

## Electronic Supplementary Information

### In Situ Growing MOFs on Ni(OH)<sub>2</sub> for Efficient Electrocatalytic Oxidation of 5-Hydroxymethylfurfural

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## Experimental Section

### *Chemicals*

All reagents were of AR grade and used without further treatment and purification. 5-Hydroxymethylfurfural, 5-hydroxymethyl-2-furancarboxylic acid, 2,5-diformylfuran, 5-formyl-2-furancarboxylic and 2,5-Furandicarboxylic acid were purchased from Aladdin Reagent Company.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , thiophene-2,5-dicarboxylate (Tdc), 4, 4'-bipyridine (Bpy), sodium hydroxide (NaOH) and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. The commercial Ni foam (NF) was obtained from Shanghai Hesun Electric Co. LTD.

### *Fabrication of $\text{Ni}(\text{OH})_2\text{-NSs/NF}$*

For a typical synthesis, 5 mmol  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 10 mmol urea and 4 mmol  $\text{NH}_4\text{F}$  were first dissolved in 35 mL deionized water under vigorous stirring. The obtained light green solution was then transferred to a 50 mL Teflon-lined autoclave. A piece of pre-treated NF ( $1 \times 2 \text{ cm}^2$ ) was immersed in the solution, and the autoclave was sealed and heated to  $120 \text{ }^\circ\text{C}$  for 6 h. The obtained  $\text{Ni}(\text{OH})_2\text{-NSs/NF}$  was separated from the reaction mixture, washed thoroughly with ethanol and water and dried in oven at  $60 \text{ }^\circ\text{C}$  overnight.

### *Fabrication of $\text{S,N-MOFs@Ni}(\text{OH})_2\text{-NSs/NF}$*

For a typical synthesis, 296 mg 4, 4'-bipyridine, 280 mg thiophene-2, 5-dicarboxylate and 132 mg NaOH were dissolved in 20 mL deionized water. A piece of the as-synthesized  $\text{Ni}(\text{OH})_2\text{-NSs/NF}$  was immersed in the above solution for 6 h under room temperature to allow the formation of  $[\text{Ni}-(\text{Tdc})(\text{Bpy})]_n$  MOFs on  $\text{Ni}(\text{OH})_2\text{-NSs/NF}$  surface. The resultant  $\text{S,N-MOFs@Ni}(\text{OH})_2\text{-NSs/NF}$  was washed thoroughly with ethanol and water and dried in oven at

60 °C overnight.

### ***Characterizations***

The morphology of samples was characterized by field emission scanning electron microscopy (SU 8020) and transmission electron microscopy (JEOL-2010). X-ray diffraction (XRD) patterns were recorded by a Philips X-Pert Pro diffractometer with a Ni-filtered monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Brunauer-Emmett-Teller (BET) surface areas and pore structure properties were obtained using a surface area and porosity analyzer (Autosorb iQ Station 2). X-ray photoelectron spectra (XPS) were recorded by an ESCALAB 250 system. The thickness of the as-synthesized nanosheets was measured by atomic force microscopy (AFM; PARKNX10). FT-IR spectra were obtained from a Thermo Nicolet NEXUS FI-IR spectrophotometer using a KBr pellet method.

### ***Electrochemical measurements***

All electrochemical measurements were performed using a two-compartment H-type electrochemical cell with a Nafion membrane separator. All Electrochemical data were recorded by an electrochemical workstation (CHI 760E) using a three-electrode electrochemical system with a  $1 \times 1 \text{ cm}^2$  S,N-MOFs@Ni(OH) $_2$ -NSs/NF or (Ni(OH) $_2$ -NSs/NF or bare NF working electrode, a Hg/HgO reference electrode and a Pt mesh counter electrode in the 1.0 M KOH electrolyte solution with and without 10 mM HMF.

### ***Products analysis***

The concentrations of HMF and oxidation products were determined by HPLC using a 4.6 mm  $\times$  150 mm Shim-pack GWS 5  $\mu$ m C-18 column and an ultraviolet-visible detector. HPLC eluents were mixtures of solvents A and B. Solvent A was 5% aqueous ammonium formate

solution and solvent B was methanol. Separation and quantification were performed using an isocratic elution with 60% A and 40% B over 10 min at a flow rate of 0.6 mL min<sup>-1</sup>.

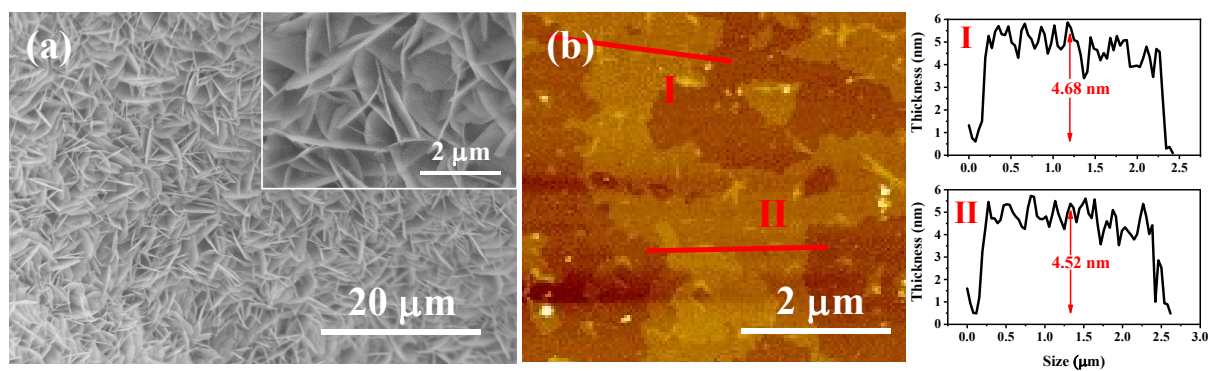
The product yields and faradaic efficiencies (FE) were calculated based on the following equations:

