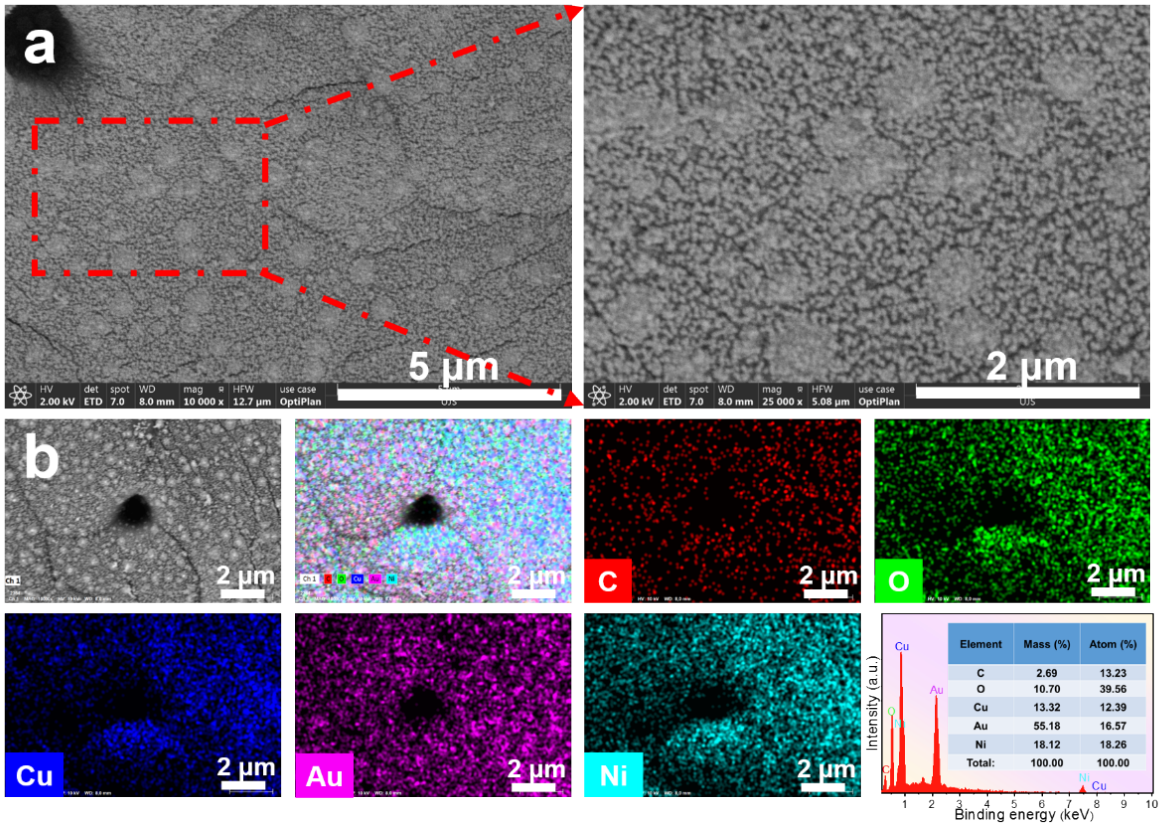


Fig. S2. SEM (a) and EDS-mapping (b) images of the activated CF-Ni MOF/Au.

