Electronic Supplementary Information (ESI)

Cu_2B_2 Monolayer with Planar Hypercoordinate Motifs: an Efficient Catalyst for CO Electroreduction to Ethanol

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Computional Details on Dissolution Potential and Overpotential

To evaluate the stability of Cu_2B_2 monolayer in strong acidic media, we computed the dissolution potentials (U_{dis}, in V) of Cu in Cu_2B_2 monolayer at pH=0, which was defined as: $U_{dis} = U_{Cu}^{0} + \left[E_{Cu,bulk} - \left(E_{Cu_2B_2} - E_{d-Cu_2B_2}\right)\right]/ne$, where U_{Cu}^{0} is the standard dissolution potential of Cu in the bulk form (0.34 V), d-Cu_2B_2 is the defective Cu_2B_2 monolayer by dissolving (removing) one Cu to solutions, and *n* is the coefficient for the aqueous dissolution reaction: $Cu + 2H^+ \leftrightarrow Cu^{2+} + H_2$, namely, *n* equals to 2. According to this definition, the U_{dis} value of Cu in Cu_2B_2 monolayer is computed to be about 1.76 V.

On the other hand, the overpotential (η) value was obtained according to the following equation: $\eta = U_0 - U_L$, where U_0 is the computed equilibrium potential of COR to C_2H_5OH production ($U_0 = -(\Delta G)/n$), and U_L is the limiting potential of COR on Cu_2B_2 monolayer (−0.59 V). Since the ΔG value for CO reduction to C_2H_5OH ($2CO + 8H^+ + 6e^- \rightarrow C_2H_5OH + H_2O$ in Fig. 5a) was computed to be −1.85 eV, the computed U_0 is [− (−1.85)/8) = 0.23 V]. Thus, the negative overpotential (−η) of COR on Cu_2B_2 monolayer is –[0.23 V – (−0.59 V)] = −0.82 V, which is much smaller than the U_{dis} value of Cu (1.76 V), suggesting that Cu within the Cu_2B_2 framework can survive under the realistic experimental conditions of CORR, and thus ensuring their excellent long-term stability.

Table S1. The computed free energy changes of each possible elementary step during the electrochemical reduction of CO to C_2H_5OH on Cu_2B_2 monolayer.

Elementary step	Free energy change (ΔG)
$CO\ (g) \rightarrow {}^*CO$	**–0.77**
${}^*CO + H^+ + e^- \rightarrow {}^*COH$	**0.59**
${}^*CO + H^+ + e^- \rightarrow {}^*CHO$	0.71
${}^*COH + H^+ + e^- \rightarrow {}^*CHOH$	**–0.01**
${}^*COH + H^+ + e^- \rightarrow {}^*C + H_2O$	1.28
${}^*CHOH + H^+ + e^- \rightarrow {}^*CH_2OH$	**–0.22**
${}^*CHOH + H^+ + e^- \rightarrow {}^*CH + H_2O$	1.74
${}^*CH_2OH + H^+ + e^- \rightarrow {}^*CH_2 + H_2O$	**–0.77**
${}^*CH_2OH + H^+ + e^- \rightarrow CH_3OH^*$	0.04
${}^*CH_2 + CO\ (g) + e^- \rightarrow {}^*CH_2CO$	**–0.20**
${}^*CH_2CO + H^+ + e^- \rightarrow {}^*CH_2CHO$	**–0.59**
${}^*CH_2CO + H^+ + e^- \rightarrow {}^*CH_3CO$	–0.39
${}^*CH_2CO + H^+ + e^- \rightarrow {}^*CH_2COH$	0.04
${}^*CH_2CHO + H^+ + e^- \rightarrow {}^*CH_2CH_2O$	**–0.68**
${}^*CH_2CHO + H^+ + e^- \rightarrow {}^*CH_3CHO$	0.18
${}^*CH_2CHO + H^+ + e^- \rightarrow {}^*CH_2CHOH$	2.29
${}^*CH_2CH_2O + H^+ + e^- \rightarrow {}^*CH_3CH_2O$	**0.07**
${}^*CH_2CH_2O + H^+ + e^- \rightarrow {}^*CH_2CH_3O$	0.54
${}^*CH_2CH_2O + H^+ + e^- \rightarrow {}^*CH_2CH_2OH$	1.06
${}^*CH_3CH_2O + H^+ + e^- \rightarrow CH_3CH_2OH + {}^*$	**0.53**

