Supplementary Materials

Improved Methanol-to-Formate Electrocatalytic Reaction by Engineering of Nickel Hydroxide and Iron Oxyhydroxide Heterostructures

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SEM Characterization

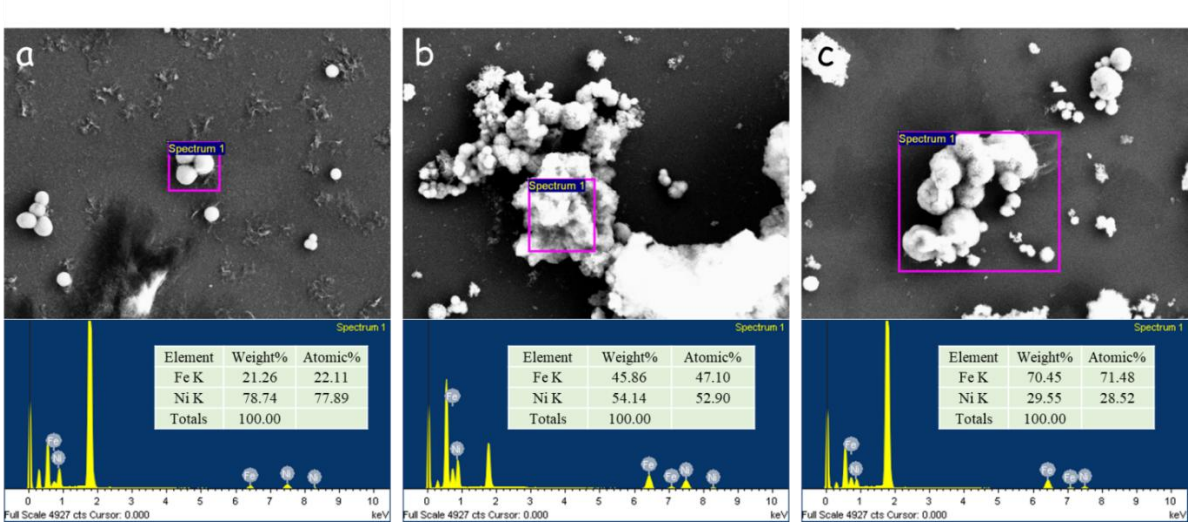

Figure S1. SEM-EDS results for the samples obtained from Ni/Fe ratio with (**a**) 3:1, (**b**) 1:1, and (**c**) 1:3 in the precursor.

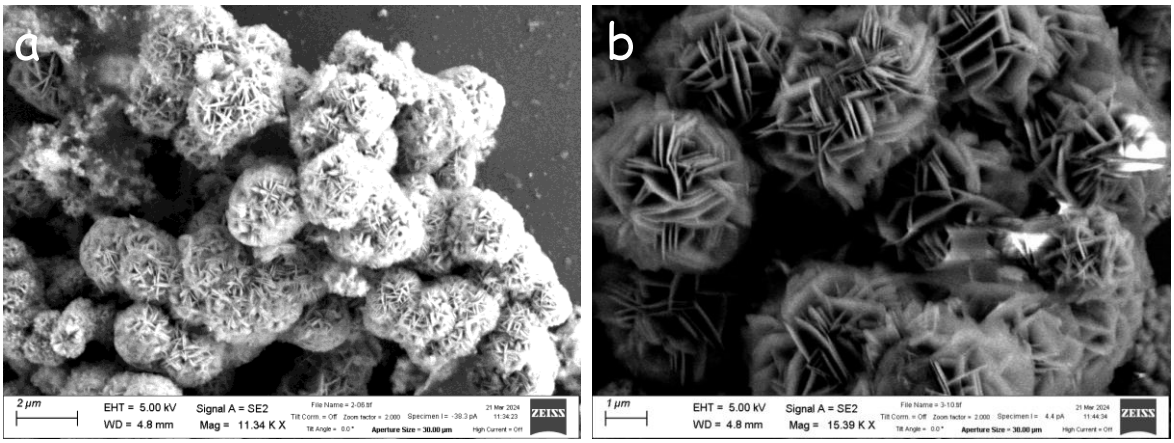

Figure S2. Representative SEM images for (**a**) $Ni_{0.75}Fe_{0.25}$ and (**b**) $Ni_{0.25}Fe_{0.75}$ based NFHs.