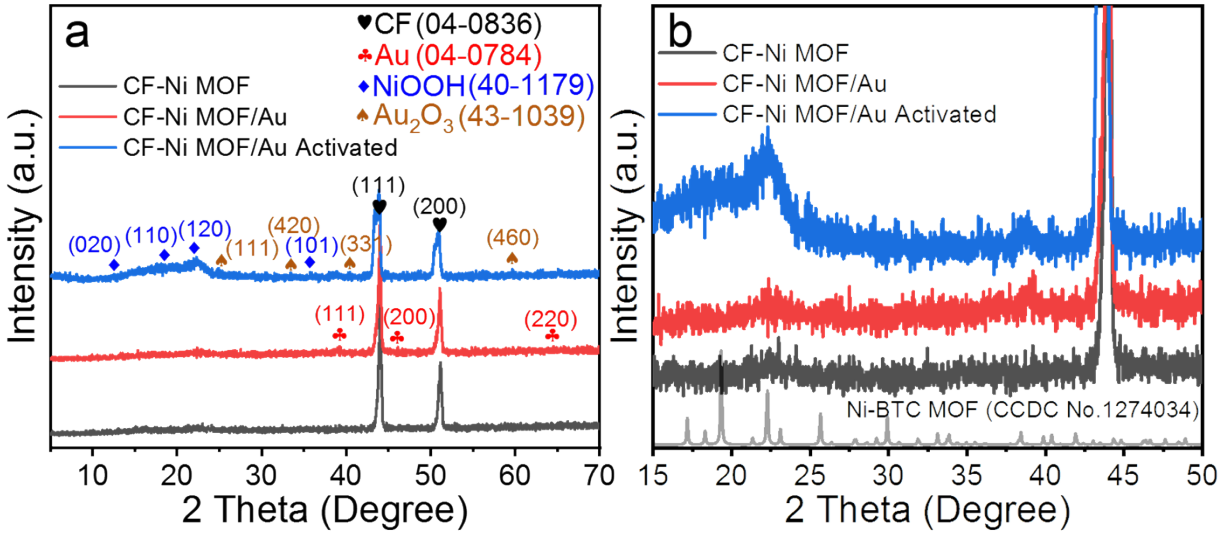


Fig. S3. XRD patterns of CF-Ni MOF, CF-Ni MOF/Au, activated CF-Ni MOF/Au (a). The partially enlarged view for XRD patterns (b).