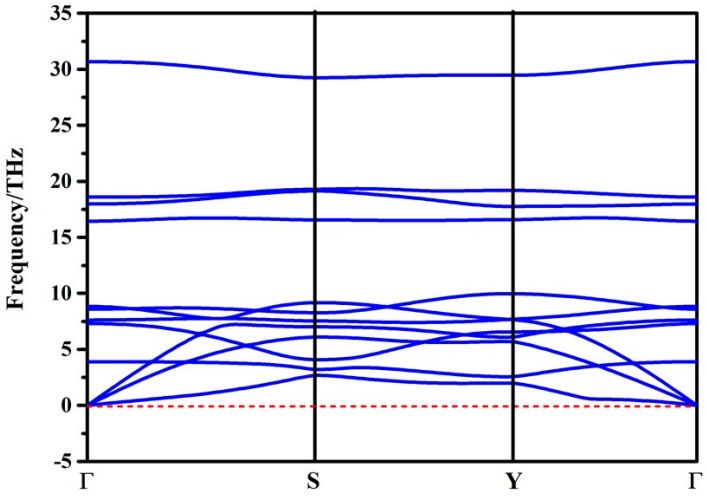

Figure S1. The computed phonon dispersions of the predicted Cu_2B_2 monolayer.

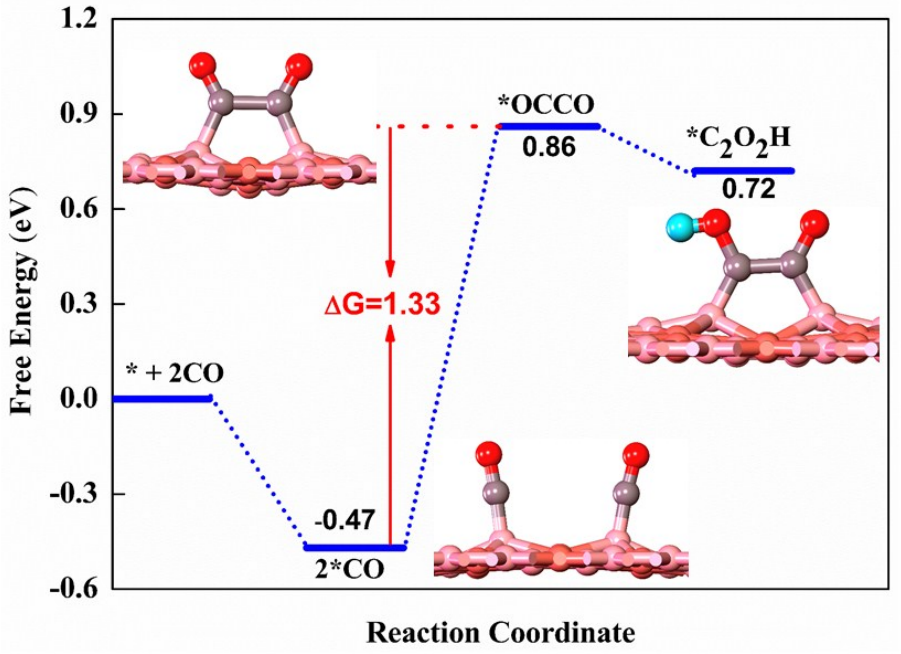

Figure S2. The computed free energy profiles for the C–C coupling through the CO direct dimerization on Cu_2B_2 monolayer and the corresponding structures of the reaction intermediates. Bronze, pink, gray, red, and cyan balls represent Cu, B, C, O, and H atoms, respectively.

