Supporting Information

Engineering atomic-scale synergy of Ni and Mn dual-atom catalysts for highly efficient CO_2 electroreduction

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Experimental Section

Chemicals and reagents

Manganese (II) nitrate ($Mn(NO_3)_2 \cdot 4H_2O$, 98%, AR, Macklin); nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99%, AR, AEX); zinc (II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99%, AR, AEX); 2-methylimidazole (2-MeIM, Aladdin); lsopropyl alcohol (AR, Tianjin Fuyu Fine Chemical Co., Ltd); Potassium bicarbonate ($KHCO_3$, AR, Tianjin DaMao Chemical Regent Factory); Methylalcohol (CH_3OH, Yongda Chemical Regengt Co., Ltd); Ethanol (C_2H_5OH, AR, Sinopharm Chemical Reagent Co., Ltd); Nafion solution (5.0 wt%, D520), Nafion membrane (N-117, Sigma-Aldrich); carbon paper (Maya Reagent). All chemicals were used directly in the experiments without any further treatment.

The calculation of TOF

Calculate the turnover frequency (TOF, h^{-1}) of the sample based on the following formula:

$$TOF = \frac{JS/NF}{m_{cat}\omega/M_{metal}} \times 3600$$

J: partial current density for CO production (A/cm^2);

S: geometric surface area of the working electrode (cm^2);

N: the number of electron transfer for CO production, which is 2 for CO;

F: Faradaic constant, 96485 C mol^{-1};

m_{cat}: the mass of the catalyst on the electrode(g);

ω: metal loading in the catalyst based on ICP-OES results;

M_{metal}: atomic mass of Ni (58.69 g mol^{-1}) for Ni_1-NC, atomic mass of Mn (55.00 g mol^{-1}) for Mn_1-NC, and atomic mass of 57.88 g mol^{-1} for Ni_1Mn_1-NC (based on the ratio of Ni and Mn).

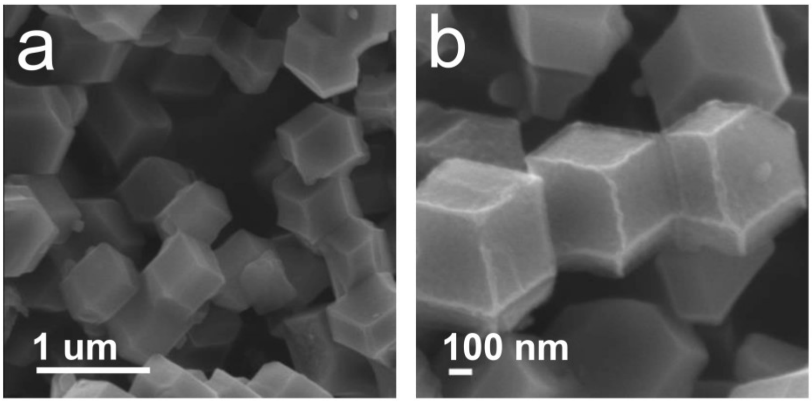

Fig. S1. (a, b) SEM image of the NC.

