Supporting Information

Tuning CO Binding Strength via Engineering Copper/Borophene Interface for Highly Efficient Conversion of CO into Ethanol

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Free Energy Calculation:

The free energies for all the states are calculated by:

$$G = E + ZPE + \int C_p dT - TS$$

Where the zero point energies (ZPE), enthalpic temperature correction ($\int C_p dT$) and entropy correction (TS) were computed on the basis of vibration analysis obtained by standard methods and used to convert the electronic energies in to free energies at 298.15 K[1] (Table S1); gase-phase free energies were obtained by standard methods as well (Table S2).

The computational hydrogen electrode (CHE) model was applied to include the electrode potential correction to the free energy of each state, by considering the electrochemical proton-electron transfer being a function of the applied electrical potential.[2, 3] In this model, the free energy of a proton-electron pair at 0V vs RHE is defined to be equal to ½ of the H_2 free energy at 101,325 Pa. The free energy of each intermediate, calculated at 298.15 K, is then a function of the electrode potential (U) according to G(U) = G(0V) − neU, where e is the elementary charge of an electron, n is the number of proton-electron pairs transferred to the investigated intermediate or final states. The application

of this equation to an elementary reaction pathway results in the electrode potential corrected free energy pathway, therefore provides a venue to evaluate at which potential a certain CO electroreduction pathway opens, as well as defining the potential dependent reaction step. In the current study, the relative free energies of the reaction intermediates were taken only as an indication the starting point of different pathways in the electroreduction of CO, since reaction barriers were not considered. As indicated in earlier studies, barriers for proton transfer to adsorbates from solution are normally low enough to be surmountable at room temperatures[4]
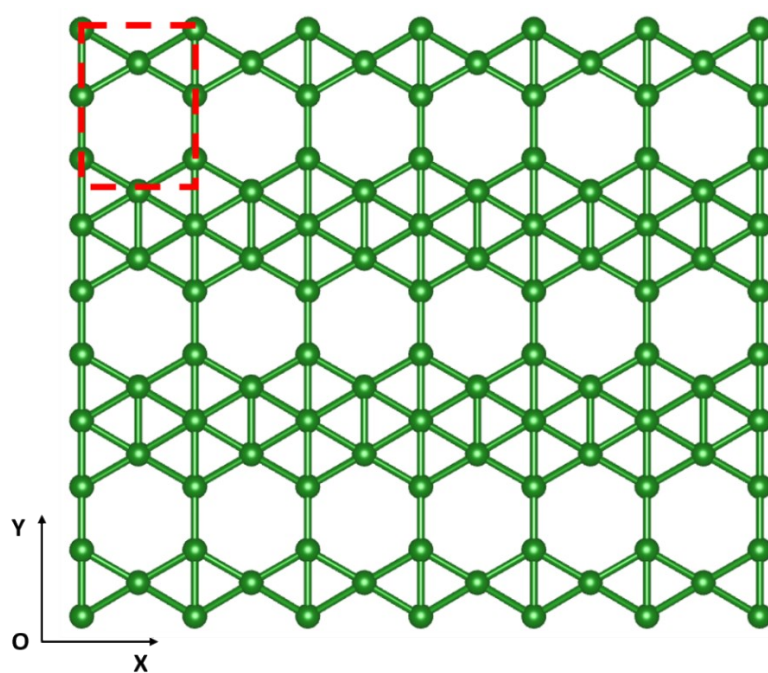