$$Yield (\%) = \frac{\text{Moles of Formed Product}}{\text{Moles of Initial HMF}} \times 100\% \quad (1)$$

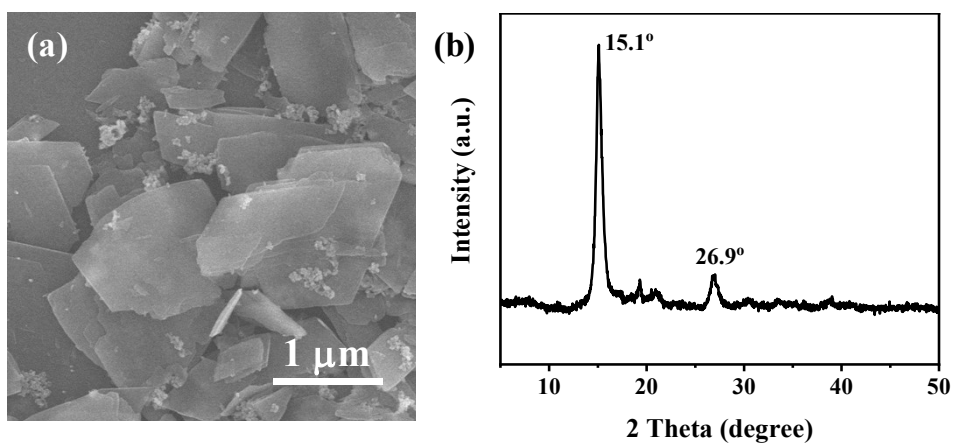
$$FE (\%) = \frac{6 F \times (\text{Moles of Formed FDCA})}{Q} \times 100\% \quad (2)$$

Where,  $Q$  is the total transferred charge and  $F$  is Faraday constant (96485 C mol<sup>-1</sup>). The quantity of product is determined by HPLC analysis.