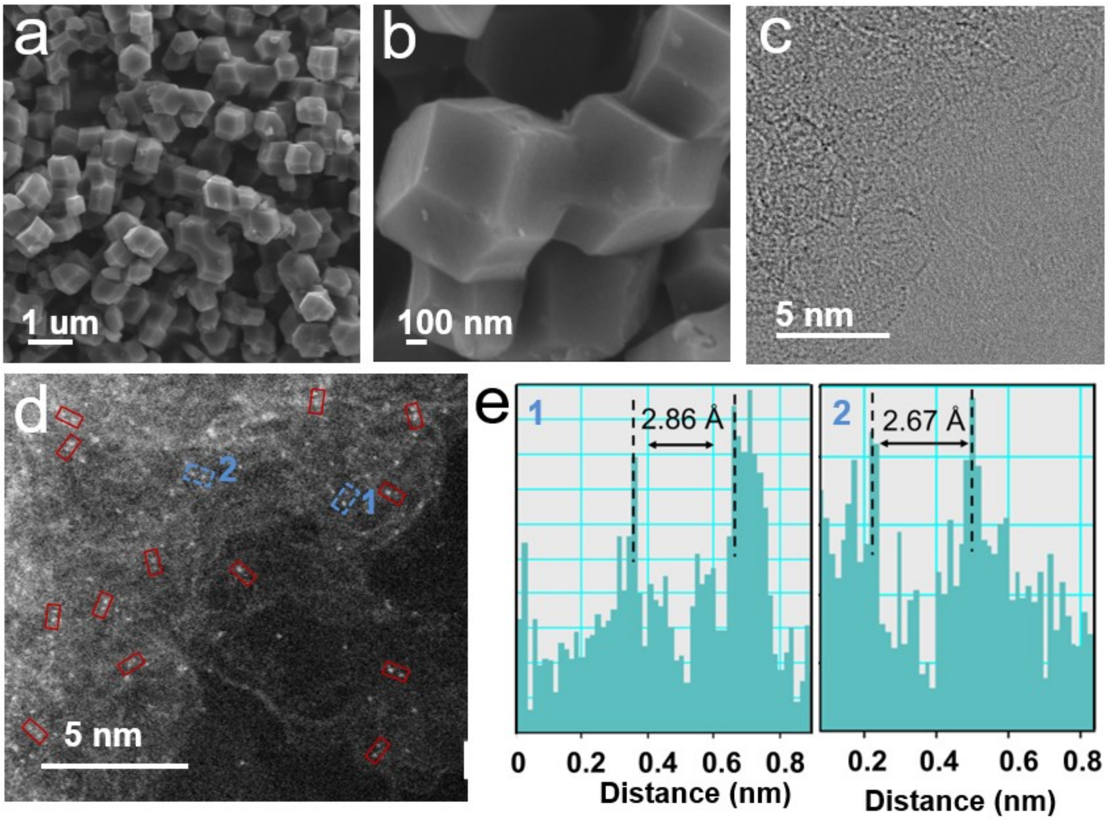

Fig. S2. (a, b) SEM image of Ni_1Mn_1-NC. (c) HRTEM image of Ni_1Mn_1-NC. (d) AC-HAADF-STEM image of Ni_1Mn_1-NC. (e) intensity spacing diagram.