Figure S1 the β_{12} borophene nanosheet with a peculiar distribution of filled and empty hexagons structure
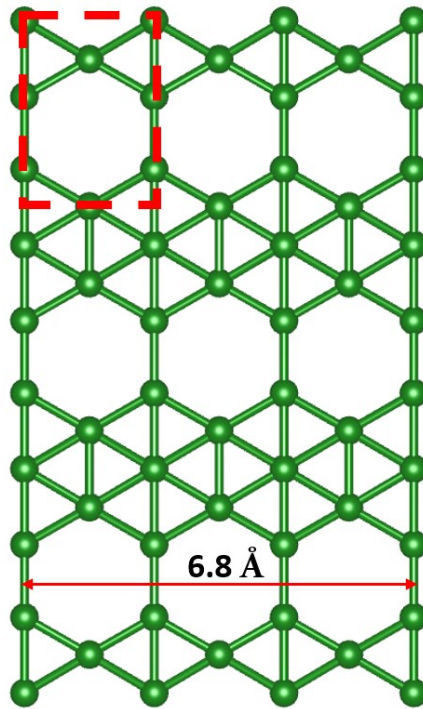
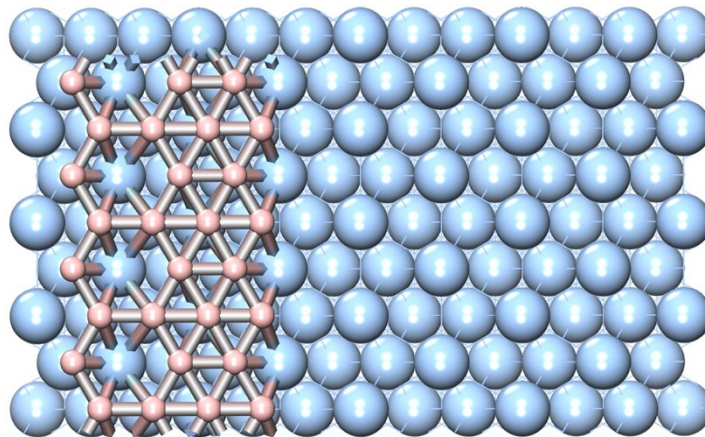**Figure S2** the β_{12} borophene nanoribbon

Figure S3 the atomic structure of borophene nanoribbon on Ag (111) surface.
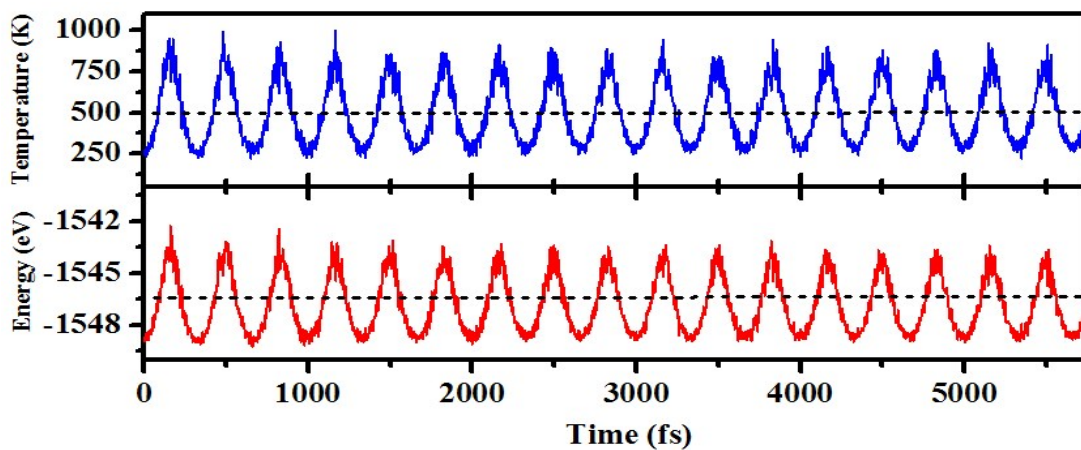
Figure S4 variations of temperature and energy versus the AIMD simulation time for borophene nanoribbon on Cu (111) surface at T = 500 K.
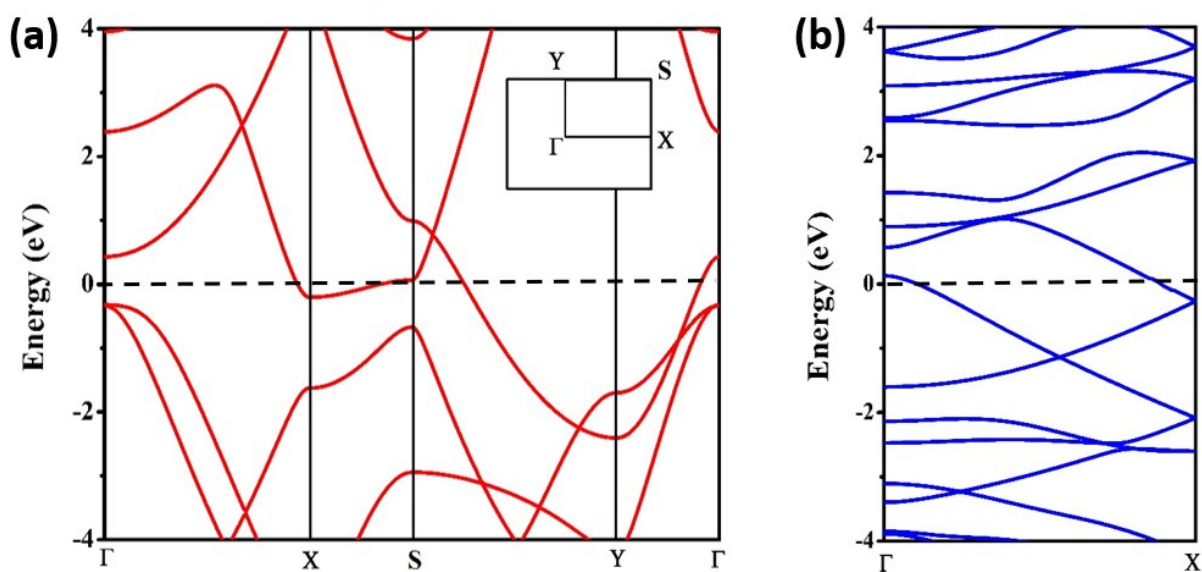

