Supplementary Information for

Boosting HMF oxidation performance *via* decorating ultrathin nickel hydroxide nanosheets with amorphous copper hydroxide islands

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EXPERIMENTAL SECTION

Synthesis of Ni_xCu_{1-x}(OH)₂ nanosheets (NSs): The Ni_xCu_{1-x}(OH)₂ NSs was synthesized using NiCl₂·6H₂O and CuCl₂ as the cation source. As an example to illustrate the process, 0.45 mM NiCl₂·6H₂O and 0.05 mM CuCl₂·2H₂O were dissolved into 20 ml deionized water. After stirring for 5 minutes, 80 μ l NH₃·H₂O was added into the mixture and stirred for another 5 minutes. Finally, the reaction flask was immersed in the oil bath and maintained at 60 °C for 24 h. After the flask was cooled down room temperature, the product was collected by centrifugation and washed three times with water and one time with ethanol and vacuum dried at 60 °C for 12 h. The Ni_xCu_{1-x}(OH)₂ samples with different Ni/Cu ratio were prepared by adjusting the ratio of NiCl₂ and CuCl₂.

Structural Characterization

The crystal structure and morphology were characterized by X-ray diffraction (XRD, Rigaku Miniflex-600) equipped with a Cu K α radiation ((provide the instrument) λ =0.15406 nm, 40 kV). TEM images were captured using a Titan G2 60-300 electron microscope. HAADF-STEM images and elemental mapping results were recorded on a JEOL ARM-200F microscope with spherical aberration corrector operated at 200 kV. The valence states of Ni and Cu were identified by X-ray photoelectron spectroscopy (XPS) using an Escalab 250Xi equipped with an A1 Ka (1486.6 eV) excitation source.. The thickness of the samples was evaluated by atomic force microscope (AFM, XE-100, Park Systems). To conduct the thickness test, the sample was dispersed on a Si substrate and the AFM test was carried out under a scan rate of 0.5 Hz at 25 °C in the air.

Electrode preparation and electrocatalytic characterization

To prepare the catalyst ink, 4 mg of catalysts was dispersed into 1 ml of ethanol and sonicated to form a uniform dispersion. In another vial, 4 mg of carbon black was uniformly dispersed in 0.98 ml of ethanol. The catalyst-contained solution was then added into the carbon black solution to form a mixed solution. Finally, 0.02 ml of Nafion (5 wt %) was added to the mixed solution to adjust the solution's viscosity. To prepare the electrode for electrocatalytic characterization, the catalyst ink was air brushed to a carbon paper (1 cm×2 cm) with the mass loading controlled at 1 mg cm⁻². The electrocatalytic performance was conducted using a three-

electrode configuration, where carbon paper loaded with catalyst was applied as the working electrode, a platinum wire was used as the counter electrode, and an Ag/AgCl (saturated KCl) electrode work as the reference electrode. The conversion from the potential *vs* Ag/AgCl to the potential *vs* RHE is expressed as: (E *vs* RHE) = E (*vs* Ag/AgCl) +0.197+0.0591×pH. The electrochemical tests were performed in an H-type divided cell with Nafion 117 membrane as the separator. All the electrochemical tests were carried out in 1.0 M KOH solution unless otherwise noted. Electrochemical active surface area (ECSA) was measured by cyclic voltammetry (CV) in a potential window of 0.97-1.08 V (*vs* RHE) at different scan rate from 10 to 100 mV s⁻¹.

HPLC analysis

HPLC analysis was carried out using a Shimadzu Prominence LC-2030C system with an ultraviolet visible detector set at 265 nm. A mixture of methanol and 5 mM ammonium formate with volumetric ratio of 3:7 was used as the mobile phase, and the flow rate was controlled at 0.6 mL min⁻¹. In each measurement, 10 ul of electrolyte after electrolysis was first diluted to 2 ml with ultrapure water.

The FDCA yield and faradaic efficiency were calculated by the following equations:

$$FDCA \text{ yield} = \frac{n(FDCA \text{ formed})}{n(HMF \text{ initial})}$$
(1)

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(1)
Faradaic efficiency = $\frac{6 \cdot F \cdot N \cdot n(FDCA)}{Q} = \frac{6 \cdot F \cdot N(FDCA)}{J \cdot S \cdot t}$ (2)
Faradaic efficiency = $\frac{6Fn(FDCA)}{Q} = \frac{6Fn(FDCA)}{JSt}$

Where F is the Faraday-constant (96485 C mol⁻¹), n is the mol number of reactants calculated from the concentration measured by HPLC.

Theoretically, the oxidization of one HMF molecular to FDCA needs six electrons, therefore, the coulomb amount required for complete conversion of HMF to FDCA was calculated by the following equation:

$$C = \frac{6n(HMF)N}{6.25 \times 10^{18}}$$



Fig. S1 Transmission electron microscope (TEM) images of the as-synthesized Ni_{1-x}Cu_x(OH)₂ NSs. (a) Ni(OH)₂ NSs; (b) Ni_{0.95}Cu_{0.05}(OH)₂ NSs; (c) Ni_{0.8}Cu_{0.2}(OH)₂ NSs.



Fig. S2 AFM image and height profiles of Ni(OH)₂ (a and b), $Ni_{0.95}Cu_{0.05}(OH)_2$ (c and d), and $Ni_{0.8}Cu_{0.2}(OH)_2$ (e and f).