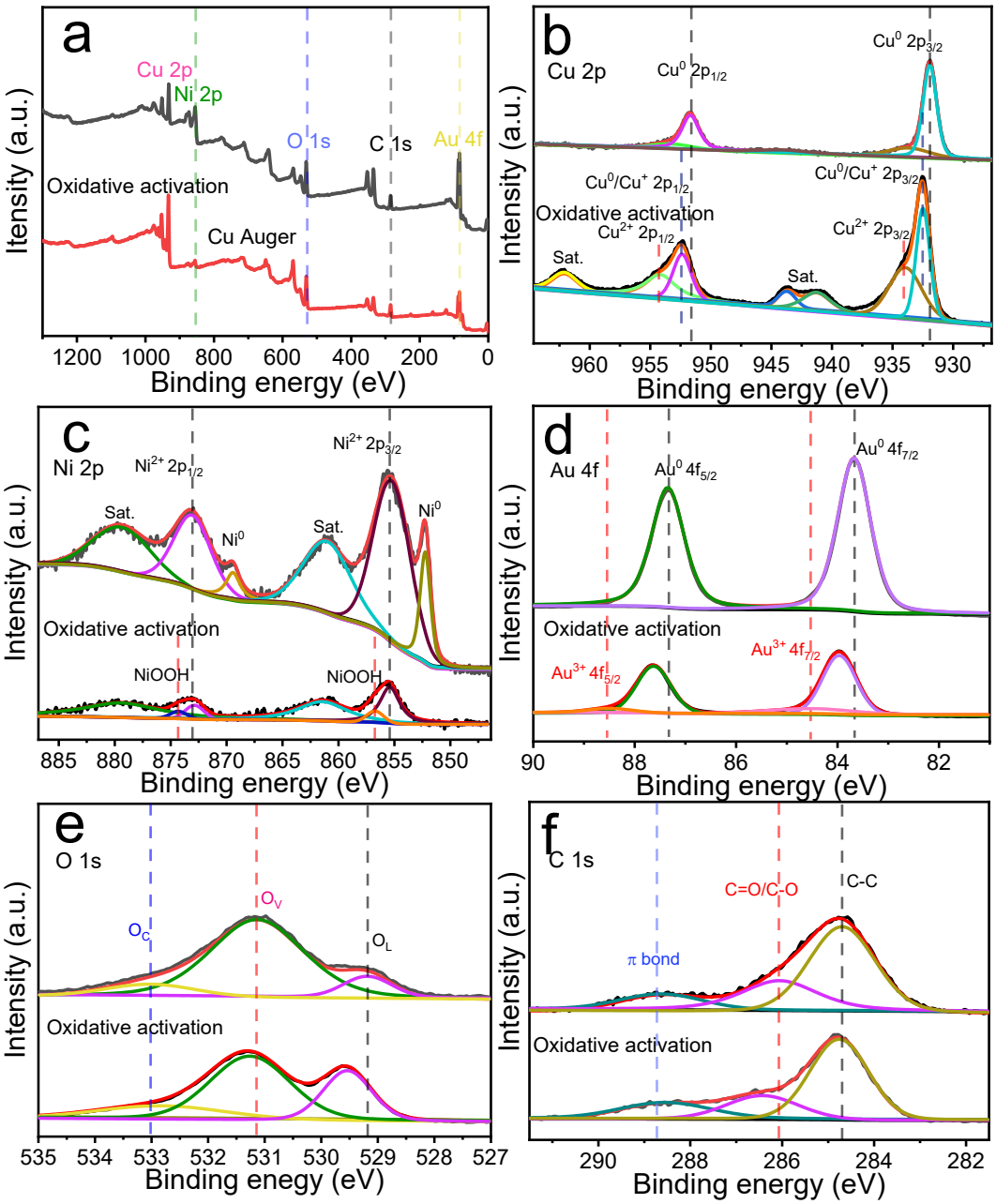
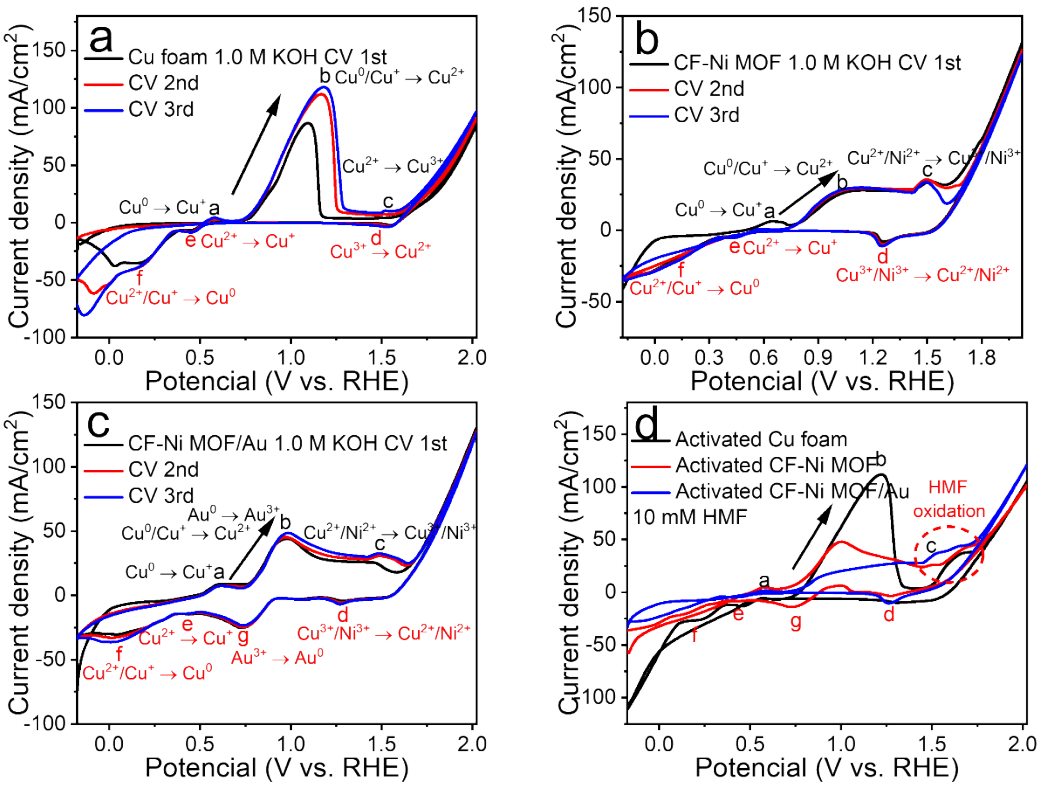