Figure S5 band structure of (a) borophene nanosheet and (b) borophene nanoribbon. The Fermi level is set to zero.
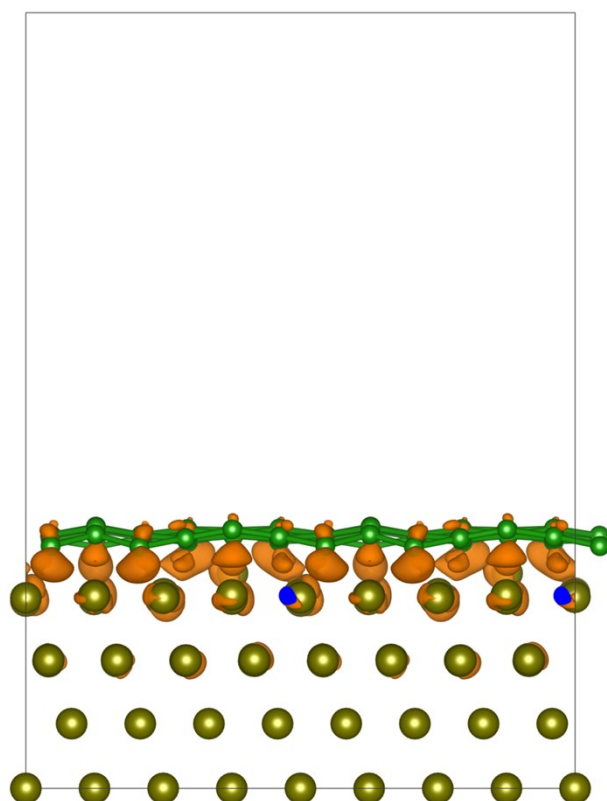
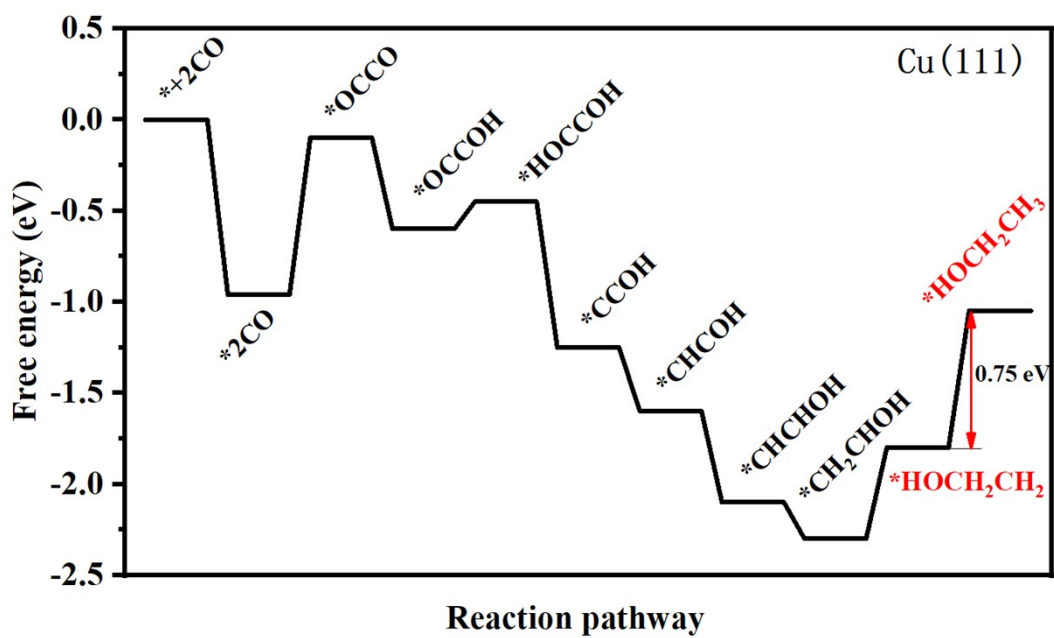**Figure S6** the charge distribution at the Cu-B interface.

