

Supporting Information

Core-shell Si doped NiFe LDH/C electrocatalyst for methanol oxidation reaction

Yuanhao Li[#], Siwei Wang[#], Haonan Li, Qijing Bu^{*}, Huijuan Li^{*}, and Qingyun Liu^{*}

College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, China

[#]These authors contributed equally to this work

Electrochemical test methods

1 Preparation of working electrode

Prior to use, the glassy carbon electrode surface was sequentially polished with alumina polishing powders, ultrasonically treated in a mixed solution of deionized water and ethanol for 10 minutes. The working electrode was prepared as follows: 4 mg of catalyst, 480 μL of deionized water and 500 μL of anhydrous ethanol, and 20 μL of Nafion solution (5 wt%) were mixed. The mixture was then subjected to ultrasonic dispersion for 30 minutes to ensure homogeneity. Subsequently, 3 μL of the uniformly dispersed catalyst ink was precisely deposited onto the pre-polished glassy carbon electrode (GCE). Finally, the coated electrode was air-dried at room temperature to form the working electrode, which was directly employed for the subsequent electrochemical testing.

2 Electrochemical testing

All electrochemical tests were conducted using a CHI760E electrochemical workstation with a three-electrode system. The L-shaped glassy carbon electrode (GCE), Hg/HgO and a platinum sheet ($10 \times 10 \times 0.1$ mm) were acted as the working electrode, the reference electrode and the counter electrode. The N_2 saturated 1 M KOH + 1 M CH_3OH was used as electrolyte. All cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were carried out at the potential in the range from 0 V vs. SCE to 0.6 V vs. SCE with the scan rate of 50 mV s^{-1} . The tafel plots were derived from LSV data using the classical Tafel equation: $\eta = b \log|j| + a$, in which η represents the overpotential, j denotes the current density, b is the Tafel slope, and a is the

intercept. The electrochemical impedance spectroscopy (EIS) was performed at a constant potential of 0.55 V vs. SCE with the frequency range from 1 Hz to 100 kHz. The stability was characterized by the chronoamperometry test which is carried out at 0.55 V vs. SCE for 10 h. The electrochemical surface area (ECSA) is determined by CV curves at different scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mV s⁻¹. The potential range is typically a 0.1 V window centered at open-circuit potential (OCP) of the system. The double-layer charging current (i_c) is equal to the product of the scan rate (v) and the electrochemical double-layer capacitance according to the following equation: $i_c = v \times C_{dl}$. Therefore, the slope of the straight line derived from the i_c as a function of v , is equal to C_{dl} . The ECSA values are calculated according to the corresponding C_{dl} depending on the formula: $ECSA = C_{dl}/C_s$.

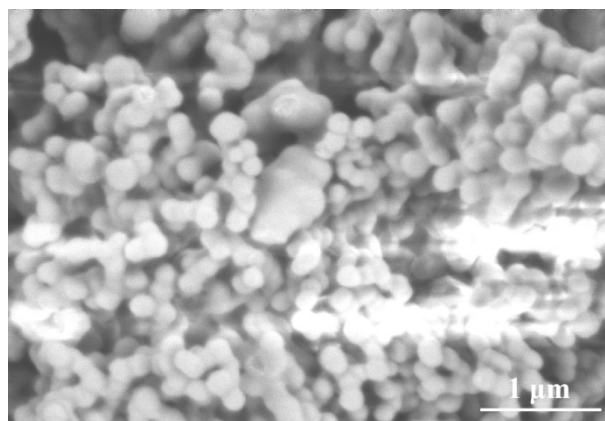


Fig. S1 SEM image of carbon square.

