Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Rational Design of Dual-Metal-Site Catalysts for Electroreduction of Carbon Dioxide

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Computational details of micro-kinetics simulations

To give an intuitive demonstration of the CRR activity of DMSCs, we further constructed a micro-kinetics model for the conversion of CO_2 to CO, of which the reaction process is summarized as:

$$CO_2(g) + * + H^+ + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} COOH^* \qquad (S1)$$

$$COOH^* + H^+ + e^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CO^* + H_2O \qquad (S2)$$

$$CO^* \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} CO(g) + * \qquad (S3)$$

where k_i (i = 1-3) is rate constant, and k_{-i} is rate constant of the reverse reaction. Based on steady-state approximation, the dynamical coverage rate of $*_{DMSC}$, COOH* and CO* can be written as:

$$\frac{\partial\theta_{*DMSC}}{\partial t} = -k_1\theta_{*DMSC}P_{CO_2(g)} + k_{-1}\theta_{COOH*} + k_3\theta_{CO*} - k_{-3}\theta_{*DMSC}P_{CO(g)}$$

(S4)

$$\frac{\partial\theta_{COOH*}}{\partial t} = k_1\theta_{*DMSC}P_{CO_2(g)} - k_{-1}\theta_{COOH*} - k_2\theta_{COOH*} + k_{-2}\theta_{CO*}$$

(S5)

$$\frac{\partial\theta_{CO*}}{\partial t} = k_2\theta_{COOH*} - k_{-2}\theta_{CO*} - k_3\theta_{CO*} + k_{-3}\theta_{*DMSC}P_{CO(g)}$$

(S6)

where θ is the coverage of the reaction intermediate, *t* is the time, and $P_{CO_2(g)}$ and $P_{CO(g)}$are the pressure of $CO_2(g)$ and CO(g), respectively. For the simulated kinetic volcano and polarization curves presented in the main text, we set $P_{CO_2(g)}= P_{CO(g)} =$ 1 atm and 0.5 atm, respectively. Besides, these coverages on a DMSC should be satisfied the following condition：

$$1 = \theta_{*DMSC} + \theta_{CO*} + \theta_{COOH*} \qquad (S7)$$

On the basis of the transition state theory, for electrochemical step, the rate constant

k_i can be written as[1]

$$k_i = A\,exp\left(-\frac{E_{a,i}}{k_BT}\right)exp\left(-\frac{\beta e(U-U_i^0)}{k_BT}\right) \quad (S8)$$

where A is a pre-exponential factor, $E_{a,i}$ is the activation energy for the proton transfer, U_i is the reversible potential of step i deduced by $U_i = -\Delta G_i/e$, β is the symmetric factor taken as 0.5. k_B is the Boltzmann constant, and h is Planck constant. It is assumed that the $E_{a,i}$ to be material-independent in the electrochemical process, such that an effective pre-exponential factor, $A' = A\exp\left(-\frac{E_{a,i}}{k_BT}\right)$, can be applied to simplify the expression of rate constant:

$$k_i = A'exp\left(-\frac{\beta e(U-U_i^0)}{k_BT}\right) \quad (S9)$$

$A' = 3.6\times10^4\ s^{-1}$ is adopt here to reproduce the experimental polarization curve on Au surface with ~5% steps in the sample.[2] In addition, the rate constant for chemical step of CO* desorption is expressed as,

$$k_3 = v\,exp\left(-\frac{E_{co}}{k_BT}\right) \quad (S10)$$

where E_{CO} is the binding energy of CO* and $v = 10^{13}\ s^{-1}$ is a conventional pre-factor for CO desorption.

The equilibrium constant (K_i), which depends on the electrode potential (U), is calculated by,

$$K_i = exp\left(-\frac{eU+\Delta G_i}{k_BT}\right) \quad (S11)$$

For all reaction steps, the k_{-i} can be calculated from the its rate constant and equilibrium constant; that is,

$$k_{-i} = \frac{k_i}{K_i} \quad (S12)$$

These rate equations are solved at steady state, and then we can get the turn over frequency (TOF).

Finally, the current density (j) can be calculated by:

$$j = e\rho TOF_{e^-} \tag{S13}$$

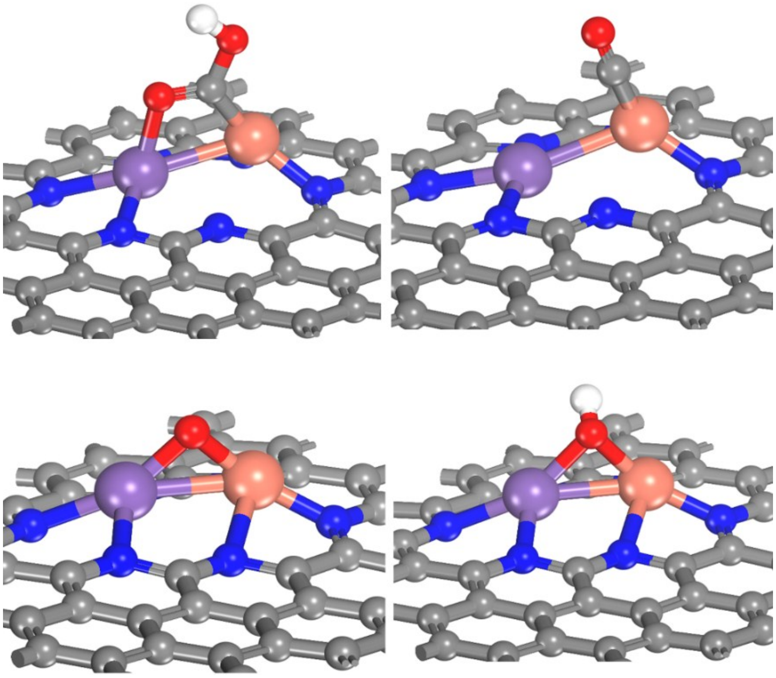

Fig. S1 The most stable configurations of key intermediates adsorption on Cu/Mn DMSC in the process of CO_2 electroreduction. Grey, dark blue, orange and purple balls represent C, N, Cu and Mn atoms, respectively

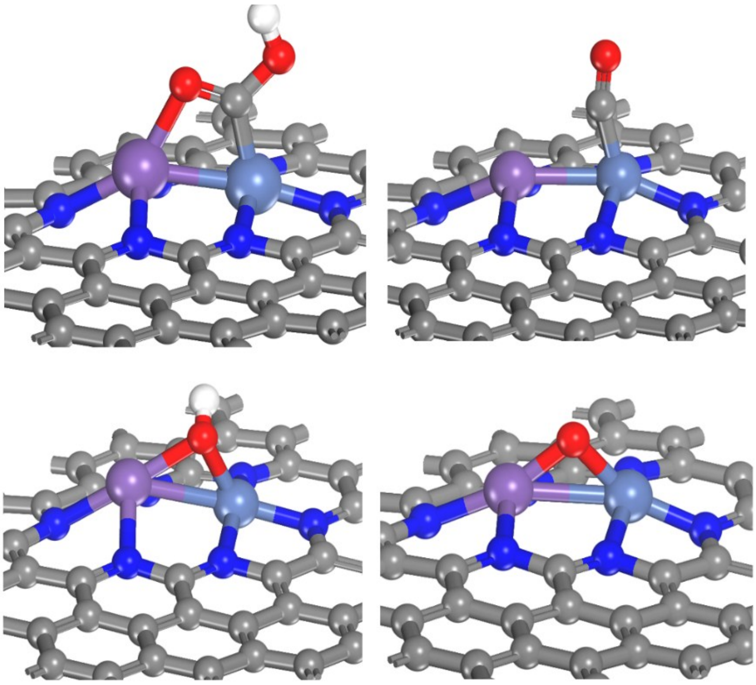

Fig. S2 The most stable configurations of key intermediates adsorption on Ni/Mn DMSC in the process of CO_2 electroreduction. Grey, dark blue, light blue and purple balls represent C, N, Ni and Mn atoms, respectively

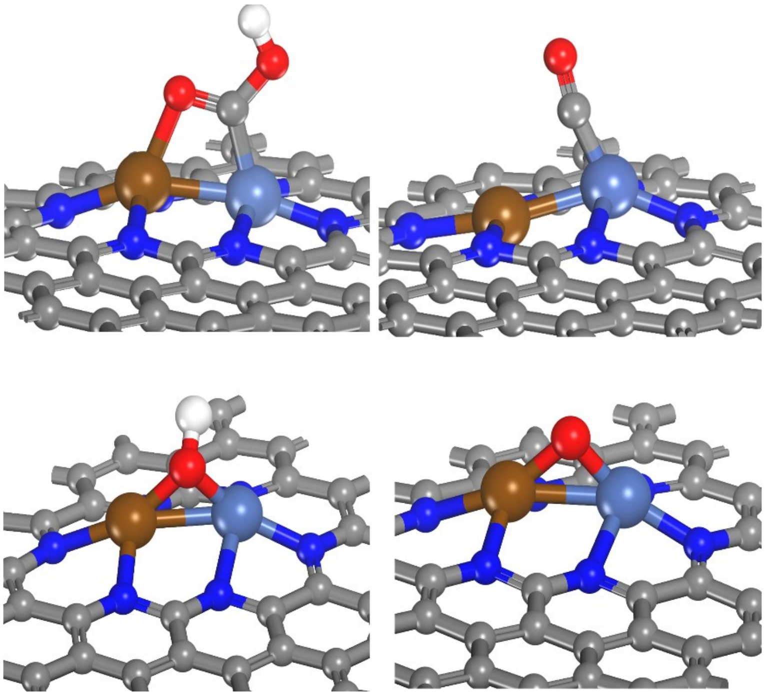

Fig. S3 The most stable configurations of key intermediates adsorption on Ni/Fe DMSC in the process of CO_2 electroreduction. Grey, dark blue, light blue and brown balls represent C, N, Ni and Fe atoms, respectively