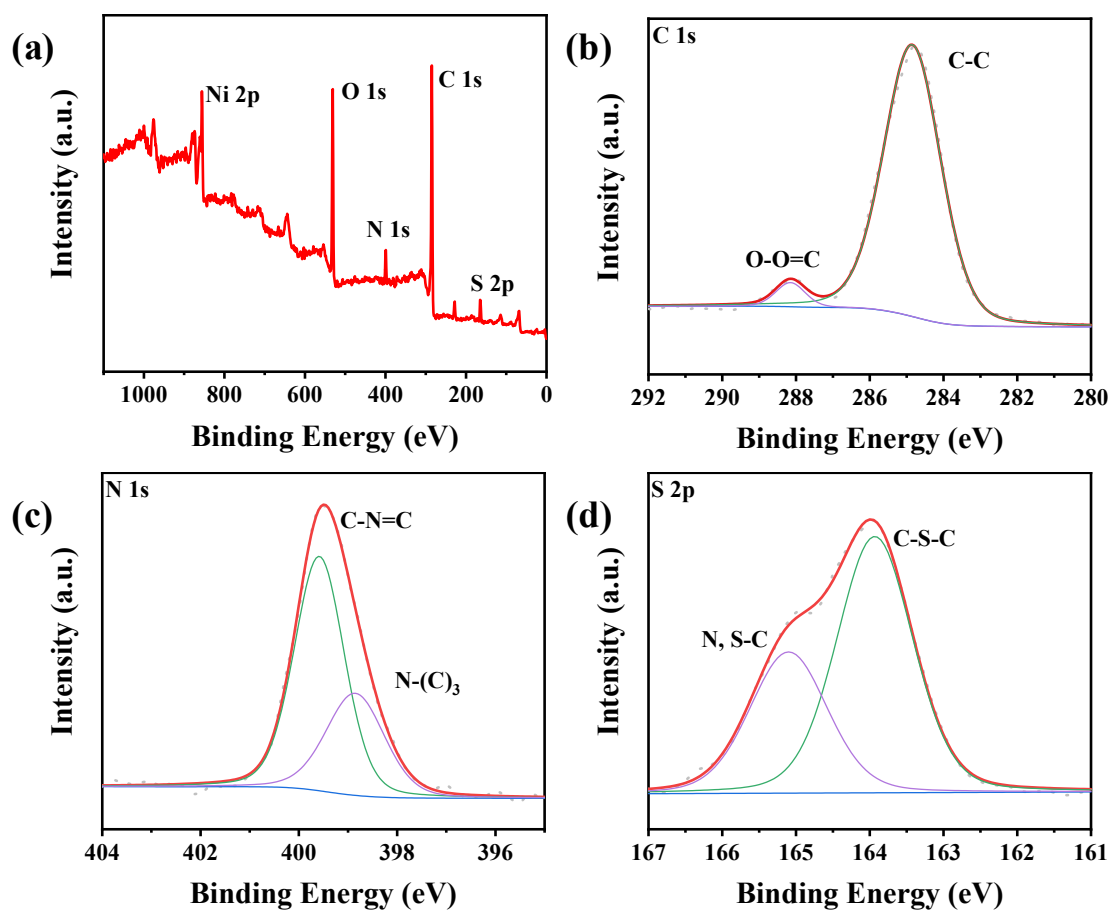
## Figures and Tables



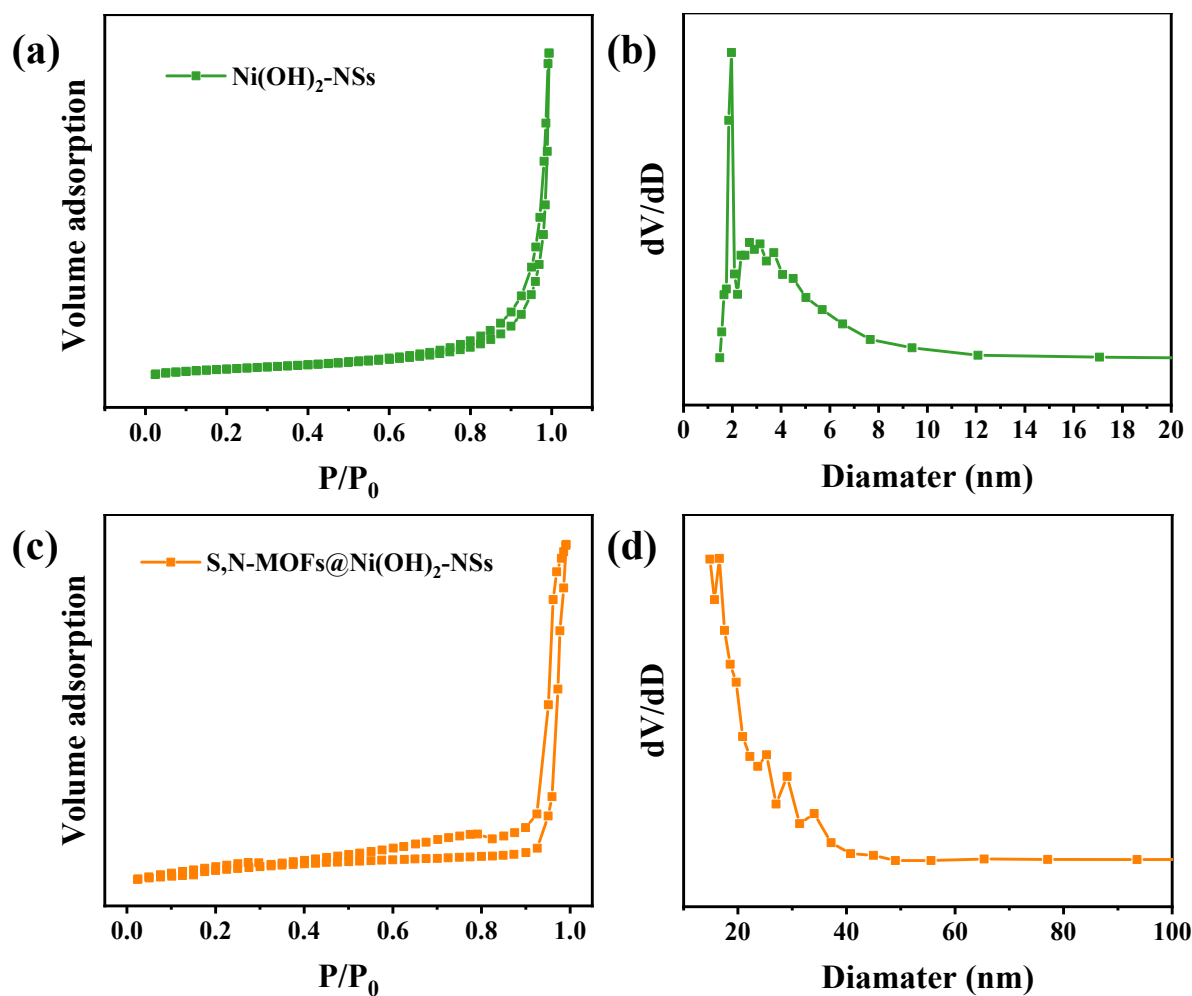
**Fig. S1** (a) FESEM images and (b) AFM image and the corresponding thickness profiles of the as-synthesised Ni(OH)<sub>2</sub>-NSs/NF.



**Fig. S2** (a) SEM image and (b) XRD pattern of the as-synthesised free-standing [Ni-(Tdc)(Bpy)]<sub>n</sub> MOFs-NSs. The free-standing [Ni-(Tdc)(Bpy)]<sub>n</sub> MOFs NSs were synthesized by adding 228 mg NiCl<sub>2</sub>·6H<sub>2</sub>O to a 20 mL aqueous solution containing 296 mg of Tdc, 280 mg of Bpy and 132 mg of NaOH.