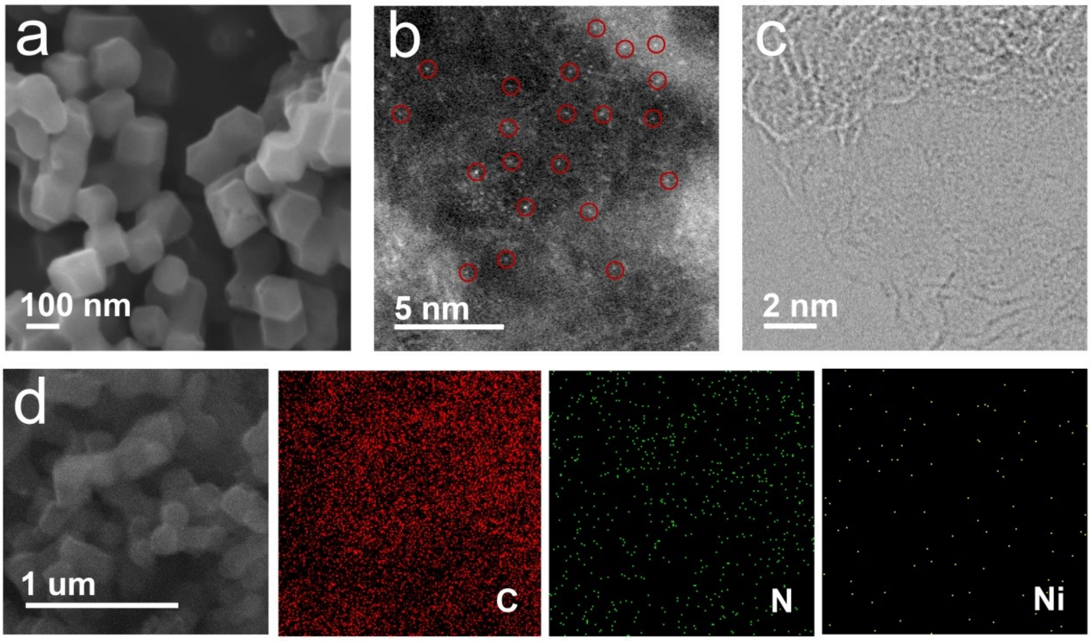

Fig. S3. (a) SEM image of Ni_1-NC. (b) AC-HAADF-STEM image of Ni_1-NC. (c) HR TEM image of Ni_1-NC. (d) EDS mappings of the Ni_1-NC.

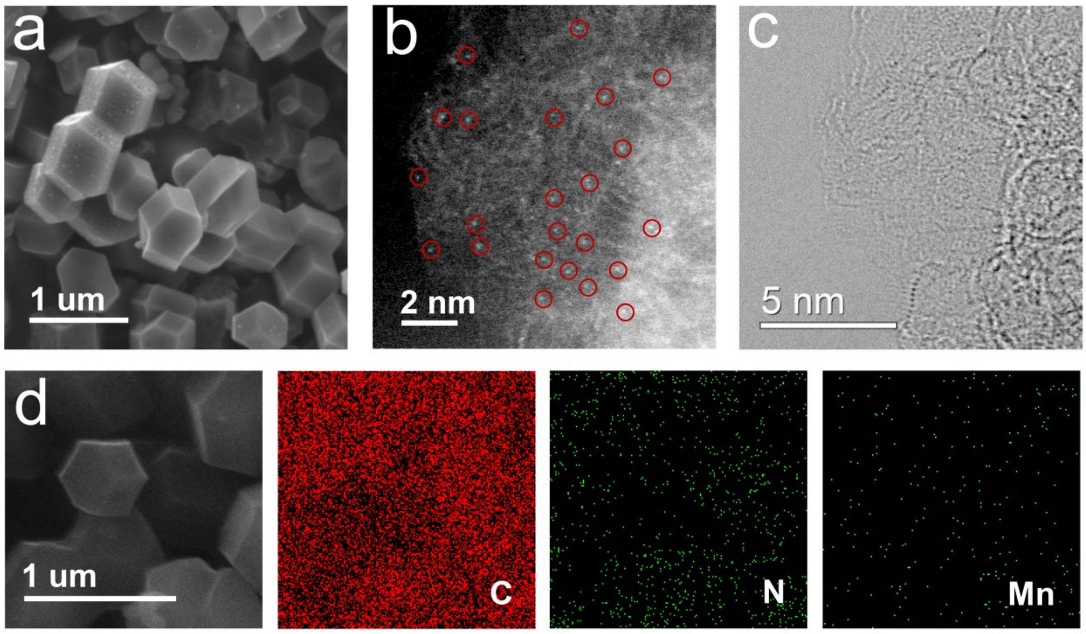

Fig. S4. (a) SEM image of Mn_1-NC. (b) AC-HAADF-STEM image of Mn_1-NC. (c) HRTEM image of Mn_1-NC. (d) EDS mappings of the Mn_1-NC.