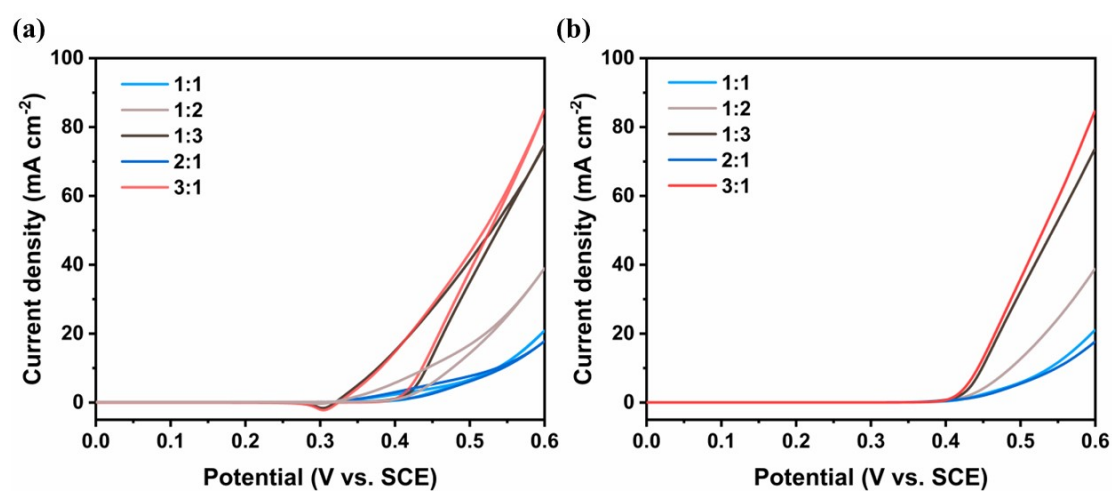


Fig. S2 a) CV curves for NiFe-LDH/C. b) LSV curves for NiFe-LDH/C.

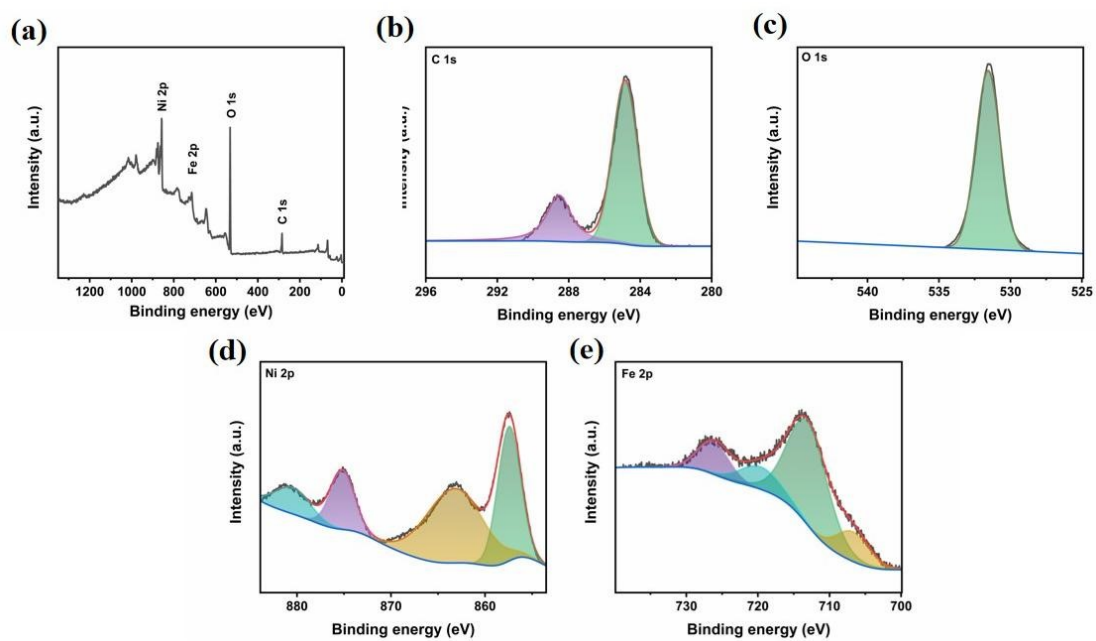


Fig. S3 XPS spectra of NiFe-LDH/C: a) full spectrum, b) C 1s, c) O 1s, d) Ni 2p, e) Fe 2p high-

resolution spectra.

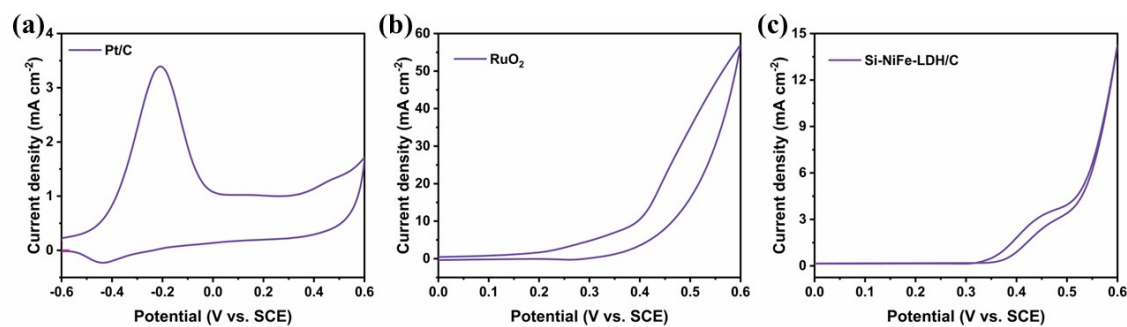


Fig. S4 CV curves for commercial a) Pt/C and b) RuO₂ catalysts, c) CV curves of Si-NiFe-LDH/C synthesized by conventional methods.