Fig. S4. Full-scan XPS spectra of CF-Ni MOF/Au and activated CF-Ni MOF/Au (a). XPS spectra of Cu 2p (b), Ni 2p (c), Au 4f (d), O 1s (e) and C 1s (f) of CF-Ni MOF/Au and activated CF-Ni MOF/Au.



a. $2Cu + 2OH^- \rightarrow Cu_2O + H_2O + 2e^-$

b. $Cu_2O + 2OH^- \rightarrow 2CuO + H_2O + 2e^-$

$Cu + 2OH^- \rightarrow CuO + H_2O + 2e^-$

$Cu + 2OH^- \rightarrow Cu(OH)_2 + 2e^-$

$2Au + 6OH^- \rightarrow Au_2O_3 + 3H_2O + 6e^-$

c. $CuO + OH^- \rightarrow CuOOH + e^-$

$Cu(OH)_2 + OH^- \rightarrow CuOOH + H_2O + e^-$

$Ni^{2+} + 3OH^- \rightarrow NiOOH + H_2O + e^-$

d. $CuOOH + H_2O + e^- \rightarrow Cu(OH)_2 + OH^-$

$CuOOH + e^- \rightarrow CuO + OH^-$

$NiOOH + H_2O + e^- \rightarrow Ni^{2+} + 3OH^-$

e. $2CuO + H_2O + 2e^- \rightarrow Cu_2O + 2OH^-$

f. $Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^-$

$CuO + H_2O + 2e^- \rightarrow Cu + 2OH^-$

$Cu(OH)_2 + 2e^- \rightarrow Cu + 2OH^-$

g. $Au_2O_3 + 3H_2O + 6e^- \rightarrow 2Au + 6OH^-$

Fig. S5. CV curves of Cu foam (a), CF-Ni MOF (b) and CF-Ni MOF/Au (c) in 1.0 M KOH solution. CV curves of Cu foam, CF-Ni MOF and CF-Ni MOF/Au in the presence of 10 mM HMF (d). (Scan rate: 5 mV/s).

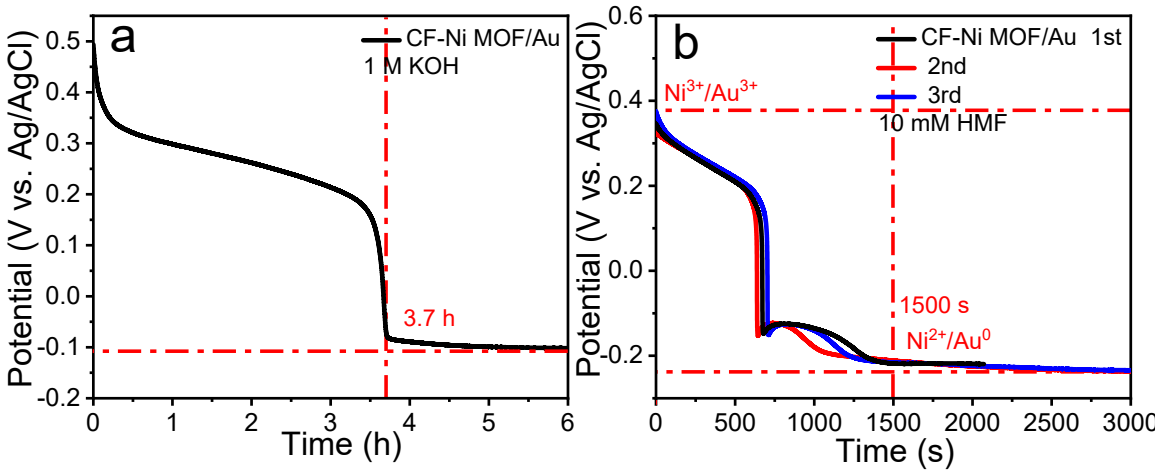


Fig. S6. OCPT of CF-Ni MOF/Au in 1.0 M KOH solution (a). Three consecutive OCPTs of CF-Ni MOF/Au in 10 mM HMF (b).

