

Electronic Supplementary Material

Rare-earth metal– N_6 centers in porous carbon forelectrocatalytic CO_2 reduction

Xianshi Zeng^{a,b}, Luliang Liao^a, Meishan Wang^{c*}, Hongming Wang^{a*}

^a Institute for Advanced Study, Nanchang University, Nanchang 330031, China;
zengxueliang@163.com(X.Z); 15279011738@163.com(L.L); hongmingwang@ncu.edu.cn(H.W)

^b School of Physics and Materials Science, Nanchang University, Nanchang 330031, China.

^c School of Integrated Circuits, Ludong University, Yantai 264025, China;
mswang1971@163.com(M.W)

1. Raw materials and reagents

Potassium citrate, europium nitrate pentahydrate, dicyandiamide, glucose, isopropanol, potassium bicarbonate and dilute hydrochloric acid were purchased from Sinopharm Chemical Reagent Co.. Nafion (5wt%) purchased from Shanghai Aladdin Reagent Co.. Ultrapure water (18.2 $\text{M}\Omega$ cm) was obtained from a Milli-Q water purification system (Millipore), All reagents are analytically pure and can be used without further purification.

2. Synthesis of rare earth Eu single atom catalysts

First, the porous carbon (PC) carrier (prepared by pyrolysis of potassium citrate) was ultrasonically dispersed in a solution containing europium nitrate and glucose (chelating agent). After washing and drying, it was mixed with dicyandiamide (nitrogen source) and ground well, and the mixture was pyrolyzed in a tube furnace under Ar atmosphere to obtain Eu- N_6C rare earth monoatomic catalyst. The process is shown in Figure S1.

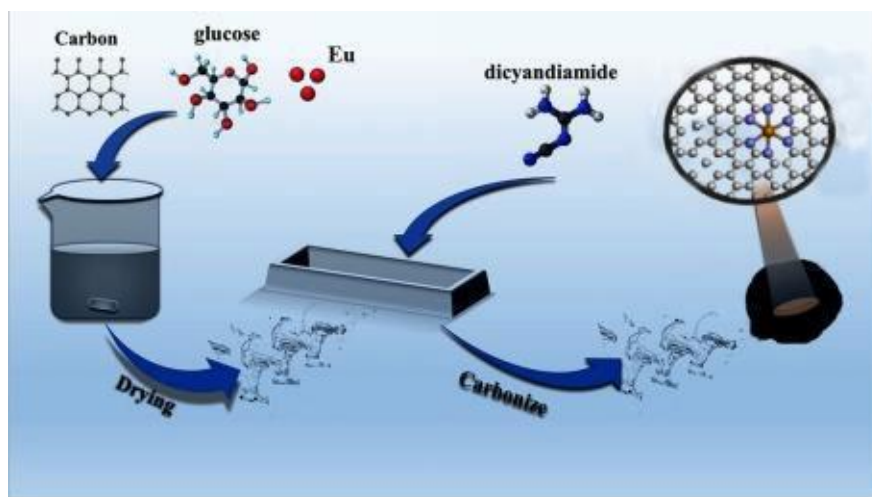


Figure S1 Schematic diagram of Eu- N_6C synthesis

2.1 Synthesis of Pc carrier

Potassium citrate (3mmol) was put into a small porcelain boat and pyrolyzed in a tube furnace at 800°C under Ar atmosphere. After cooling to room temperature, the black solid obtained was washed with hydrochloric acid solution (0.5M) and ultrapure water respectively and dried at 70°C. The black powder was obtained as Pc carrier.

2.2 Synthesis of Eu-N₆C

60 mg Pc, 0.3 mmol europium nitrate and 6.7 mmol glucose were added into 5 mL ultrapure water, sonicated for 30 min, washed with ultrapure water and dried at 60°C. The dried powder was ground with dicyandiamide in a mass ratio of 1:5, and the obtained powder was put into a tube furnace and heated to 800°C under Ar gas flow (50 SCCM). After 2h of pyrolysis, black powder was obtained.

3. Electrochemical performance test of Eu-N₆C

3.1 Preparation of working electrode

The working electrodes were prepared by making a homogeneous ink of the catalyst and then applying it dropwise on carbon paper. Briefly, 1 mg of catalyst was dispersed in isopropanol (0.2 mL) solution, then 20 μL of 5 wt% Nafion solution was added and the mixture was sonicated for 1 h to prepare a homogeneous catalyst ink. Finally, the ink was uniformly applied dropwise on carbon paper (1 × 1 cm) to make a catalyst loading of 1 mg.cm⁻².