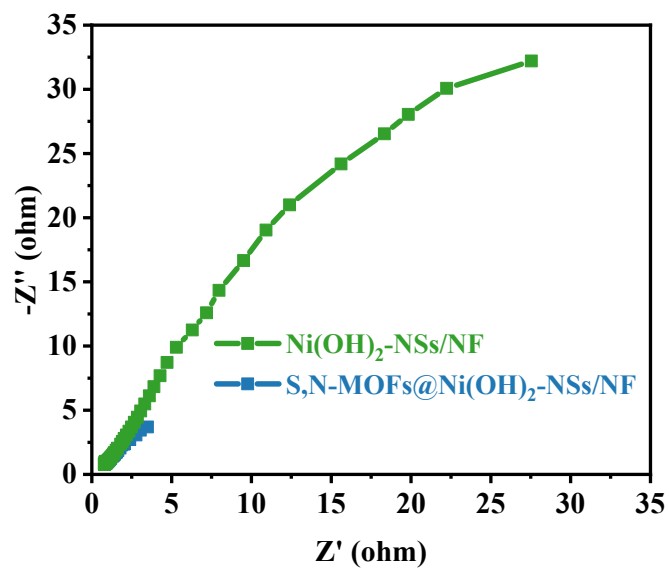


**Fig. S3** XPS spectra of S,N-MOFs@Ni(OH)<sub>2</sub>-NSs. (a) Survey spectrum; (b) C 1s spectrum; (c) N 1s spectrum and (d) S 2p spectrum.

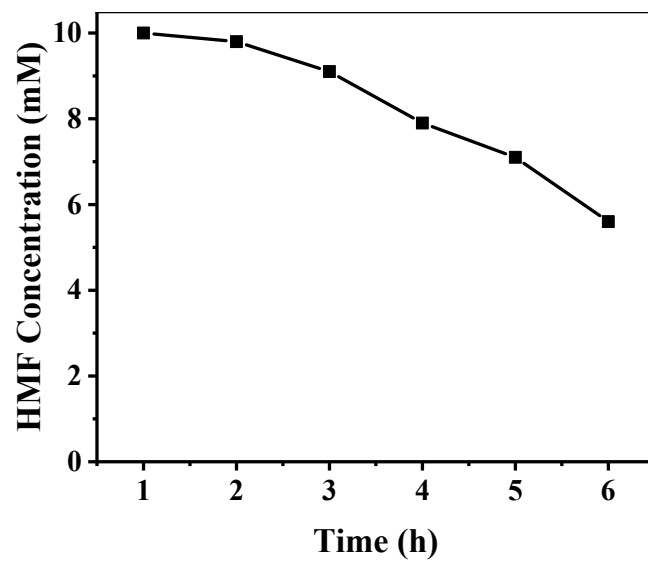


**Fig. S4**  $\text{N}_2$  adsorption-desorption isotherms and corresponding pore size distributions of (a-b)  $\text{Ni(OH)}_2\text{-NSs}$  and (c-d)  $\text{S,N-MOFs@Ni(OH)}_2\text{-NSs}$ , respectively.