Fig. S3 XPS survey spectra of Ni(OH)₂ (a), Ni_{0.95}Cu_{0.05}(OH)₂ (b), Ni_{0.9}Cu_{0.1}(OH)₂ (c), Ni_{0.8}Cu_{0.2}(OH)₂ (d).



Fig. S4 High resolution XPS spectra. (a) Ni 2p and (b) Cu 2p (b) for $Ni_{0.95}Cu_{0.05}(OH)_2$ NSs, Ni 2p (c) and Cu 2p (d) for $Ni_{0.8}Cu_{0.2}(OH)_2$ NSs.



Fig. S5 LSV curves of the $Ni_{0.9}Cu_{0.1}(OH)_2$ nanosheet at a scan rate of 10 mV s⁻¹ in 1 M KOH with varied HMF concentration.



Fig. S6 LSV curves of the $Ni_{1-x}Cu_x(OH)_2$ nanosheets at a scan rate of 10 mV s⁻¹ in 1 M KOH without HMF.



Fig. S7 The CV curves of $Ni(OH)_2$ (a), $Ni_{0.95}Cu_{0.05}(OH)_2$ (b), $Ni_{0.9}Cu_{0.1}(OH)_2$ (c) and $Ni_{0.8}Cu_{0.2}(OH)_2$ (d) at different scan rates from 10 to 100 mV s⁻¹.



Fig. S8 Change of current density plotted against the scan rate at 1.02 V (*vs* RHE) for Ni(OH)₂ (a), Ni_{0.95}Cu_{0.05}(OH)₂ (b), Ni_{0.9}Cu_{0.1}(OH)₂ (c), Ni_{0.8}Cu_{0.2}(OH)₂ (d).



Fig. S9 Tafel slopes of Ni(OH)₂ (a), Ni_{0.95}Cu_{0.05}(OH)₂ (b), Ni_{0.9}Cu_{0.1}(OH)₂ (c), Ni_{0.8}Cu_{0.2}(OH)₂ (d).



Fig. S10 HPLC test result of pure HMF (a), FDCA (c) and standard curve line of HMF(b), FDCA(d).



Fig. S11 HPLC measurements of pure HMFCA(a), FFCA(b), DFF(c), various electrolysis charge of HPLC chromatograms (d).



Fig. S12 Color of the electrolyte after HMF constant potential electrolysis



Fig. S13 Stability of the $Ni_{0.9}Cu_{0.1}(OH)_2$ catalyst during the HMF oxidation. The arrow indicates the point where the electrolyte containing 5 mM HMF was refreshed.



Fig. S14 Conversion and yield of HMF oxidation by $Ni_{0.95}Cu_{0.05}(OH)_2$ with respected to passed charges at 1.45 V vs RHE.



Fig. S15 Conversion and yield of HMF oxidation by $Ni_{0.8}Cu_{0.2}(OH)_2$ with respected to passed charges at 1.45 V vs RHE.



Fig. S16 Summary of the FDCA selectivity of $Ni_{(1-x)}Cux(OH)_2$ nanosheet with passed charges of 116 C at 1.45 V vs RHE.

Samples	Ni (%)	Cu (%)	O (%)
Ni(OH) ₂	28.18	/	53.36
Ni _{0.95} Cu _{0.05} (OH) ₂	27.33	1.67	55.49
Ni _{0.9} Cu _{0.1} (OH) ₂	14.36	1.67	48.9
Ni _{0.8} Cu _{0.2} (OH) ₂	17.17	4.39	45.16

Table S1: Atomic ratios of elements in Ni_{1-x}Cu_x(OH)₂ nanosheets determined by XPS analysis

Table S2: Atomic ratios of elements in Ni_{1-x}Cu_x(OH)₂ nanosheets determined by ICP-MS

Samples	Ni (mg/L)	Cu (mg/L)	Ni:Cu (mole ratio)	
Ni _{0.95} Cu _{0.05} (OH) ₂	112.4	6.703	18.15	
Ni _{0.9} Cu _{0.1} (OH) ₂	69.44	9.003	8.35	
Ni _{0.8} Cu _{0.2} (OH) ₂	51.04	10.71	4.72	

Table S3: HMF oxidation performance of $Ni_{0.9}Cu_{0.1}(OH)_2$ nanosheet in this work and several representative results with high performance from recent published works.

Cat.	Electrolyte	C _{HMF} (mM)	E/V (vs RHE)	FE _{FDCA} (%)	Ref.
СоООН	0.1M KOH	5	1.56	35.1	1
NiOOH	1 M NaOH	5	1.67	84	2
Ni/NiOOH (foam)	0.1M Na ₂ SO ₄	0.65	1.66	80	3

NiCoFe-LDHs	1 M NaOH	10	1.52	~ 90	4
MnO _x	$1 \text{ M H}_2 \text{SO}_4$	20	2.0	53.8	5
nanocrystalline Cu	0.1 M KOH	5	1.62	96.4	6
NiFe LDH Nanosheet	1 M KOH	10	1.23	99.4	7
CuCo ₂ O ₄	1 М КОН	50	1.45	94	8
Ni _x B-modified NF	1 M KOH	10	1.45	100	9
Ni3N@C	1 М КОН	10	1.45	98	10
Ni _{0.9} Cu _{0.1} (OH) ₂	1 М КОН	5	1.45	91.2	This work

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