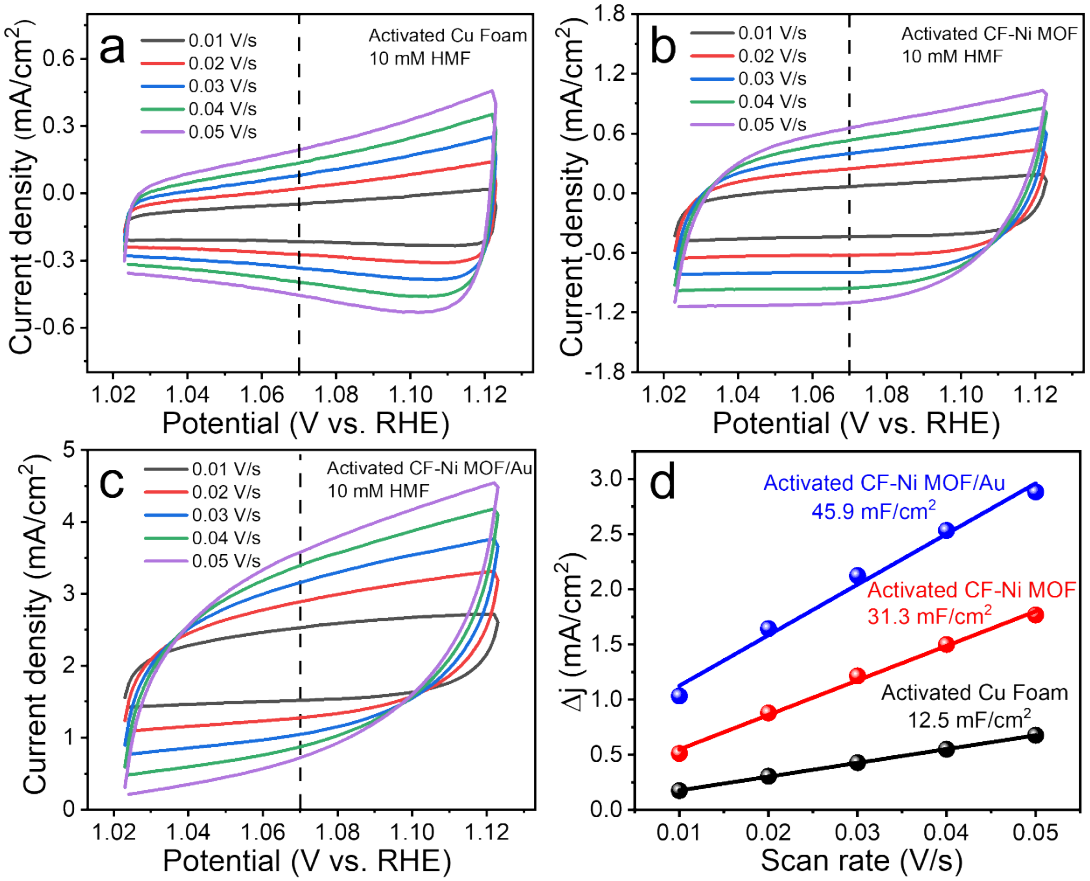


Fig. S7. CV curves of the activated CF (a), CF-Ni MOF (b) and CF-Ni MOF/Au (c) in the presence of 10 mM HMF at different scan rates. Current density vs. scan rates (d).