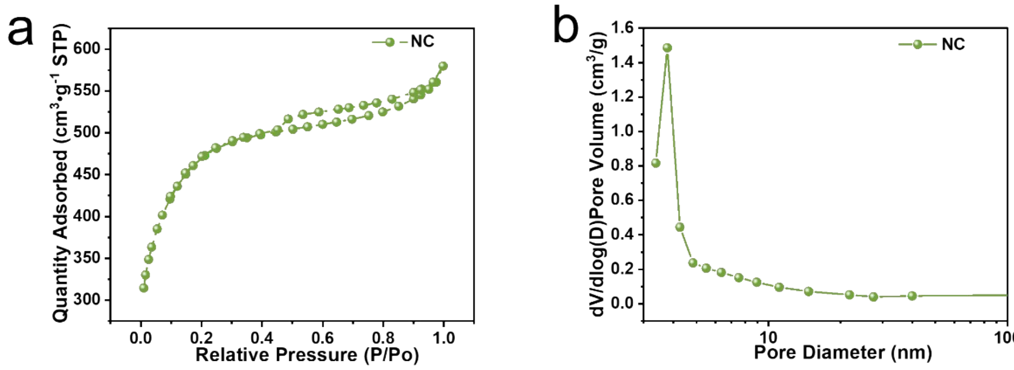

Fig. S5. (a) N_2 adsorption and desorption isotherm of NC. (b) Pore size distribution of NC.

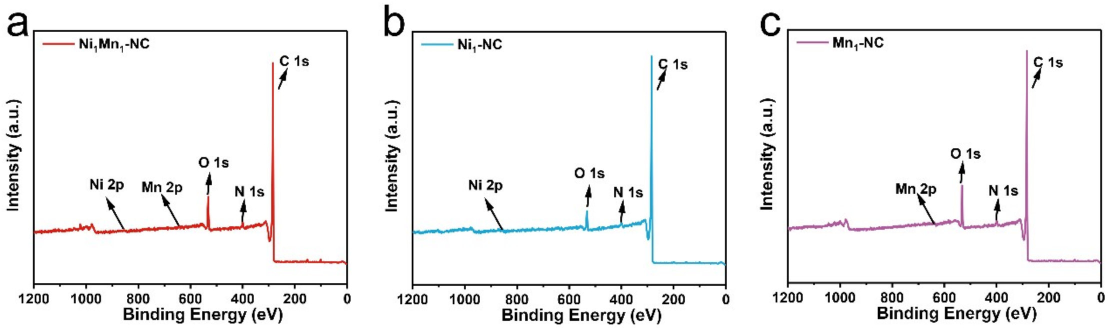

Fig. S6. XPS spectra for the survey scan of (a) Ni_1Mn_1-NC. (b) Ni_1-NC. and (c) Mn_1-NC.

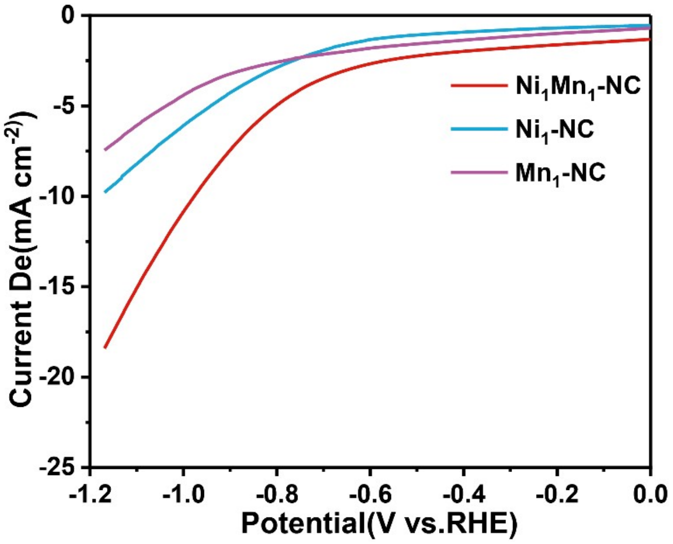

Fig. S7. LSV curves measured in Ar-saturated 0.5 M $KHCO_3$ electrolyte.