Standard IC Curve

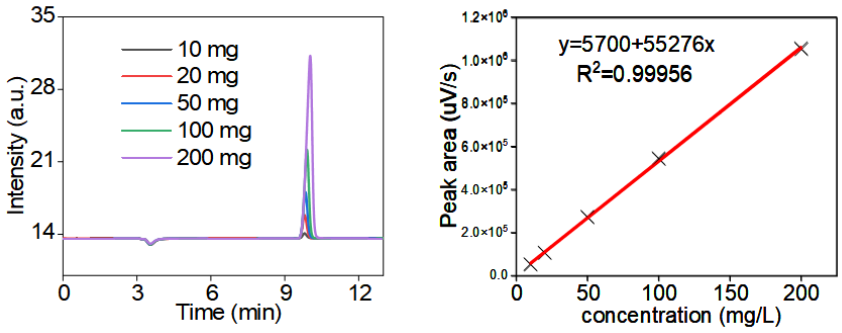

Figure S3. Standard IC profile for formate concentration and the corresponding fiting formate peak area and concentration.

Electrochemical Characterization

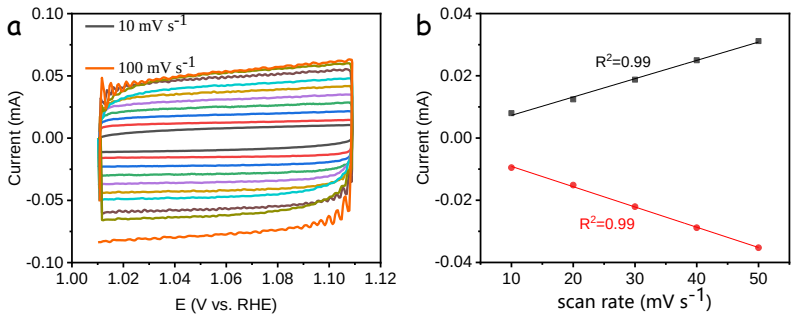

Figure S4. Determination of ECSA curves in 1 M KOH for the $Ni_{0.75}Fe_{0.25}$-based electrode.

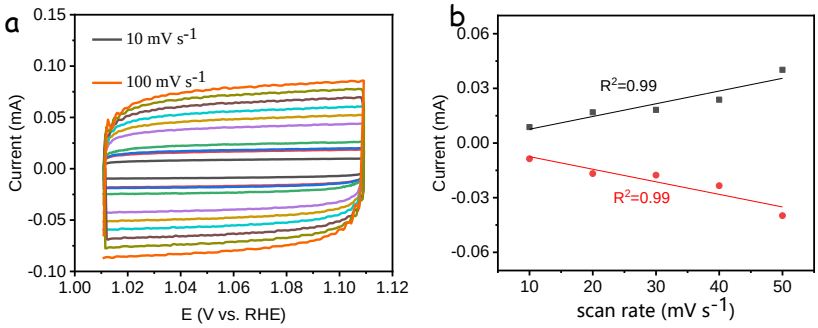

Figure S5. Determination of ECSA curves in 1 M KOH for the $Ni_{0.25}Fe_{0.75}$-based electrode.

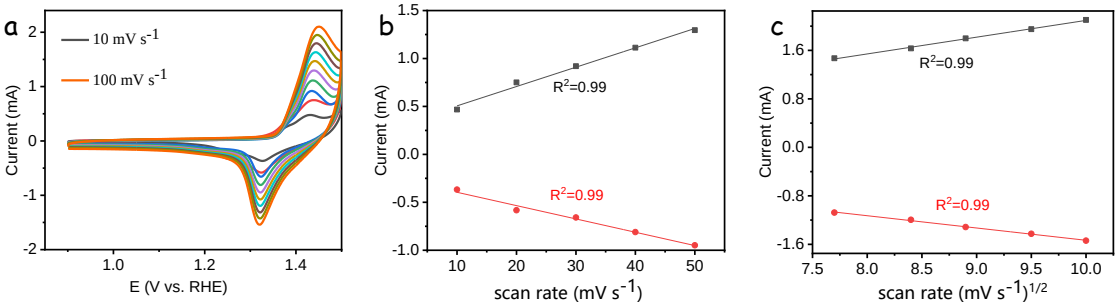

Figure S6. Intrinsic property for the $Ni_{0.75}Fe_{0.25}$-based electrode in 1 M KOH (**a**) CVs, (**b**) surface coverage of redox species (Γ*), and (**c**) diffusion coefficient (D).