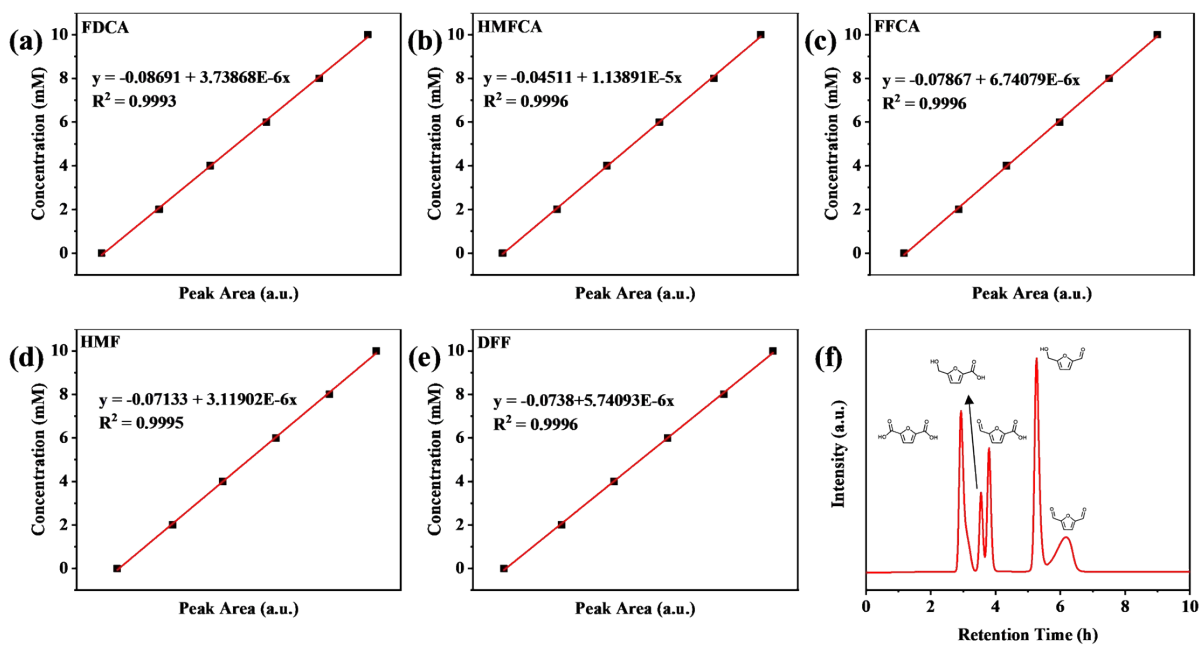




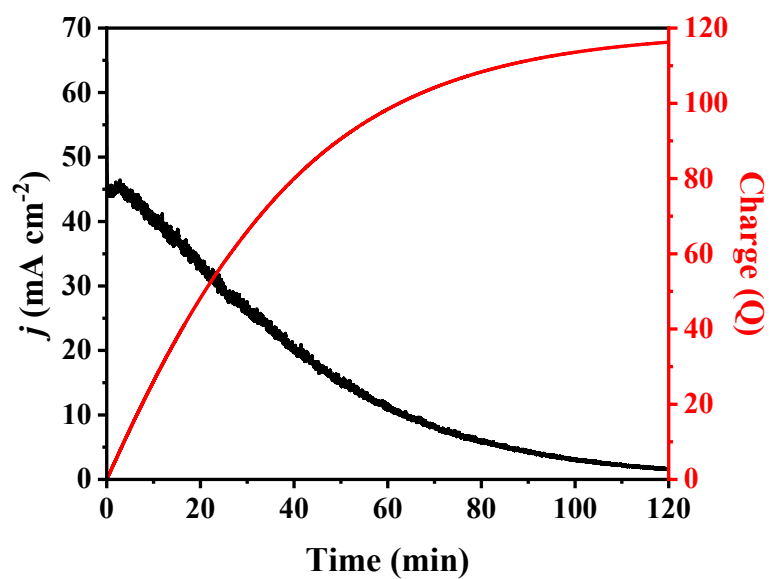
**Fig. S5** Nyquist plots of  $\text{Ni(OH)}_2\text{-NSs/NF}$  and  $\text{S,N-MOFs@Ni(OH)}_2\text{-NSs/NF}$  at 1.4 V (vs. RHE) in 1.0 M KOH containing 10 mM HMF.



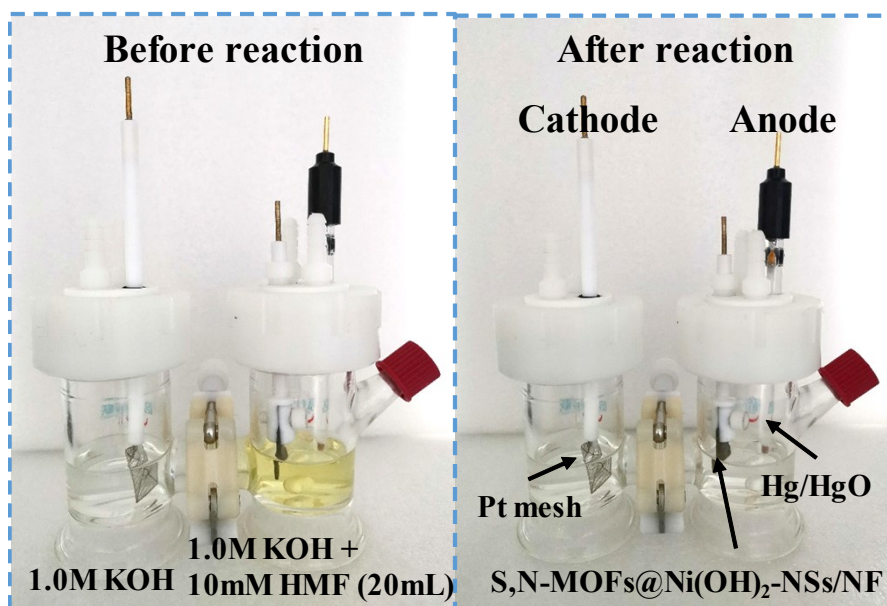
**Fig. S6** Self-degradation of HMF (10 mM) in 1.0 M KOH electrolyte in absence of electrocatalyst.



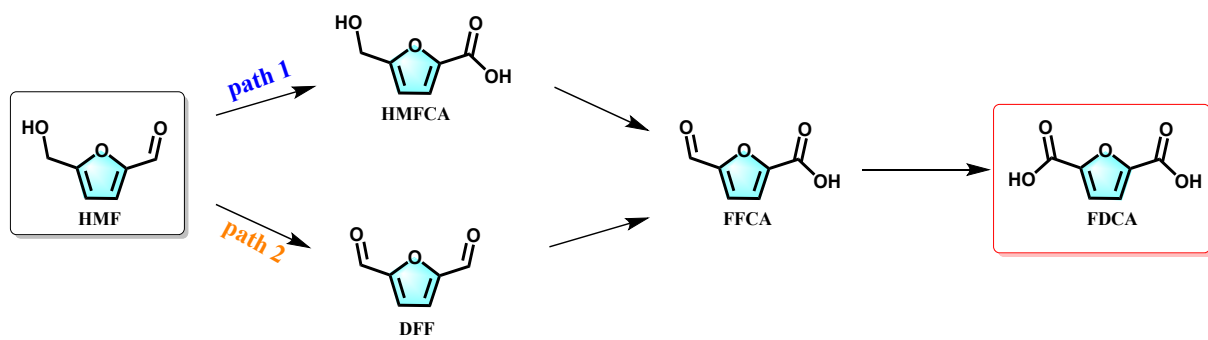
**Fig. S7** (a-e) HPLC calibration curves of standard HMF, FDCA, DFF, FFCA and HMFCA samples; (f) HPLC curves from a mixed solution containing HMF, FDCA, DFF, FFCA and HMFCA.