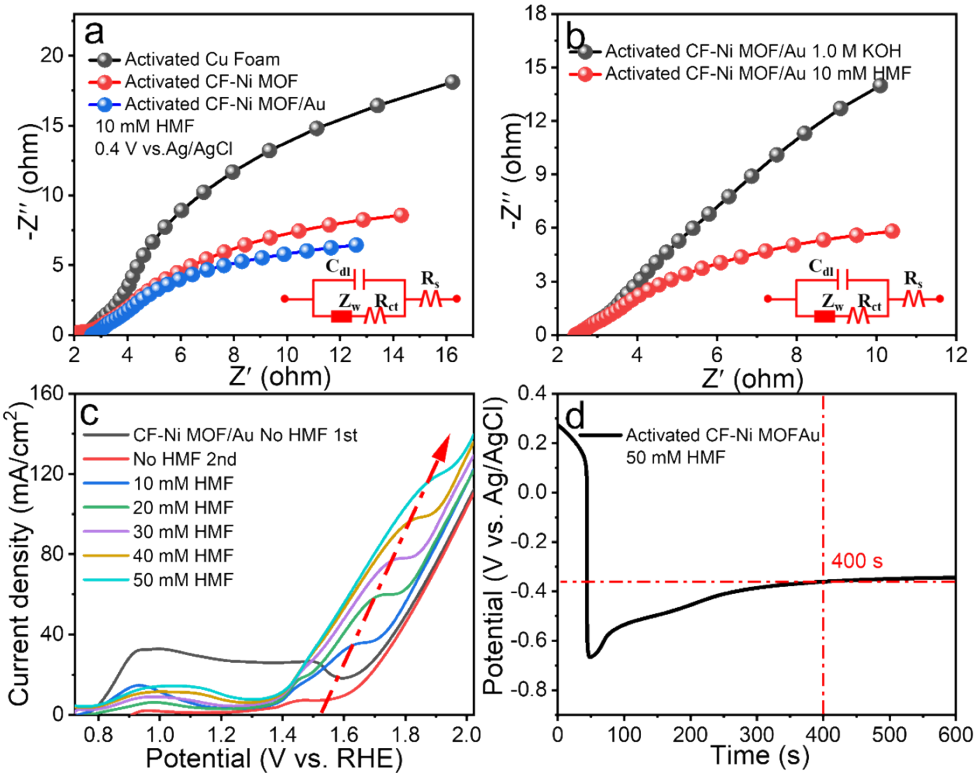


Fig. S8. EIS plots (1.42 V vs. RHE) of CF, CF-Ni MOF and CF-Ni MOF/Au in the presence of 10 mM HMF (a). EIS plots (1.42 V vs. RHE) of CF-Ni MOF/Au in the absence or presence of 10 mM HMF (b). LSV curves of CF-Ni MOF/Au at different concentration of HMF (c). OCPT experiment of the activated CF-Ni MOF/Au in the presence of 50 mM HMF (d).

