Supporting Information

Instruments

XRD was performed with Shimadzu XRD-6000 X-ray diffraction instrument. Scanning electron microscopy (SEM) images were collected on a SU8010 scanning electron microscope operating. Energy dispersive X-ray spectroscopy (EDS) was performed on the catalysts as-grown on Ni foam substrates with the SEM described above equipped with a Thermo-Fisher EDS detector. X-ray photoelectron spectroscopy (XPS) was conducted on a K-alpha XPS spectrometer (KRATOS AXIS Ultra DLD) with a microfocused monochromated Al Kα X-ray source.

Fabrication of the NiMn-LDH electrocatalysts

Ni foam (NF) was treated by hydrochloric acid, ethanol and water to remove surface impurities.

In a typical reaction for Ni₁Mn₃-LDH preparation, 50 mL of aqueous solution containing Ni(NO₃)₂·6H₂O (0.5 mmol), MnCl₂·4H₂O (1.5 mmol) and hexamethylenetetramine (2.5 mmol) was transferred to a 100 mL Teflon-lined stainless steel autoclave. Then, a piece of the pre-treated NF was put into the autoclave, which was maintained at 90 °C for 6 h. When the reaction was completed, the NF/Ni₁Mn₃-LDH electrode was obtained by washing with deionized water and dried at 60 °C for 12 h. By varying the molar ratio of Ni(NO₃)₂·6H₂O to MnCl₂·4H₂O (the sum of molar quantity of Ni²⁺ and Mn²⁺ were kept at 2 mmol), Ni₁Mn₅-LDH, Ni₁Mn₁-LDH, Ni₀Mn, and NiMn₀ were prepared.

Electrochemistry

Linear sweep voltammetry and Cyclic Voltammetry curves were recorded by CH Instrument 660E electrochemical potentiostat with NF/NiMn-LDH electrode as working electrode, Ag|AgCl (KCl_{sat.}) as reference electrode, Pt wire as counter electrode. The electrolyte was KOH solution (1 M) with or without 10 mM HMF. The potentials versus RHE were converted by the reference of $E_{RHE} = E_{Ag|AgCl} + 0.197 + 0.0592 \times pH$.

The electrochemical HMF oxidation were carried out using a electrochemical workstation (CH instrument) with an H-type electrochemical cell at room temperature. 25 mL of KOH solution with 10 mM HMF was used as the electrolyte. The products were analyzed by HPLC (Waters 486) equiped with a reversed-phase ZORBAX Eclipse XDB-C18 column (4.6 × 250 mm).

The conversion of HMF and yields of its oxidation products can be calculated with the equations:

$$Con. of \ HMF(\%) = \frac{c_0 HMF - c_t HMF}{c_0 HMF} \times 100\%$$

$$Yield \ of \ FDCA(\%) = \frac{c_t A}{c_0 HMF} \times 100\%$$

$$Select \ of \ FDCA(\%) = \frac{c_t A}{c_0 HMF - c_t HMF} \times 100\%$$



Figure S1. EDS of Ni1Mn5-LDH.



Figure S2. XPS survey spectrum spectra of the Ni1Mn5-LDH



Figure S3. Nyquist plots of NF/NiMn and NF/Ni1Mn5-LDH electrodes in 1.0 m KOH with 10 mm HMF.



Figure S4. Plot of HMF conversion and products yielded by Ni₁Mn₅-LDH against reaction time in 1.0 M KOH solution containing 10 mM HMF at 1.35 V (vs RHE)



Figure S5. SEM images of NF/Ni1Mn5-LDH after five repetition reactions.



Figure S6. XRD patterns of Ni_1Mn_5 -LDH before and after five repetition reactions.



Figure S7. HPLC chromatograms recorded during electrochemical HMF oxidation catalyzed by Ni₁Mn₅-LDH at 1.4 V (vs RHE) in 1.0 M KOH with 10 mM HMF.

Catalyst	C _{HMF}	Reaction Time	Potential	Conv.	FDCA yield	FE
	(mM)	(min)	(V vs RHE)	(%)	(%)	(%)
Ni(OH)2 ^[1]	5	240	1.67	-	71	90
$NiB_x@NF^{[2]}$	10	100	1.64	99.8	>99	99
$Ni_2P/NF^{[3]}$	10	<150	1.423	100	98-100	98
Ni ₂ S ₃ /NF ^[4]	10	-	1.423	98	98	100
Ni ₃ N@C ^[5]	10	-	1.45	100	98	99
NiFe-LDH ^[6]	10	90	1.33	98	98	98.6
NiCoFe-LDHs ^[7]	10	240	1.52	10	-	-
Ni1Mn5-LDH	10	60	1.40	97	95	97
(this work)						

Table S1. Comparisons of catalytic performances for electrochemical oxidation of HMF at room temperature.

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