3.2 Testing Methodology

The CO₂RR performance of the materials was evaluated in a three-electrode system with Ag/AgCl electrode as the reference electrode, graphite electrode as the counter electrode, and 0.5 M (pH = 7.2) KHCO₃ solution as the electrolyte, using an H-type electrolytic cell with a proton exchange membrane. All potentials were calibrated as relative to the reversible hydrogen electrode (RHE) potential using the following equation: $E_{VS\ RHE} = E_{VS\ Ag/AgCl} + 0.197 + 0.0591 \times pH$, as described in the following test method.

Before conducting electrochemical tests, 35 mL of KHCO₃ solution was added to each end of the H-type electrolytic cell, and high-purity CO₂ was passed into the cathode chamber of the electrolytic cell at a rate of 20 ml/min for at least 30 min to saturate the electrolyte, while the catalyst was then activated by cyclic voltammetry and scanned until the curves largely overlapped, indicating the completion of catalyst activation. The voltage setting for this step ranges from -0.62 V to -1.72 V vs Ag/AgCl. The linear scanning voltammetry (LSV) curves of the catalysts were measured at a scan rate of 2 mv s⁻¹ in CO₂-saturated or Ar-saturated electrolytes, with potential settings in the same range as the catalyst activation step. The LSV curves were used to initially

determine the required setting potential for the next step of potentiostatic electrolysis. The catalysts were then tested for Faraday efficiency of each reduction product using the chrono-current (i-t) method, with the gaseous products detected online by gas chromatography and the liquid products quantified using NMR.

3.3 Quantitative analysis method of reduction products

The reduction products obtained by electrocatalytic CO₂ reduction are available in gas phase and liquid phase, which are quantified by gas chromatography and NMR, respectively. The Faraday efficiency of the gas-phase product was calculated using the following equation.

$$FE = \frac{Q_x}{Q_{tot}} \times 100\% = \frac{\left(\frac{v}{60S/min} \right) \times \left(\frac{y}{24000cm/mol} \right) \times N \times F}{j} \times 100\%$$

Where $v = 20\text{mL}/\text{min}$ refers to the flow rate of the incoming CO₂, y refers to the concentration of the gas in the quantitative ring of 1 mL gas chromatography, N is the number of electrons transferred for the reaction to produce 1 mol of a particular gas product. For CO and H₂, the value of N is 2, $F = 96485\text{ C}/\text{mol}$ is the Faraday constant, and j is the current density recorded during the constant voltage electrolysis.

The liquid phase products were quantified using the liquid NMR test method with a pressed water peak. The ratios of the samples to be tested for NMR are shown below. 300 μL of electrolyte after the end of electrolysis was placed into the NMR tube. Then 200 μL of heavy water and 2 μL of dimethylsulfoxide (internal standard) were added to it with a pipette, and the mixture was mixed by a mixer to produce the NMR sample.