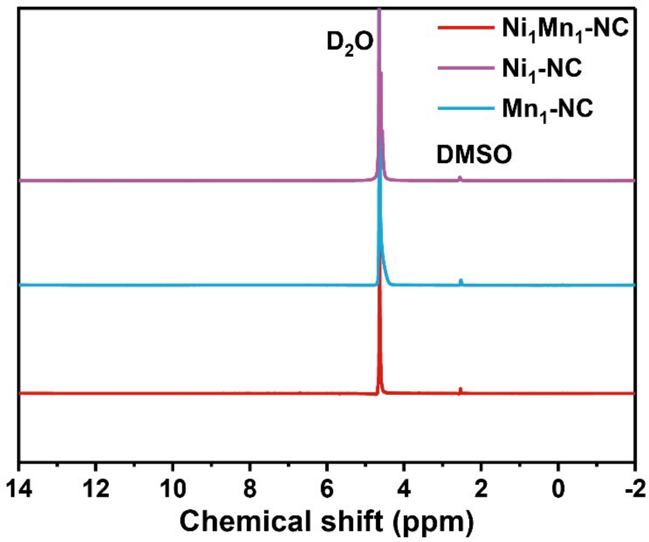

Fig. S8. The [1]H NMR spectra of liquid products on Ni_1Mn_1-NC, Ni_1-NC, and Mn_1-NC at -0.7 V vs. RHE.

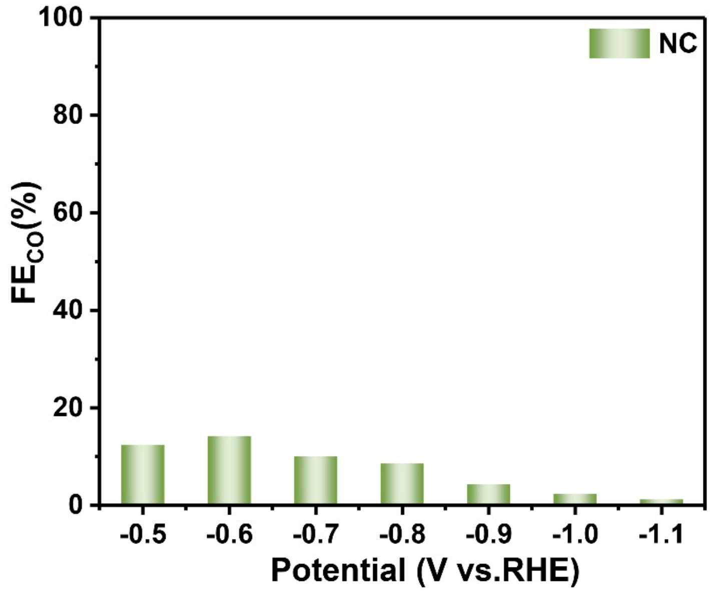

Fig. S9. FE_{CO} of the NC at different potentials performed in 0.5 M $KHCO_3$ electrolyte.

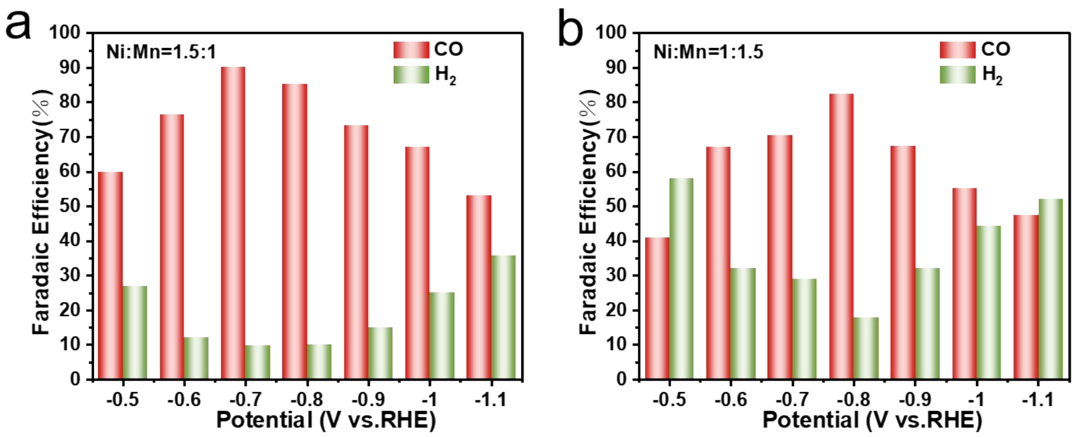

Fig. S10. The FE_{CO} of Ni_1Mn_1-NC with Ni:Mn molar ratios of (a) 1.5:1 and (b) 1:1.5.