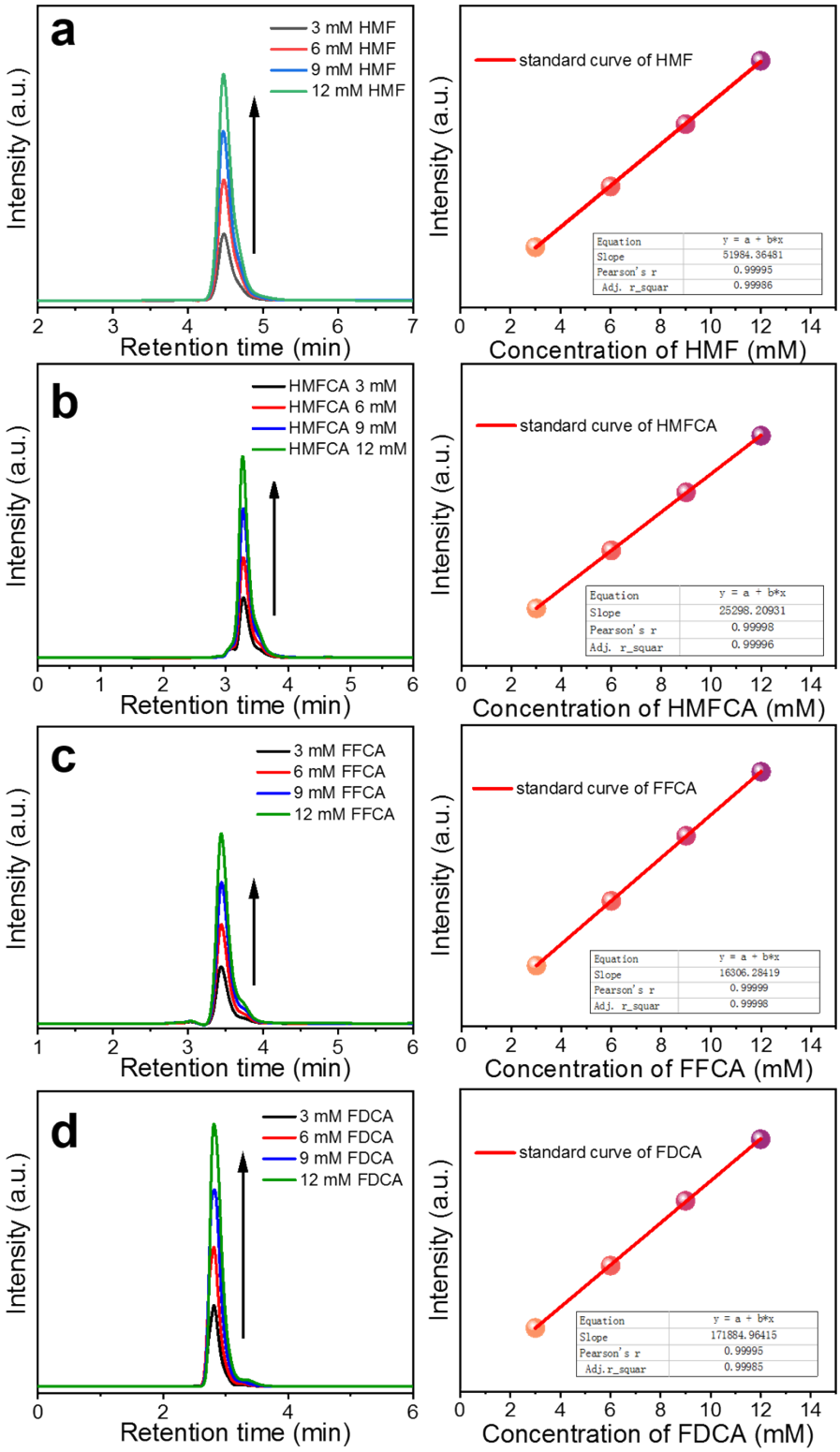


Fig. S9. Calibration curves of HMF (a), HMFCA (b), FFCA (c) and FDCA (d).

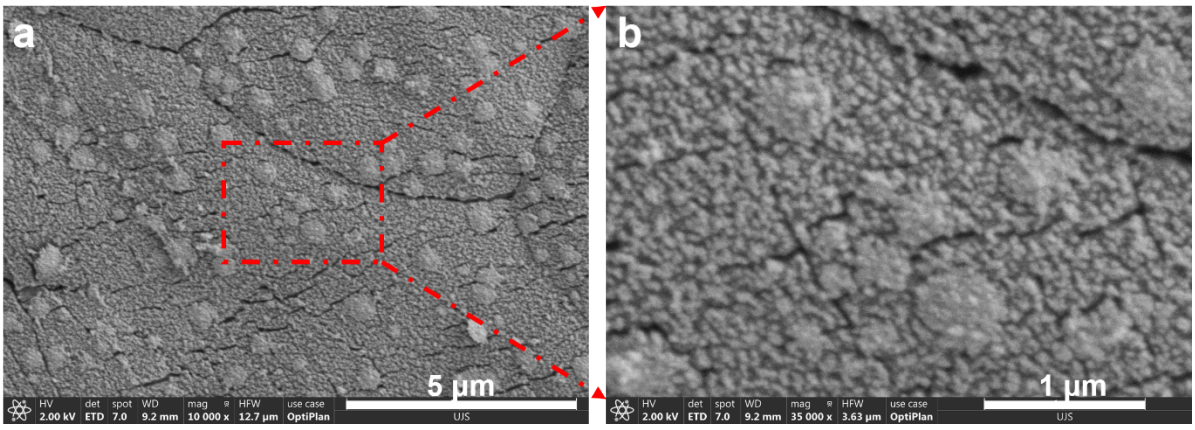


Fig. S10. SEM images of the activated CF-Ni MOF/Au after the five successive electrocatalytic HMF oxidations.

Fig. S11. Electrocatalytic mechanism of NiOOH/Au^{3+} species for HMF oxidation.