Supplementary Information

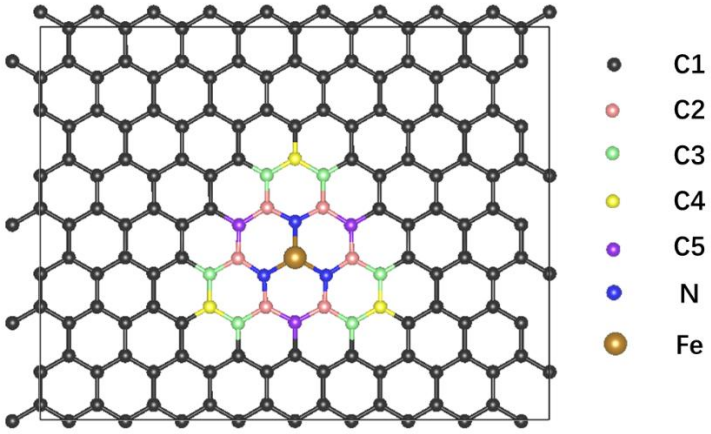

Fig. S 1 Atomic type setting. All environment C atoms share the same parameters (C1), while all symmetrically unique central atoms have their unique parameters (C2, C3, C4, C5, N, Fe)

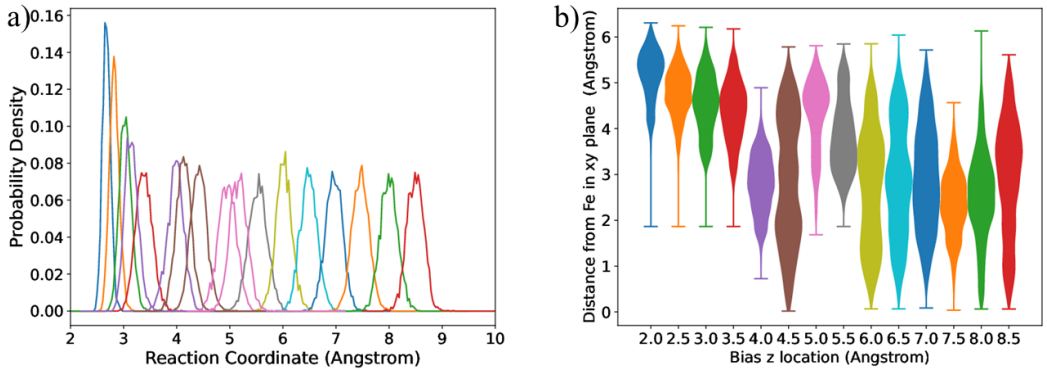

Fig. S 2 The distribution of CO_2 position under different bias potentials :(a) Reaction coordinate distribution in different windows for constP condition (7V). The reaction coordinate is defined as the distance between the C in CO_2 and electrode surface. (b) The violin plot of the distance between C in CO_2 and doped Fe atom in xy plane.

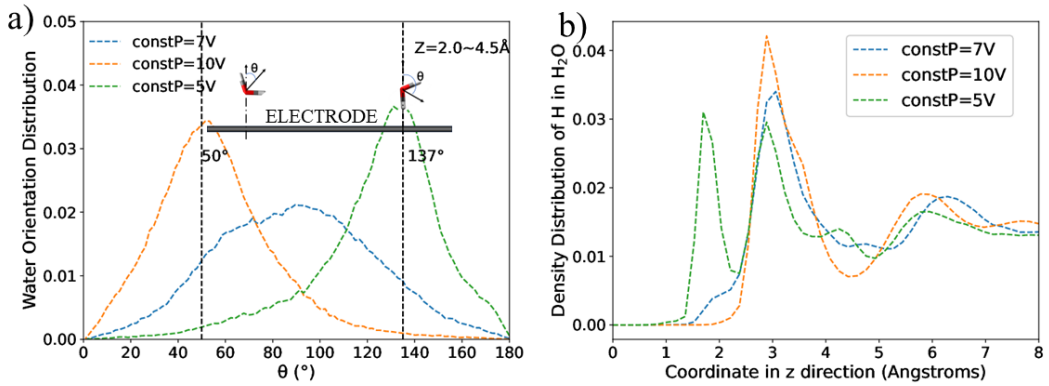

Fig. S 3 Comparison of water orientation under different bias potential: (a) The probability distribution of the water orientation within inner water layer (within 2.0~4.5 Å from the electrode surface). The θ stands for the angle between the bisector of adsorbed water molecules and the surface normal. Two vertical dash lines at 50° and 137° stand for most probable θ for positively and negatively charged electrode, respectively, and the corresponding configuration are shown around the vertical dash line, the black thick horizontal line stands for electrode surface. (b) probability density distribution of distance between oxygen atom in water and electrode surface.

Table S 1 parameters in Fe-N-C electrode model

	χ (kJ·mol^{-1}·e^{-1})	J (kJ·mol^{-1}·e^{-2})	η (angstrom)	ε (kJ·mol^{-1})	σ (nm)
C1	651.12496677	-4164.829436	0.10928332	0.69067923	0.29762701
C2	510.40392156	-6598.437796	0.07218767	0.69067923	0.29762701
C3	645.92171508	-23412.16716	0.02274385	0.69067923	0.29762701
C4	644.80942378	-4078.440621	0.11069275	0.69067923	0.29762701
C5	648.81564144	-4341.428043	0.10515459	0.69067923	0.29762701
N	1785.28391366	-5086.041613	0.06959997	0.09944425	0.31275400
Fe	479.4279537	-11302.57032	0.04676696	0.51379945	0.19529668

Table S 2 Adsorption energy of CO_2 on electrode calculated by DFT and classical forcefield

Adsorption Site	DFT ($kJ \cdot mol^{-1} \cdot$)	Classical Forcefield ($kJ \cdot mol^{-1}$)
C	-8.37	-17.95
Fe	-18.91	-26.64

Both DFT and calculation under our classical forcefield consider only one CO_2 molecule and the electrode. The DFT setup uses identical computational details under vacuum conditions.

Link 1 DMFF/dmff/admp/qeq.py at devel · deepmodeling/DMFF · GitHub