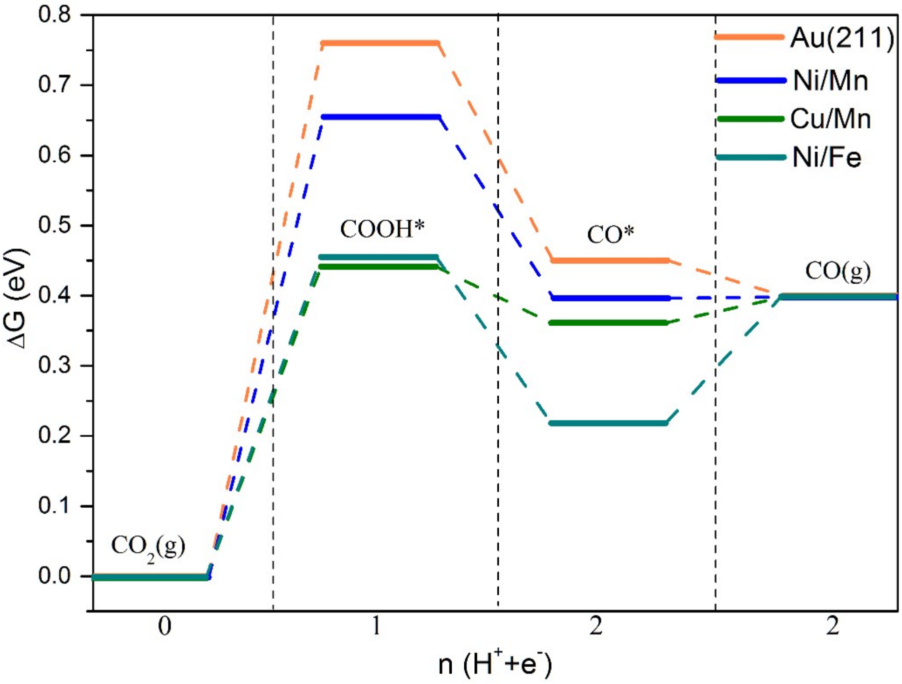

Fig. S4 The free energy diagrams of CO_2 reduction on Cu/Mn, Ni/Mn and Ni/Fe DMSCs at 0 V vs RHE. The free energy diagram of Au(211) was also plotted for comparison.

Table S1. The calculated dissolution potentials (U_{dis}) of transition metal atoms (M_1 or M_2) in M_1/M_2-N_6/C DMSCs for the dissolution reaction of $M_1(M_2) + nH^+ \leftrightarrow M_1(M_2)^{n+} + n/2H_2$. U_{dis} is defined as $U_{dis} = U_{M1}{}^0 + [E_{M1,\ bulk} - (E_{M1/M2\text{-}N6\text{-}C} - E_{M2\text{-}N6\text{-}C})]$ or $U_{dis} = U_{M2}{}^0 + [E_{M2,\ bulk} - (E_{M1/M2\text{-}N6\text{-}C} - E_{M1\text{-}N6\text{-}C})]$. $U_{M1}{}^0$ and $U_{M2}{}^0$ are the standard dissolution potentials of M_1 and M_2 in the bulk phase.[3]

M	$U_M{}^0$ (V)	U_{dis} (V)
Ni@Ni/Fe DMSC	–0.26	0.43
Fe@Ni/Fe DMSC	–0.45	0.24
Cu@Cu/Mn DMSC	0.34	0.72
Mn@Cu/Mn DMSC	–1.18	-0.36
Ni@Ni/Mn DMSC	–0.26	0.37
Mn@Ni/Mn DMSC	–1.18	-0.13

Table S2. The calculated formation energies (E_f) of heteronuclear Cu/Mn, Ni/Mn and Ni/Fe DMSCs and compared to those of homonuclear Cu/Cu, Mn/Mn, Fe/Fe/ and Ni/Ni DMSCs. E_f is defined as $E_f = E_{M1/M2\text{-}N6\text{-}C} - \mu_{M1} - \mu_{M2} - n\mu_C - m\mu_N$, where $E_{M1/M2\text{-}N6\text{-}C}$ is the total energy of DMSC, μ_{M1} and μ_{M2} are the chemical potentials of M_1, M_2, carbon and N atoms, respectively. n and m are the number of C and N atoms in the supercell, respectively. The total energies of bulk metals, graphene and nitrogen molecule were computed to obtain the chemical potentials for corresponding elements.

DMSC	Cu/Mn	Ni/Mn	Fe/Ni	Cu/Cu	Mn/Mn	Ni/Ni	Fe/Fe
E_f (eV/atom)	0.093	0.102	0.120	0.104	0.118	0.121	0. 162

References

[1] S. Vilekar, I. Fishtik, R. Datta, *J. Elecrochem. Soc*. 2010, **157**, B1040-B1050.

[2] M. P. Andersson, F. Abild-Pedersen, I. N. Remediakis, T. Bligaard, G. Jones, J. Engbaek, O. Lytken, S. Horch, J. H. Nielsen, J. Sehested, *J. Catal*. 2008, **255**, 6-19.

[3] J. Greeley, J. K. Nørskov, *Electrochimica Acta*, 2007, **52**, 5829-5836