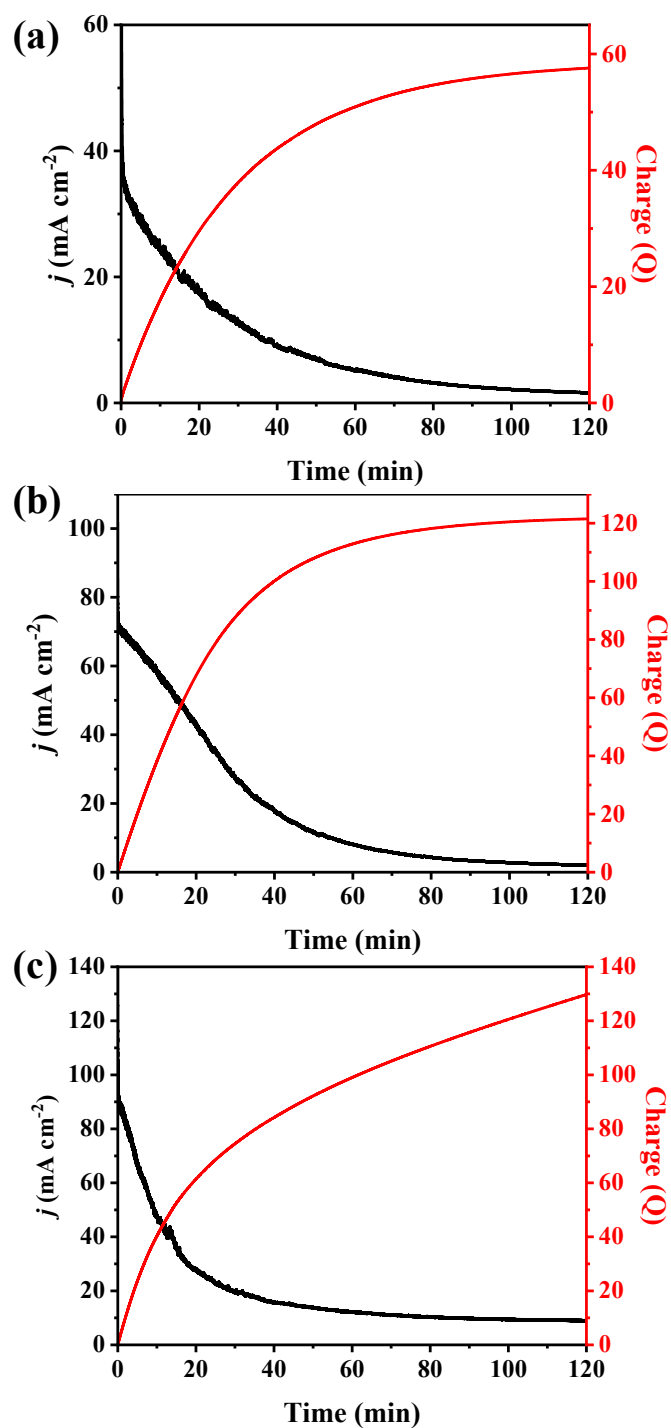
**Fig. S8** Chronoamperometric curve and the plot of the transferred charge against reaction time for S,N-MOFs@Ni(OH)<sub>2</sub>-NSs/NF catalysed HOR at 1.4 V (vs. RHE) in 1.0 M KOH containing 10 mM HMF.



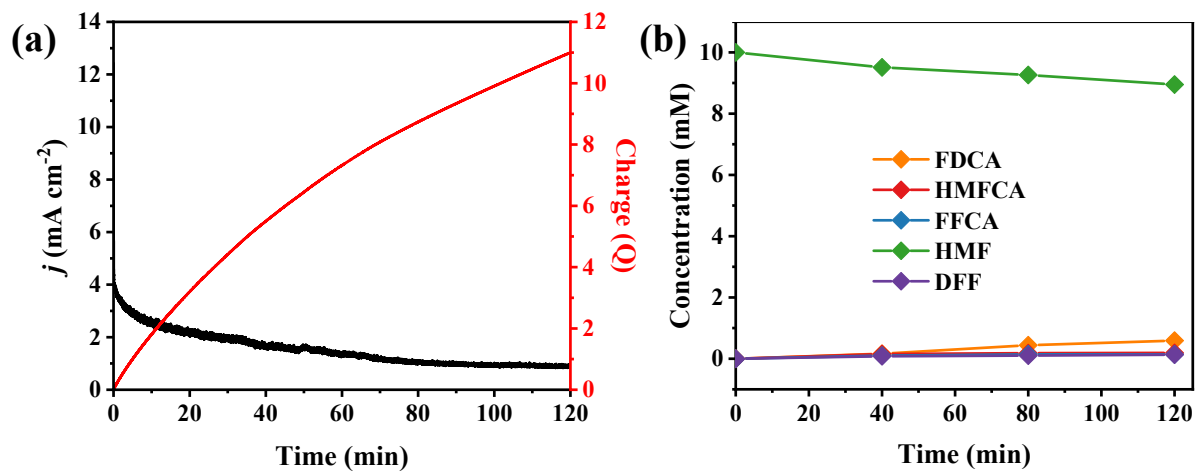
**Fig. S9** Anodic chamber solution colour change before and after 2 h HOR catalysed by S,N-MOFs@Ni(OH)<sub>2</sub>-NSs/NF at 1.4 V (vs. RHE).