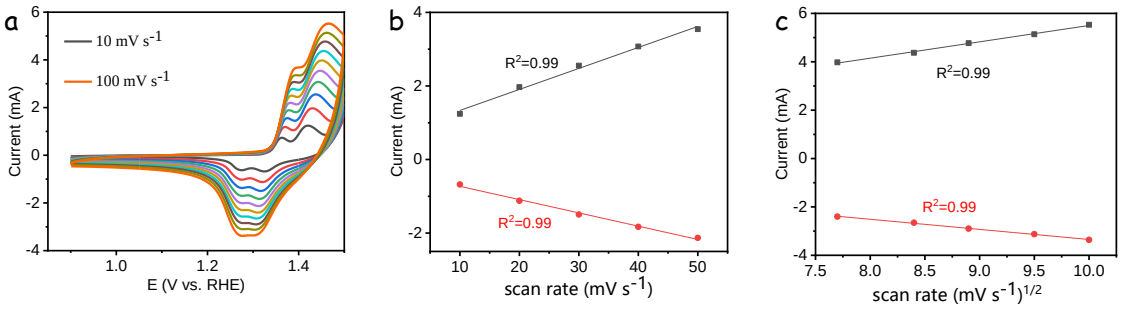

Figure S7. Intrinsic property for the $Ni_{0.25}Fe_{0.75}$-based electrode in 1 M KOH (**a**) CVs, (**b**) surface coverage of redox species (Γ*), and (**c**) diffusion coefficient (D).

Table S1. Comparison of MOR performance between this work and previously published noble-metal-free electrocatalysts.

electrocatalyst	morphology	electrolyte	MOR performance				reference
			current density (mA cm^{-2}@V. RHE)	decay	product	FE	
$Co(OH)_2$@HOS/CP	3D nanosheet	1 M KOH + 3 M methanol	~80@1.5 V	~5%@20h CP	formate	100%	[1]
Ni–Fe Oxide	porous	1 M KOH + 1 M methanol	~15@1.6 V	~5%@12h CP	formate	n.a.	[2]
$Ni_{0.75}Cu_{0.25}$ alloys	3D nanostructures	1 M NaOH + 0.5 M methanol	~45@1.6 V	~22%@0.33h	n.a.	n.a.	[3]
NiS	nanoparticles	1 M KOH + 1 M methanol	~145@1.6 V	~43%@2.78h	formate	98%	[4]
$Ni_xFe_{1-x}(OH)_2$	coreshell particle	1 M KOH + 1 M methanol	~10@1.55 V	n.a.	n.a.	n.a.	[5]
NiCo/Nickel foam	porous	1 M KOH + 2 M methanol	~82@1.5 V	~29%@12.5h	n.a.	n.a.	[6]
Ni_3S_2/CNTs	nanocrystals	1 M KOH + 1 M methanol	100@1.36 V	~1%@20h	formate	95%	[7]
$Ni_{0.75}Fe_{0.25}Se_2$	nanoparticles	1 M KOH + 1 M methanol	53.3@1.5 V	27.4%@13.9h	formate	99%	[8]
Ni/MOF	nanosheet	1 M KOH + 0.5 M methanol	100@1.44 V	18.7%@20h	formate	n.a.	[9]
$NiCo_2S_4$/CC	nanosheet	1 M KOH + 1 M methanol	~20@1.61 V	~10%@20h	formate	100%	[10]
NiO/NF	porous	1 M KOH + 2 M methanol	135@1.5 V	10%@2.78h	Formate CO_3^{2-} HCHO	n.a.	[11]
Mn-NiFe LDH/NF	nanosheet	1 M KOH + 0.5 M methanol	~300@1.5 V	~15%@120h	formate	99%	[12]
$Ni(OH)_2$/FeOOH	3D flower	1 M KOH + 1 M methanol	~95@1.6 V	~45%@12h	formate	98.5%	this work

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