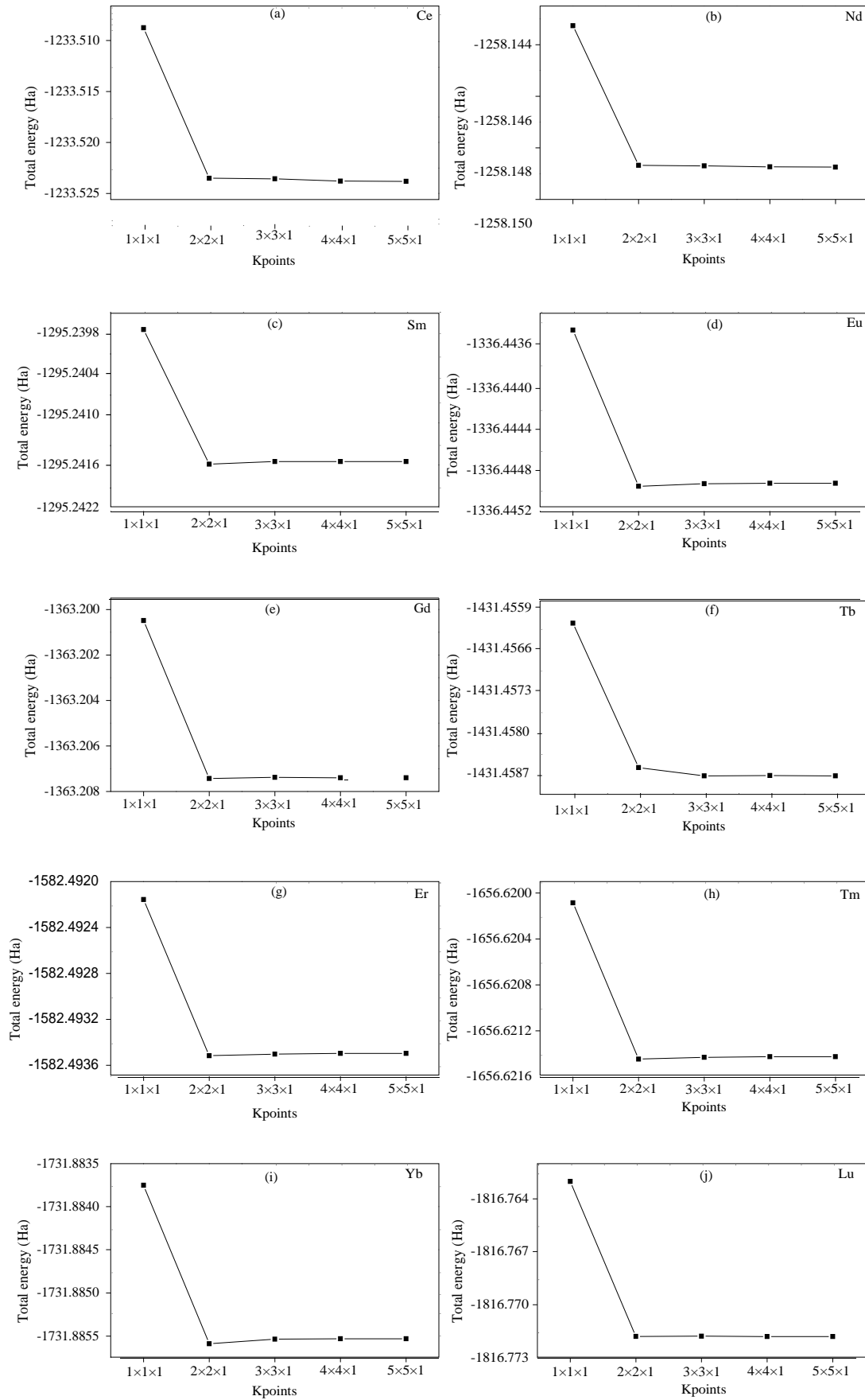


Figure S 2 The total energy of each rare-earth single-atom catalyst at different K points, where (a) is Ce-N₆C; (b) is Nd-N₆C; (c) is Sm-N₆C; (d) is Eu-N₆C; (e) is Gd-N₆C; (f) is Tb-N₆C; (g) is Er-N₆C; (h) is Tm-N₆C; (i) is Yb-N₆C; and (j) is Lu-N₆C.