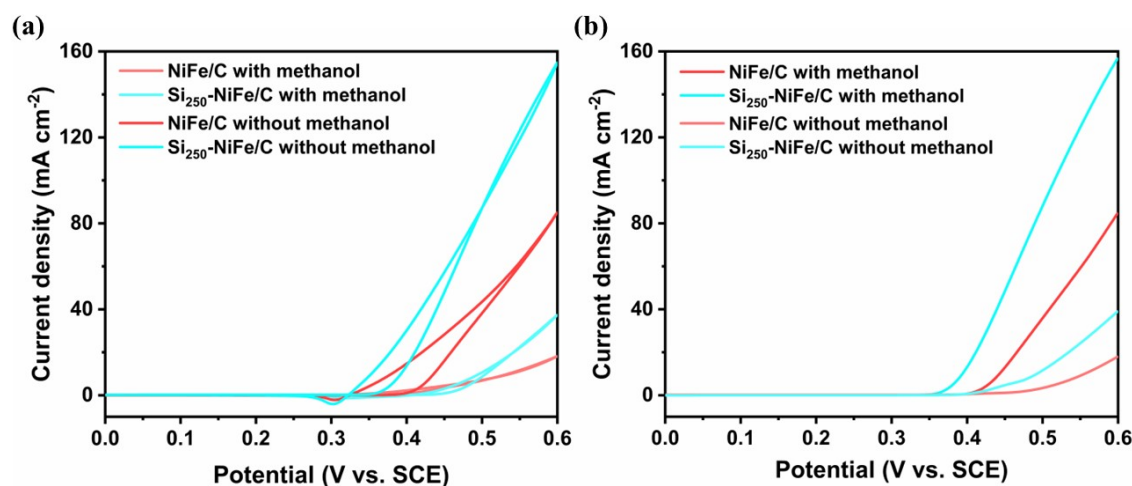


Fig. S5 a) The CV curves and b) the LSV curves of NiFe-LDH/C and Si₂₅₀-NiFe-LDH/C in 1 M KOH and 1 M KOH + 1M CH₃OH.

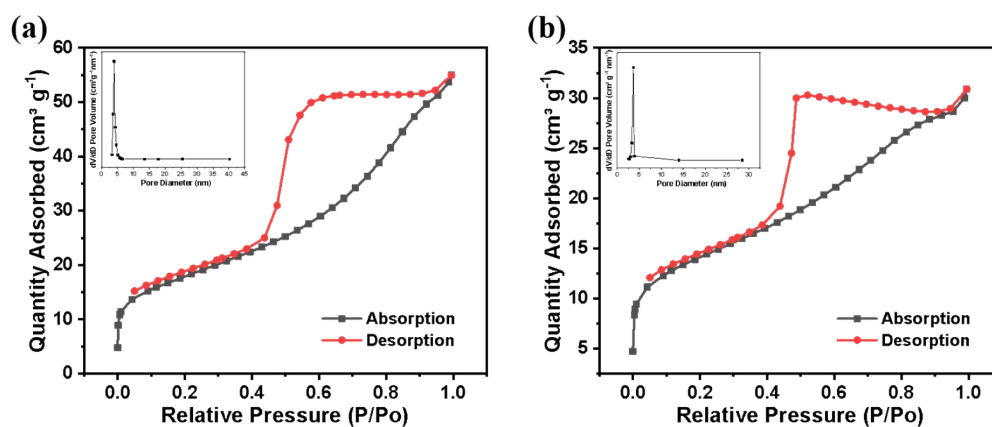


Fig. S6 The N₂ adsorption–desorption isotherm curves and pore size distribution curves of a) NiFe-LDH/C and b) Si₂₅₀-NiFe-LDH/C.

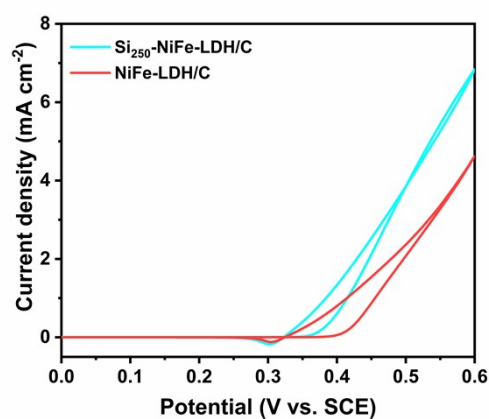


Fig. S7 The intrinsic MOR performance of Si₂₅₀-NiFe-LDH/C and NiFe-LDH/C.