**Fig. S10** Possible reaction pathways of S,N-MOFs@Ni(OH)<sub>2</sub>-NSs/NF catalysed HOR.

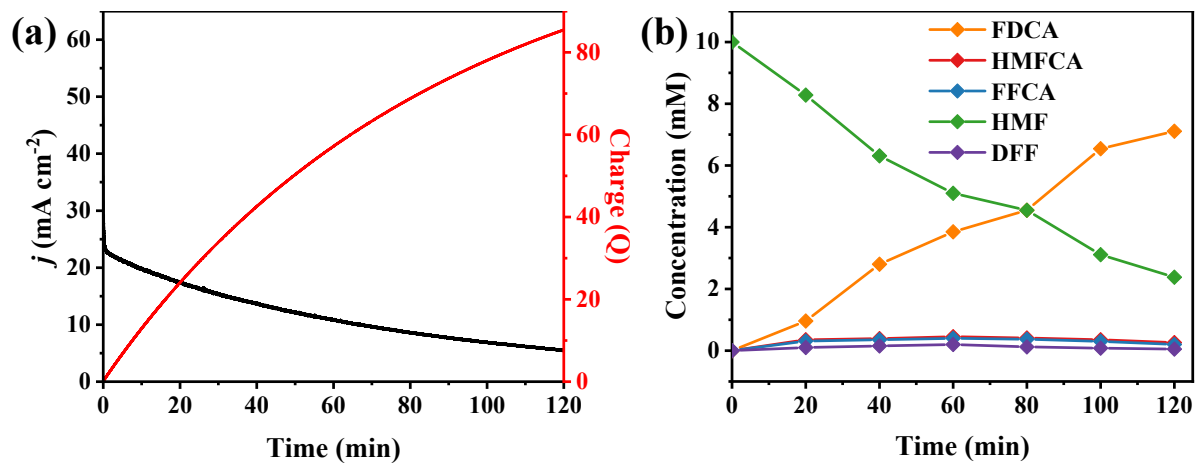


**Fig. S11** Chronoamperometric curves and the plots of the transferred charge against reaction time for S,N-MOFs@Ni(OH)<sub>2</sub>-NSs/NF catalysed HOR at 1.35, 1.45 and 1.55 V (vs. RHE), respectively.