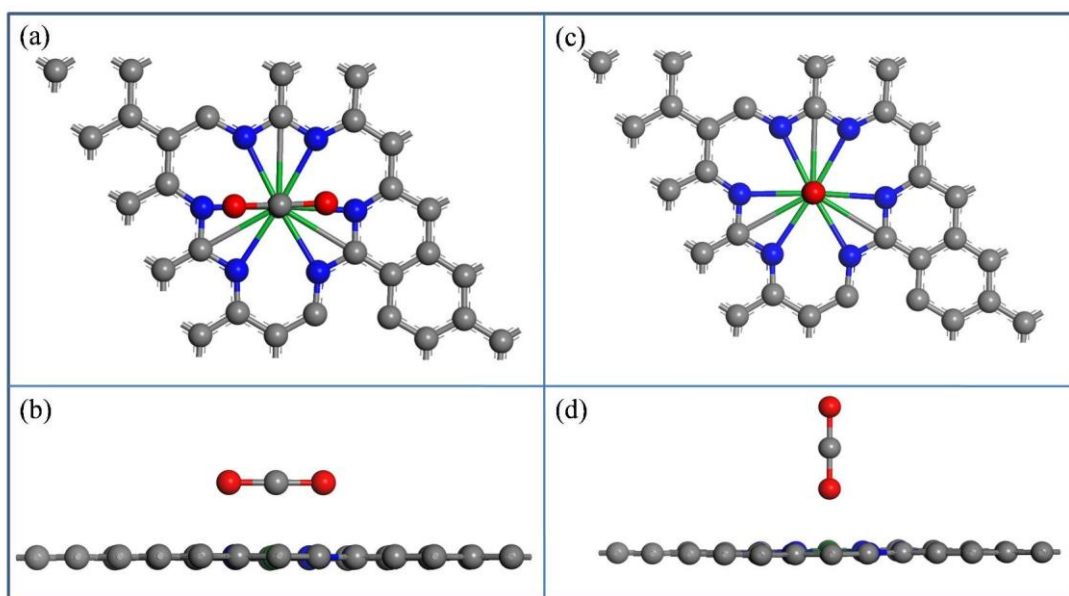


Figure S 3 Model of the adsorption structure of CO₂ molecules on rare-earth single-atom catalysts, with gray representing C atoms, blue representing N atoms, red representing O atoms, and green representing rare-earth atoms. Where (a) is the top view of C-site adsorption; (b) is the side view of C-site adsorption; (c) is the top view of O-site adsorption; (d) is the side view of O-site adsorption.

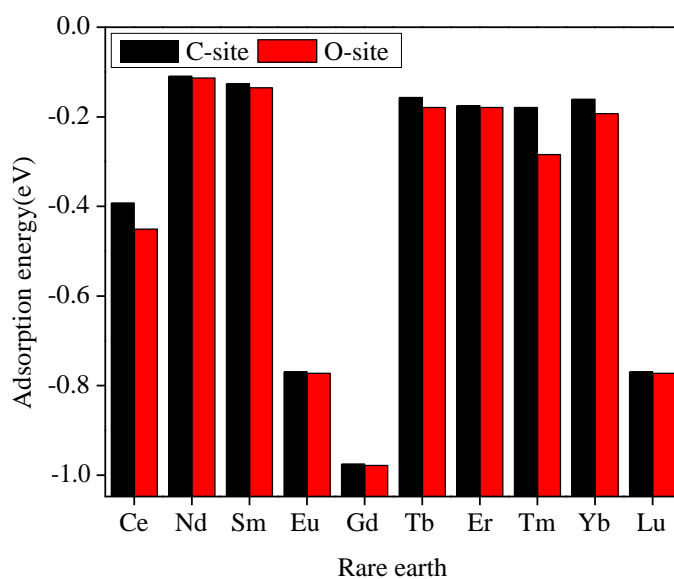


Figure S 4 Adsorption energy of carbon dioxide at C and O sites on each rare-earth single-atom catalyst

Table S. 1 The binding energy E_b of Re to the substrate N_6C in the rare-earth single-atom catalyst $Re-N_6C$, the cohesion energy E_c of rare-earth atoms in the bulk, and the formation energy of $Re-N_6C$.

Re- N_6C	E_b (eV)	E_c (eV)	E_f (eV)
Ce	-10.839	-4.576	-8.052
Nd	-10.729	-4.335	-7.943
Sm	-10.188	-3.470	-7.401
Eu	-8.670	-3.289	-5.883
Gd	-10.440	-4.425	-7.653
Tb	-10.065	-3.186	-7.277
Er	-9.848	-3.286	-7.061
Tm	-9.536	-2.825	-6.749
Yb	-8.819	-2.349	-6.032
Lu	-10.713	-4.547	-7.926

Table S. 2 The first step of protonation forms the Gibbs free energy transition of $*OCHO$, $*COOH$ or $*H$.