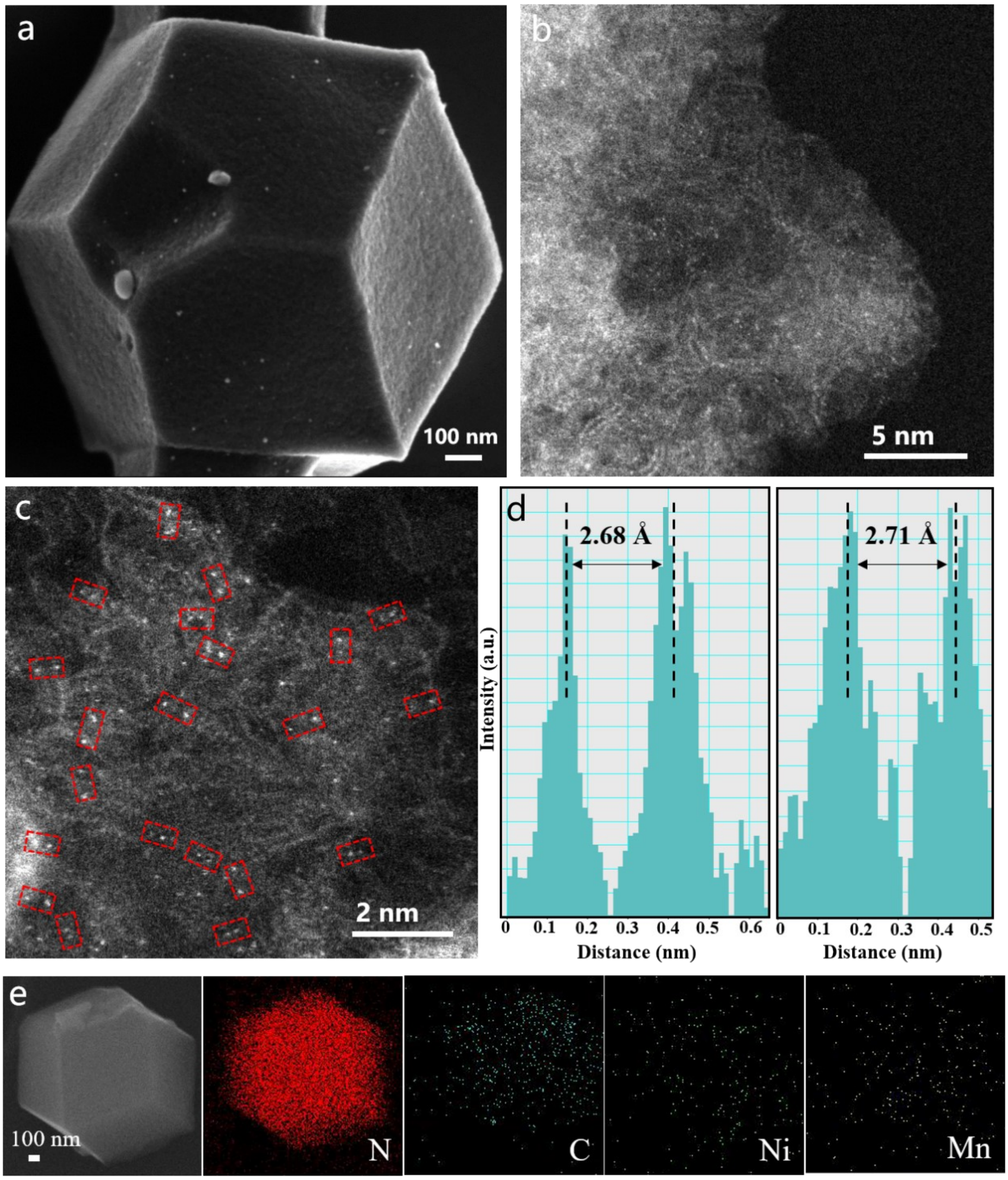

Fig. S11. (a) SEM. (b-c) AC-HAADF-STEM. (d) Intensity spacing diagram. (e) EDS mapping of Ni_1Mn_1-NC catalyst after reaction.