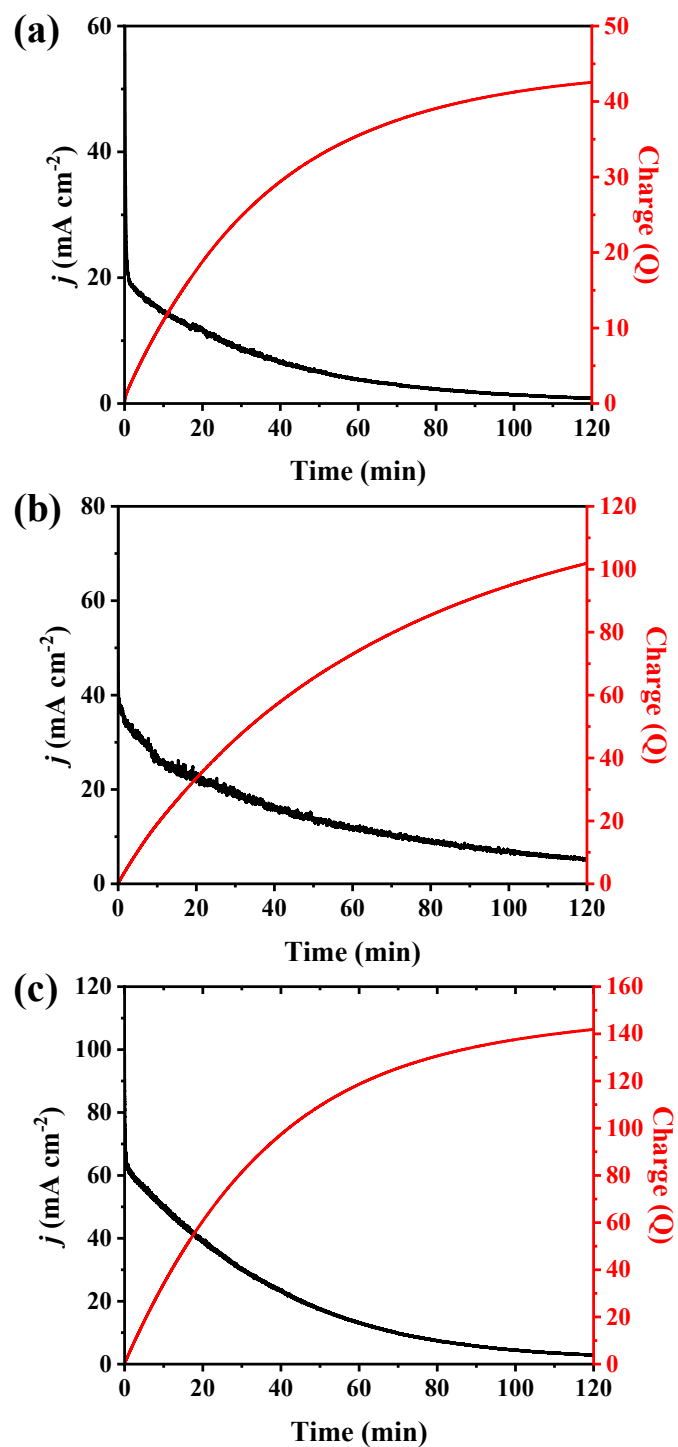


**Fig. S12** (a) Chronoamperometric curve and the plot of the transferred charge against reaction time for NF catalysed HOR at 1.4 V (vs. RHE) in 1.0 M KOH containing 10 mM HMF; (b) Corresponding HMF and oxidation products concentrations at different reaction times.

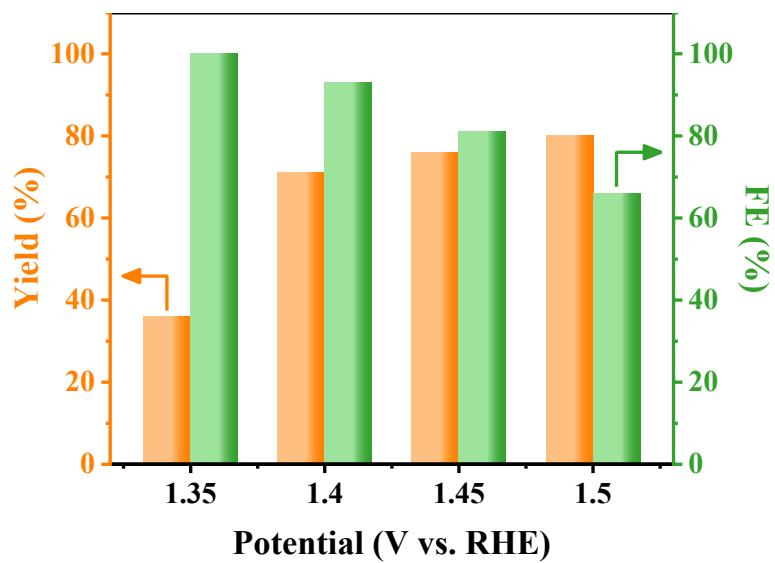




**Fig. S13** (a) Chronoamperometric curve and the plot of the transferred charge against reaction time for Ni(OH)<sub>2</sub>-NSs/NF catalysed HOR at 1.4 V (vs. RHE) in 1.0 M KOH containing 10 mM HMF; (b) Corresponding HMF and oxidation products concentrations at different reaction times.



**Fig. S14** Chronoamperometric curves and the plots of the transferred charge against reaction time for Ni(OH)<sub>2</sub>-NSs/NF catalysed HOR at 1.35, 1.45 and 1.55 V (vs. RHE), respectively.



**Fig. S15** FDCA yield and FE for Ni(OH)<sub>2</sub>-NSs/NF catalysed HOR at different potentials within 2 h in 1.0 M KOH containing 10 mM HMF.

**Table S1** Recently reported high performance electrocatalytic HOR catalysts.

Catalysts	C <sub>HMF</sub> (mM)	Potential (V vs. RHE)	Time (min)	Conv. (%)	FDCA Yield (%)	FE. (%)
Co-P/CF <sup>1</sup>	50	1.423	360	100	90	100
Ni <sub>2</sub> P NPA/NF <sup>2</sup>	10	1.423	150	100	100	98
Ni <sub>3</sub> S <sub>2</sub> /NF <sup>3</sup>	10	1.423	--	98	98	100
Ni <sub>x</sub> B <sup>4</sup>	10	1.45	30	100	98.5	100
NiFe LDH <sup>5</sup>	10	1.33	600	98.6	100	99.4
nanocrystalline Cu <sup>6</sup>	5	1.62	--	99.9	96.4	95.3
NiCo <sub>2</sub> O <sub>4</sub> <sup>7</sup>	5	1.5	53	99.6	90.8	87.5
Ni <sub>x</sub> B <sup>8</sup>	10	1.53	120	99.8	>99	99.5
Ni <sub>3</sub> N@C <sup>9</sup>	10	1.45	--	100	98	99
t-NiCo-MOF <sup>10</sup>	10	1.4	240	100	100	98
NiSe@NiO <sub>x</sub> <sup>11</sup>	10	1.423	120	98-100	93-99	
CoO-CoSe <sub>2</sub> <sup>12</sup>	10	1.43	60	99	99	97.9
CuCo <sub>2</sub> O <sub>4</sub> <sup>13</sup>	10	1.45	--	93.7	--	94
NiCoFe-LDH <sup>14</sup>	5	1.54	60	95.5	84.9	--
<b>S,N-MOFs@Ni(OH)<sub>2</sub>-NSs/NF</b>	<b>10</b>	<b>1.4</b>	<b>120</b>	<b>100</b>	<b>100</b>	<b>100</b>

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