Re- N_6C	$\Delta G[*H]$	$\Delta G[C*OOH]$	$\Delta G[O*CHO]$
Ce	0.742	0.409	-1.051
Nd	1.300	1.080	-0.831
Sm	1.401	1.122	-0.232
Eu	0.797	0.492	-0.852
Gd	-0.024	-0.277	-1.723
Tb	1.252	0.997	-0.342
Er	1.336	1.019	-0.306
Tm	1.345	1.032	-0.187
Yb	1.297	0.989	-0.283
Lu	0.166	0.097	-1.331

Table S. 3 Gibbs free energy changes for each protonation step of Ce-N₆C electrocatalytic CO₂ reduction

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	* + CO ₂ + H ⁺ + e ⁻ → *COOH	0.410
	* + CO ₂ + H ⁺ + e ⁻ → *OCHO	-1.051
2	*COOH + H ⁺ + e ⁻ → *CO + H ₂ O	-0.254
	*OCHO + H ⁺ + e ⁻ → *OCHOH	0.632
3	*CO + H ₂ O + H ⁺ + e ⁻ → *CHO + H ₂ O	0.063
	*CO + H ₂ O + H ⁺ + e ⁻ → *COH + H ₂ O	2.432
	*CO + H ₂ O → * + CO + H ₂ O	0.444
4	*CHO + H ₂ O + H ⁺ + e ⁻ → *OCH ₂ + H ₂ O	-2.048
5	*OCH ₂ + H ₂ O + H ⁺ + e ⁻ → *OCH ₃ + H ₂ O	-0.738
	*OCH ₂ + H ₂ O + H ⁺ + e ⁻ → * + HCHO + H ₂ O + H ⁺ + e ⁻	1.592
6	*OCH ₃ + H ₂ O + H ⁺ + e ⁻ → *CH ₃ OH + H ₂ O	1.205
	*OCH ₃ + H ₂ O + H ⁺ + e ⁻ → *O + CH ₄ + H ₂ O	0.412
7	*O + CH ₄ + H ₂ O + H ⁺ + e ⁻ → *OH + CH ₄ + H ₂ O	-1.089
8	*OH + CH ₄ + H ₂ O + H ⁺ + e ⁻ → * + CH ₄ + 2H ₂ O	0.559

Table S. 4 Gibbs free energy changes for each protonation step of Eu-N₆C electrocatalytic CO₂ reduction

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	*+CO ₂ +H ⁺ +e ⁻ →*COOH	0.604
2	*COOH+H ⁺ +e ⁻ →*CO+H ₂ O	-0.333
3	*CO + H ₂ O → * + CO + H ₂ O	0.440

Table S. 5 Lu-N₆C electrocatalytic CO₂ reduction for each protonation step

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	*+CO ₂ +H ⁺ +e ⁻ →*COOH	0.022
	* + CO ₂ +H ⁺ +e ⁻ →*OCHO	-1.406
2	*COOH+H ⁺ +e ⁻ →*CO+H ₂ O	-0.209
	*OCHO+H ⁺ +e ⁻ →*OCHOH	0.420
3	*CO + H ₂ O + H ⁺ + e ⁻ → *CHO + H ₂ O	0.898
	*CO + H ₂ O + H ⁺ + e ⁻ → *COH + H ₂ O	1.923
	*OCHOH + H ⁺ + e ⁻ → *CHO + H ₂ O	1.697
	*OCHOH + H ⁺ + e ⁻ → *OCH + H ₂ O	1.464
	*CO + H ₂ O → * + CO + H ₂ O	0.786
	*OCHOH → * + HCOOH	0.903

Table S. 6 Gd-N₆C electrocatalytic CO₂ reduction for each intermediate reaction

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	*+CO ₂ +H ⁺ +e ⁻ →*COOH	-0.277
	* + CO ₂ +H ⁺ +e ⁻ →*OCHO	-1.723
2	*COOH+H ⁺ +e ⁻ →*CO+H ₂ O	-0.618
	*OCHO+H ⁺ +e ⁻ →*OCHOH	0.307
3	*CO+H ₂ O+H ⁺ +e ⁻ →*CHO+H ₂ O	0.538
	*CO+H ₂ O+H ⁺ +e ⁻ →*COH+H ₂ O	0.710
	*OCHOH + H ⁺ + e ⁻ → *CHO + H ₂ O	1.060
	*OCHOH + H ⁺ + e ⁻ → *OCH + H ₂ O	1.404
4	*CHO+H ₂ O+H ⁺ +e ⁻ →*OCH ₂ +H ₂ O	-1.271
5	*OCH ₂ +H ₂ O +H ⁺ +e ⁻ →*OCH ₃ +H ₂ O	-0.651
6	*OCH ₃ +H ₂ O+H ⁺ +e ⁻ →*CH ₃ OH+H ₂ O	-0.118
	*OCH ₃ +H ₂ O+H ⁺ +e ⁻ →*O+CH ₄ +H ₂ O	0.547
7	*CH ₃ OH+H ₂ O+H ⁺ +e ⁻ →*OH+CH ₄ +H ₂ O	-0.397
	CH ₃ OH+H ₂ O→+CH ₃ OH+H ₂ O	1.247
8	*OH+CH ₄ +H ₂ O+H ⁺ +e ⁻ →*+CH ₄ +2H ₂ O	0.106