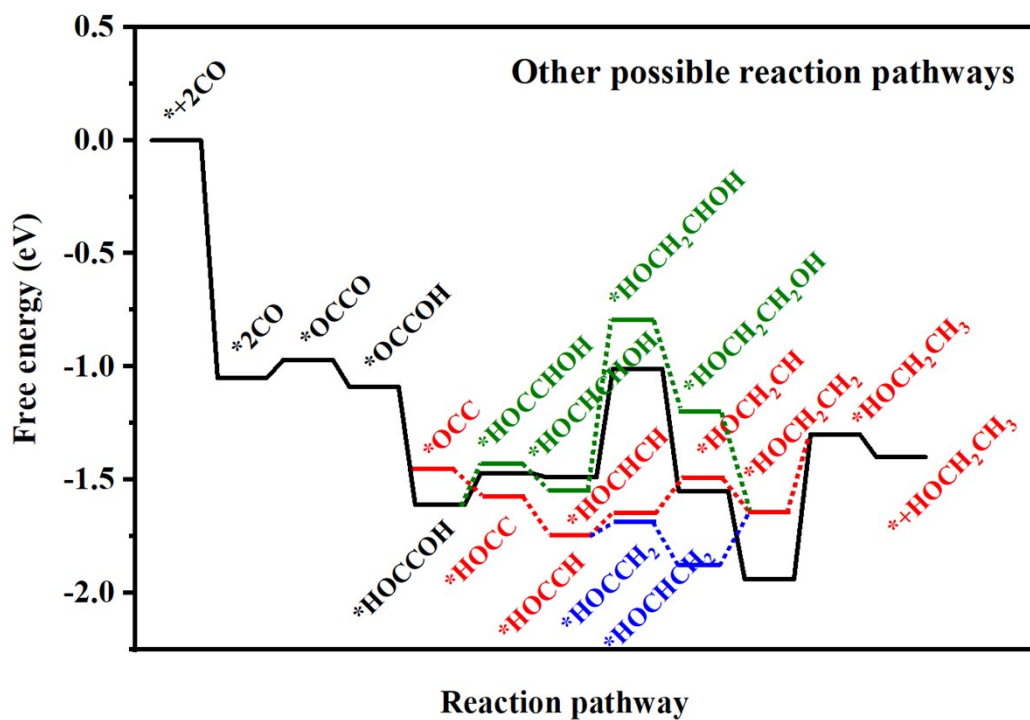**Figure S7** the reaction profile of CO on bare Cu(111) surface.

Figure S8 the other possible reaction pathways on Cu-B interface.

Table S1 Computed gas phase properties in eV.

Gas molecule	ZPE	$\int C_p dT$	-TS
CO	0.12	0.09	-0.58
C_2H_4	1.38	0.12	-0.44
CH_3CH_2OH	2.16	0.16	-0.59

Table S2 Computed corresponding thermodynamic energy corrections (in eV) for key adsorbates.

Species	ZPE	Cpdt	TS
2CO	0.429	0.128	0.259
OCCO	0.441	0.104	0.192
OCCOH	0.764	0.109	0.196
HOCCOH	1.097	0.116	0.206
OCC	0.332	0.072	0.129
HOCCHOH	1.251	0.092	0.151
HOCCH	0.983	0.078	0.135
HOCHCHOH	1.695	0.12	0.206
HOCCH$_2$	1.265	0.089	0.162
H$_2$CCH	1.134	0.051	0.079
HOCHCH$_2$	1.579	0.087	0.146
H$_2$CCH$_2$	1.443	0.067	0.129
HOCH$_2$CH$_2$	1.869	0.119	0.226
HOCH$_2$CH$_3$	2.148	0.154	0.312
H$_3$CH$_2$	1.735	0.098	0.207
HOCH$_2$CHOH	1.981	0.158	0.333

References:

1.   Cramer, C. J., *Essentials of computational chemistry: theories and models*. John Wiley & Sons: 2013.
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3.   Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S. Z., Origin of the electrocatalytic oxygen reduction activity of graphene-based catalysts: a roadmap to achieve the best performance. *J. Am. Chem. Soc.* **2014,** *136* (11), 4394-4403.
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