Electronic Supplementary Material (ESI) for Nanoscale.

Cu atomic chains supported on *β*-Borophene sheets for effective CO_2 electroreduction

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1. Computational Hydrogen Electrode (CHE) Model[1]

The chemical potential of the proton-electron pairs (H^++e^-) can be related to the chemical potential of H_2 by setting the reference potential as the reversible hydrogen electrode (RHE). In this case, at pH = 0 in the electrolyte and 1 bar of H_2 in the gas phase at 298.15 K, the reaction of eq (1) reaches equilibrium at an electrode potential of U = 0. Thus, the chemical potential of the proton-electron pairs (H^++e^-) is equal to half the chemical potential of gaseous H_2 at 0 V (vs. RHE). The effect of the applied bias U is considered in eq (2).

$$H^+ + e^- \leftrightarrow \frac{1}{2}H_2 \tag{1}$$

$$\mu(H^+) + \mu(e^-) = \frac{1}{2}\mu(H_{2(g)}) - eU \tag{2}$$

In order to get the accurate free energies of the elementary reactions, solvation corrections are included in the CHE model. The reactions are proceed in aqueous solution and the solvation corrections are well studied in previous works.[2, 3] Directly bound OH adsorbates are stabilized by 0.50 eV and indirectly bound OH containing adsorbates like COOH are stabilized by 0.25 eV. For CO or CHO containing adsorbates, the energy stabilization is 0.10 eV.

The Gibbs free energy differences (ΔG) for all electrocatalytic steps are defined as

$$\Delta G = \Delta E + \Delta E_{zpe} - T\Delta S + \Delta GpH \quad (3)$$

The entropy effects of these adsorbates are much less than those of the gas-phase species. The values of *TS* are close among the adsorbates and can be canceled out through free energy calculation. The entropy effects of the gas-phase species cannot be ignored. Therefore, we use the energies of thermodynamic experimental data as a reference and the energies are shown in Table S1 as well as the corrections.[1, 4]

Table S1 Energy data and correction of small molecules. (p = 1 bar)

	E(eV)	E_{zpe}(eV)	TS(eV)	G(eV)
H_2(g)	-6.760	0.284	0.404	-6.880
H_2O(l)	-14.226	0.566	0.672(g)	-14.332
CO(g)	-14.799	0.133	0.611	-15.277
CO_2(g)	-22.993	0.304	0.661	-23.350
HCHO(g)	-22.144	0.731	0.676	-22.089
CH_3OH(l)	-30.217	1.391	0.741(g)	-29.611
CH_4(g)	-24.030	1.219	0.576	-23.387

2. DOS of Cu_1@B, Cu_4@B and Cu_∞@B

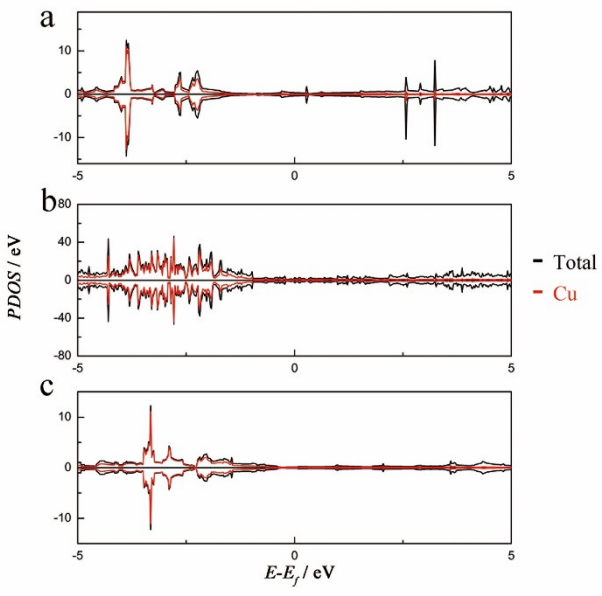

Figure. S1. Density of states for a) Cu_1@B, b) Cu_4@B and c) Cu_∞@B. Total dos and Cu orbitals are denoted as black and red, respectively.

3. Adsorption Coverage Simulation on Cu∞@B

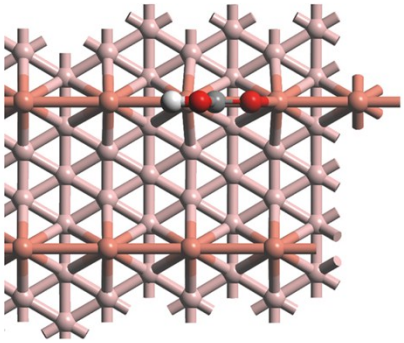

Fig. S2. COOH* adsorbates on Cu∞@B at different coverage. a) 100% coverage, b) 50% coverage with interlaced adsorptions, c) 12.5% coverage with interlaced adsorptions.

Table S2 Overpotential of COOH* Adsorption Elementary Step at Different Coverage.

Coverage	Interlaced Adsorption	E(eV)
100 %	N	0.795
50 %	N	0.207
33.3 %	N	0.184
25 %	N	0.180
50 %	Y	0.143

12.5 %		Y	1.391

4. Structure Optimization of CHO* and CO* Adsorbates

Table S3 Structure properties of CHO* intermediates

	Cu_1@B	Cu_2@B	Cu_3@B	Cu_4@B	Cu_5@B	Cu_6@B	Cu_∞@B
d(c-m) /Å	1.944	1.924	1.919	1.917	1.918	1.918	1.917
d(c=o) /Å	1.214	1.263	1.264	1.266	1.264	1.264	1.266
d(m-o) /Å		2.002	1.980	1.982	1.980	1.979	1.975

Table S4 Structure properties of CO intermediates

	Cu_1@B	Cu_2@B	Cu_3@B	Cu_4@B	Cu_5@B	Cu_6@B	Cu_∞@B
d(c-m) /Å	1.817	1.817	1.810	1.811	1.810	1.812	1.809
d(c=o) /Å	1.159	1.159	1.160	1.159	1.159	1.158	1.157

5. Energy Analyses

Table S5 Free energies of different adsorption steps on Cu_n@B sheet

Adsorbate	n(H^++e^-) transferred	Cu_1@B	Cu_2@B	Cu_3@B	Cu_4@B	Cu_5@B	Cu_6@B	Cu_∞@B
*	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
COOH	1	0.66	0.10	0.03	-0.03	-0.01	0.03	0.04
CO	2	-0.11	-0.15	-0.20	-0.20	-0.21	-0.23	-0.11
*+CO	2	0.62	0.62	0.62	0.62	0.62	0.62	0.62
CHO	3	0.90	0.42	0.32	0.27	0.28	0.31	0.33
CH2O	4	0.72	0.64	0.50	0.47	0.52	0.61	0.67
CHOH	4	1.44	1.48	1.39	1.38	1.34	1.44	1.37
*+CH2O(l)	4	0.69	0.69	0.69	0.69	0.69	0.69	0.69
OCH3	5	0.58	-0.27	-0.24	-0.24	-0.17	-0.16	-0.10
CH2OH	5	0.66	0.26	0.16	0.17	0.16	0.26	0.29
*+CH3OH(l)	6	0.05	0.05	0.05	0.05	0.05	0.05	0.05

References

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