Table S. 7 Gibbs free energy changes for each protonation step of Nd-N₆C electrocatalytic CO₂ reduction

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	*+CO ₂ +H ⁺ +e ⁻ →*COOH	0.639
	* + CO ₂ + H ⁺ + e ⁻ → *OCHO	-0.831
2	*OCHO + H + + e ⁻ →*OCHOH	0.632
3	*OCHOH + H ⁺ + e ⁻ →*CHO + H ₂ O	1.196
	*OCHOH + H ⁺ + e ⁻ → *OCH + H ₂ O	1.054
	*OCHOH → * + HCOOH	0.117

Table S. 8 Gibbs free energy changes for each protonation step of Sm-N₆C electrocatalytic CO₂ reduction

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	*+CO ₂ +H ⁺ +e ⁻ →*COOH	1.122
	* + CO ₂ + H ⁺ + e ⁻ → *OCHO	-0.232
2	*OCHO + H ⁺ + e ⁻ →*OCHOH	-0.161
3	*OCHOH + H ⁺ + e ⁻ →*CHO + H ₂ O	1.260
	*OCHOH + H ⁺ + e ⁻ → *OCH + H ₂ O	1.321
	*OCHOH → * + HCOOH	0.310

Table S. 9 Gibbs free energy changes for each protonation step of Tb-N₆C electrocatalytic CO₂ reduction

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	*+CO ₂ +H ⁺ +e ⁻ →*COOH	0.997
	* + CO ₂ + H ⁺ + e ⁻ → *OCHO	-0.342
2	*OCHO + H ⁺ + e ⁻ → *OCHOH	-0.105
3	*OCHOH + H ⁺ + e ⁻ → *CHO + H ₂ O	1.215
	*OCHOH + H ⁺ + e ⁻ → *OCH + H ₂ O	1.454
	*OCHOH → * + HCOOH	0.364

Table S. 10 Er-N₆C electrocatalytic CO₂ reduction by intermediate reaction steps and Gibbs free energy change

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	*+CO ₂ +H ⁺ +e ⁻ →*COOH	1.019
	* + CO ₂ +H ⁺ +e ⁻ →*OCHO	-0.306
2	*OCHO+H ⁺ +e ⁻ →*OCHOH	-0.180
3	*OCHOH + H ⁺ + e ⁻ → *CHO + H ₂ O	1.271
	*OCHOH + H ⁺ + e ⁻ → *OCH + H ₂ O	1.518
	*OCHOH → * + HCOOH	0.402

Table S. 11 Tm-N₆C electrocatalytic CO₂ reduction for each protonation step

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	*+CO ₂ +H ⁺ +e ⁻ →*COOH	1.032
	* + CO ₂ +H ⁺ +e ⁻ →*OCHO	-0.187
2	*OCHO+H ⁺ +e ⁻ →*OCHOH	-0.260
3	*OCHOH + H ⁺ + e ⁻ → *CHO + H ₂ O	1.263
	*OCHOH + H ⁺ + e ⁻ → *OCH + H ₂ O	2.894
	*OCHOH → * + HCOOH	0.365

Table S. 12 Yb-N₆C electrocatalytic CO₂ reduction for each protonation step

n(H ⁺ +e ⁻)transferred	Chemical reaction equation	ΔG
1	*+CO ₂ +H ⁺ +e ⁻ →*COOH	0.989
	* + CO ₂ +H ⁺ +e ⁻ →*OCHO	-0.283
2	*OCHO+H ⁺ +e ⁻ →*OCHOH	-0.254
3	*OCHOH + H ⁺ + e ⁻ → *CHO + H ₂ O	1.302
	*OCHOH + H ⁺ + e ⁻ → *OCH + H ₂ O	1.472
	*OCHOH → * + HCOOH	0.454