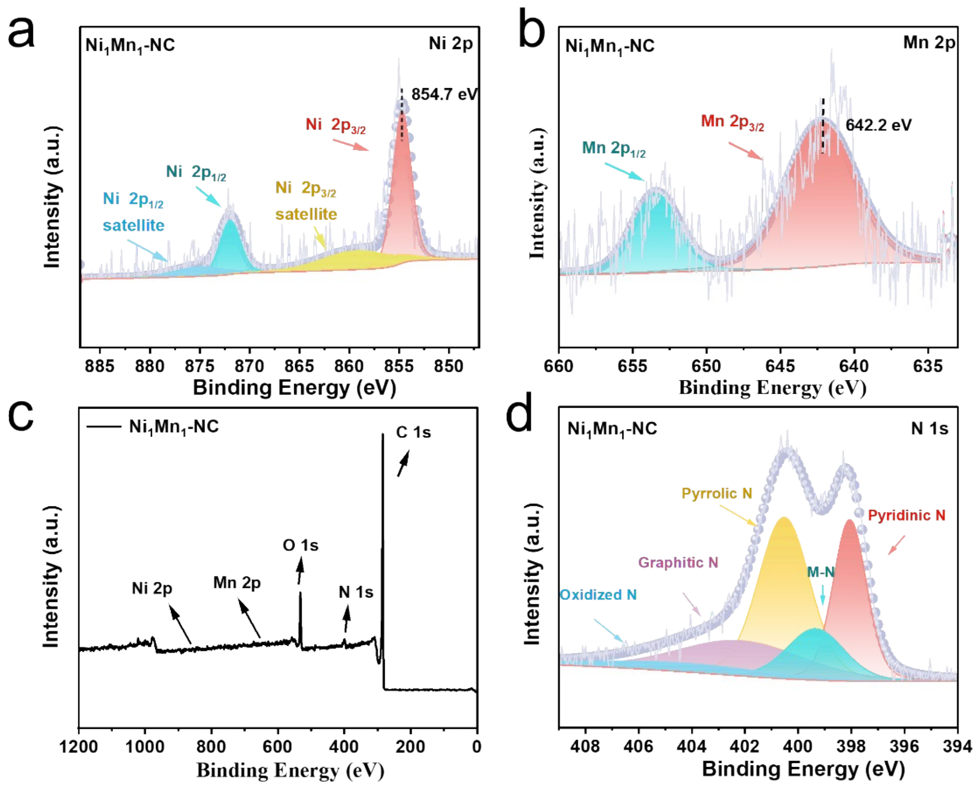

Fig. S12. (a) Ni 2p XPS spectra. (b) Mn 2p XPS spectra. (c) XPS spectra for the survey scan. (d) N 1s XPS spectra of the Ni_1Mn_1-NC catalyst after reaction.