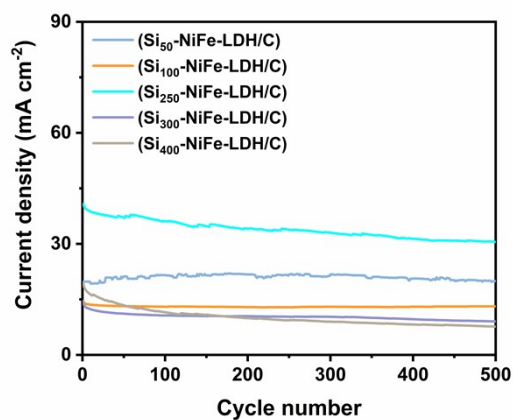


Fig. S8 The cycling performance of the Si_x-NiFe-LDH/C (Si₅₀-NiFe-LDH/C, Si₁₀₀-NiFe-LDH/C, Si₂₅₀-NiFe-LDH/C, Si₃₀₀-NiFe-LDH/C, and Si₄₀₀-NiFe-LDH/C) in 1 M KOH + 1 M CH₃OH for 500 cycles.

Table S1 Atomic ratios of Si₂₅₀-NiFe-LDH/C characterized by SEM-EDS.

Element	Weight %	Atom %
C	6.10	12.73
O	40.65	63.64
Si	1.37	1.22
Fe	12.44	5.58
Ni	39.44	16.83
Total	100	100

Table S2 Comparison of MOR performance of different catalysts.

Catalyst	Performance	Potential	Electrolyte	Scan rate (mV s ⁻¹)	Reference
Si ₂₅₀ -NiFe-LDH/C	154.77 mA	0.6 V vs.	1 M KOH+1 M	50	This work
	cm ⁻²	SCE	CH ₃ OH		
Si-NiFe-LDH/C	14.22 mA	0.6 V vs.	1 M KOH+1 M	50	This work
	cm ⁻²	SCE	CH ₃ OH		
Mn-NiFe-LDH/NF	148.9 mA	1.6 V vs.	1 M KOH+0.5	10	[1]
	cm ⁻²	RHE	M CH ₃ OH		
Pt/NiFe-LDH	18 mA cm ⁻²	0.4 E vs.	0.5 M KOH+1	50	[2]
		RHE	M CH ₃ OH		
NiFe-	15.1 mA cm ⁻²	1.6 V vs.	1 M KOH+0.5	100	[3]

LDH/300MoCN		RHE	M CH ₃ OH		
Ni-MOF/NiFe-LDH	32.66 mA cm ⁻²	0.9 V vs. Hg/HgO	1 M KOH+1 M CH ₃ OH	50	[4]
NiFe-LDH/CX/NF	400 mA cm ⁻²	0.7 V vs. Ag/AgCl	1 M KOH+0.5 M CH ₃ OH	10	[5]
Cu(OH) ₂ @FeNi(OH) _x	60 mA cm ⁻²	1.34 V vs. RHE	1 M KOH+3 M CH ₃ OH	unidentified	[6]
Pt/Ni-Fe-LDH/RGO	949.3 mA mg ⁻¹	unidentified	1 M KOH+1 M CH ₃ OH	100	[7]

Reference

- [1].Y. Ma, L. Li, Y. Zhang, et al. J. Colloid Interface Sci. 2024, 663, 971-980.
- [2].L. Li, Y. Yang, Y. Wang,et al. J. Mater. Res. Technol. 2020, 9 (3), 5463-5473.
- [3].Y. Du, Y. Zhang, X. Pu, et al. Chemosphere. 2023, 312, 137203.
- [4].W. Xia, G.Z. Guo, X.Q. Wu, et al. Solid State Chem. 2024, 336, 124783.
- [5].G.M. Abdelrazek, M.M. El-Deeb, A.A. Farghali,et al. Materials. 2021, 14 (18), 5271.
- [6].Y. Liang, Z. Song, Y. Zhang, et al. ACS Appl. Nano Mater. 2021, 4 (9), 8723-8732.
- [7].Z. Wang, F. Zhang, H. Zou, et al. J. Electroanal. Chem. 2018, 818, 198-203.