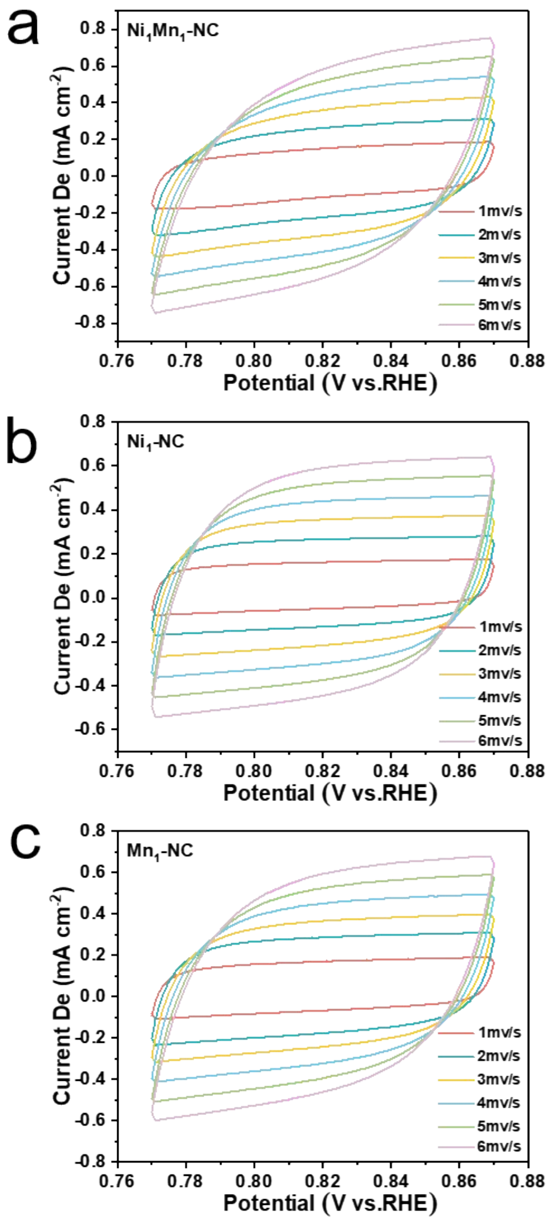

Fig. S13. The CV curves of Ni_1Mn_1-NC, Ni_1-NC, and Mn_1-NC at different scan rates.

Table S1. Physiochemical properties of the prepared Ni_1Mn_1-NC, Ni_1-NC, Mn_1-NC and N-C.

Samples	**Ni loading (wt. %)**	**Mn loading (wt. %)**	**BET surface area (m^2 g^{-1})**	**Pore diameter (nm)**	**Total pore volume (cm^3 g^{-1})**
Ni_1Mn_1-NC	0.71	0.40	1697.0	3.77	0.90
Ni_1-NC	0.61	-	1578.4	3.79	0.88
Mn_1-NC	-	0.45	1488.8	3.78	0.85
N-C	-	-	2009.5	3.77	1.17

Table S2. Performance comparison of various Ni-based single/dual-atom and Mn-based single/dual-atom catalysts for CO_2RR.

Catalyst	Cathode electrolyte	Potential (V vs. RHE)	FE_{CO} (%)	j_{CO} (mA cm^{-2})	Stability (h)	Reference
Ni_1Mn_1-NC	0.5M $KHCO_3$	-0.7	97	6.4	60	This work
Ni_1-NC	0.5M $KHCO_3$	-0.7	75	3.0	-	This work
Mn_1-NC	0.5M $KHCO_3$	-0.6	41	0.9	-	This work
Fe/Mn-NC	0.1M $KHCO_3$	-0.6	94	~8.1	12	[1]
Co_1Mn_1-NC	0.5M $KHCO_3$	-0.47	97.6	3.5	30	[2]
NiFe-DASC	0.5M $KHCO_3$	-0.8	94.5	98	30	[3]
NiN_3@CoN_3-1[#]	0.1M $KHCO_3$	-0.7	89	~3	-	[4]
Ni_2-NCNT	0.5M $KHCO_3$	-1.4	81.6	76.2	52	[5]
FeMn-N-C	0.1M $KHCO_3$	-0.5	80	~5	-	[6]
Fe_2Ni/NG	0.5M $KHCO_3$	-0.6	60.9	3.4	12	[7]
Mn-NC	0.1M $KHCO_3$	-0.8	81	1.75	10	[8]
Mn-N-C	0.1M $KHCO_3$	-0.58	70	~1	-	[9]
NiPc	0.5M $KHCO_3$	-0.7	93	2.2	10	[10]
NiSA-NGA	0.5M $KHCO_3$	-0.8	90.2	5.8	6	[11]

Reference

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