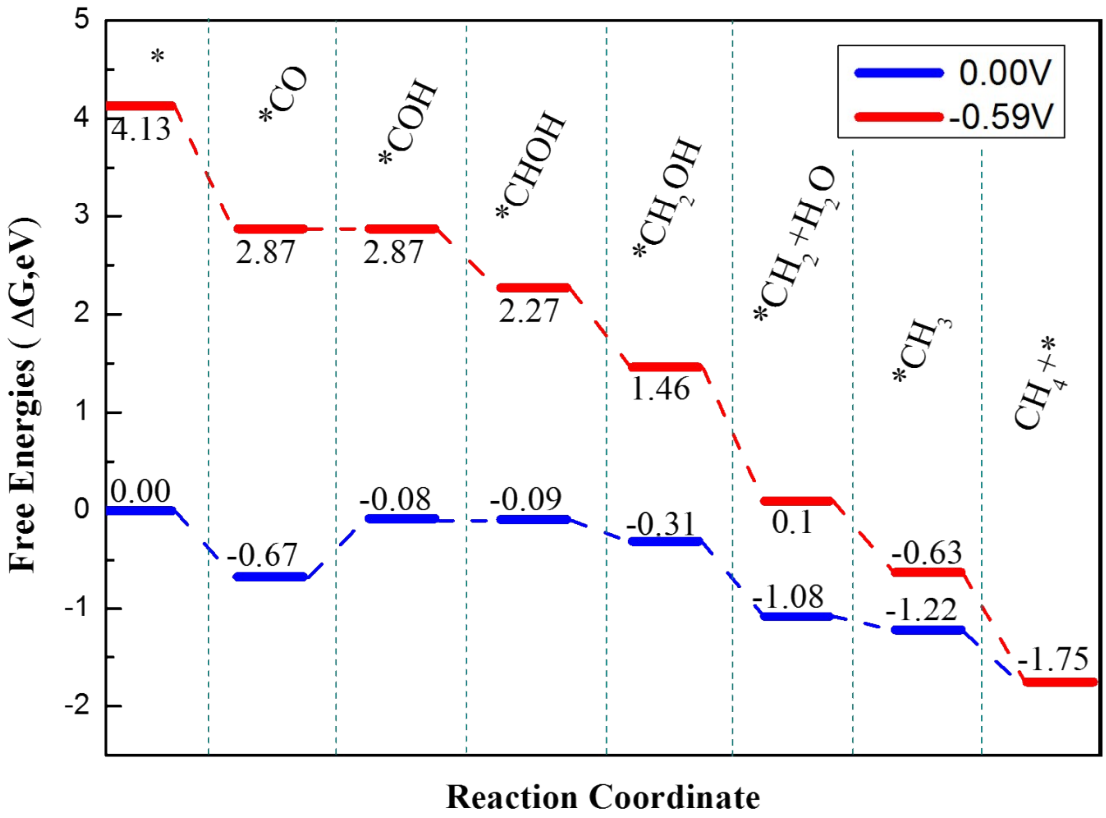

Figure S3. Gibbs free energy profiles for CO reduction to CH_4 on Cu_2B_2 monolayer surface at zero and applied potentials.

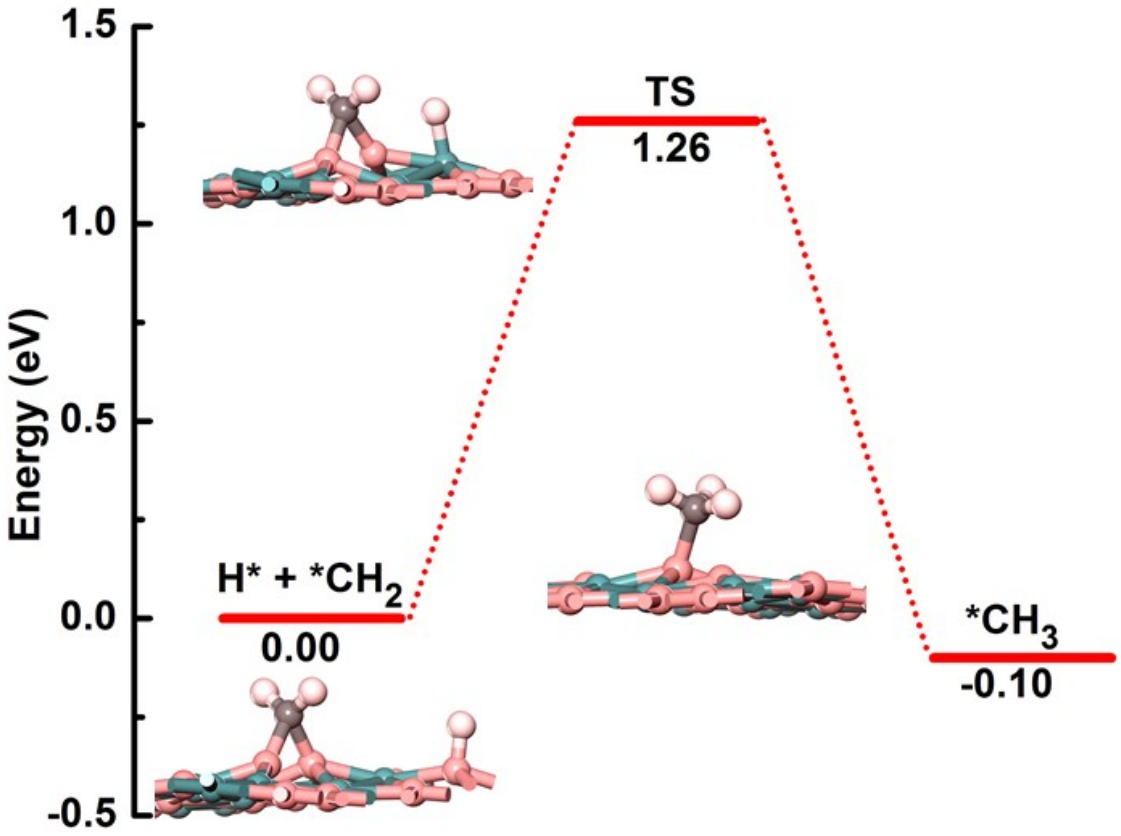

Figure S4. The kinetic reaction pathway of the hydrogenation of $^{*}CH_2$ species to $_{*}CH_3$ species. TS denotes the transition state.

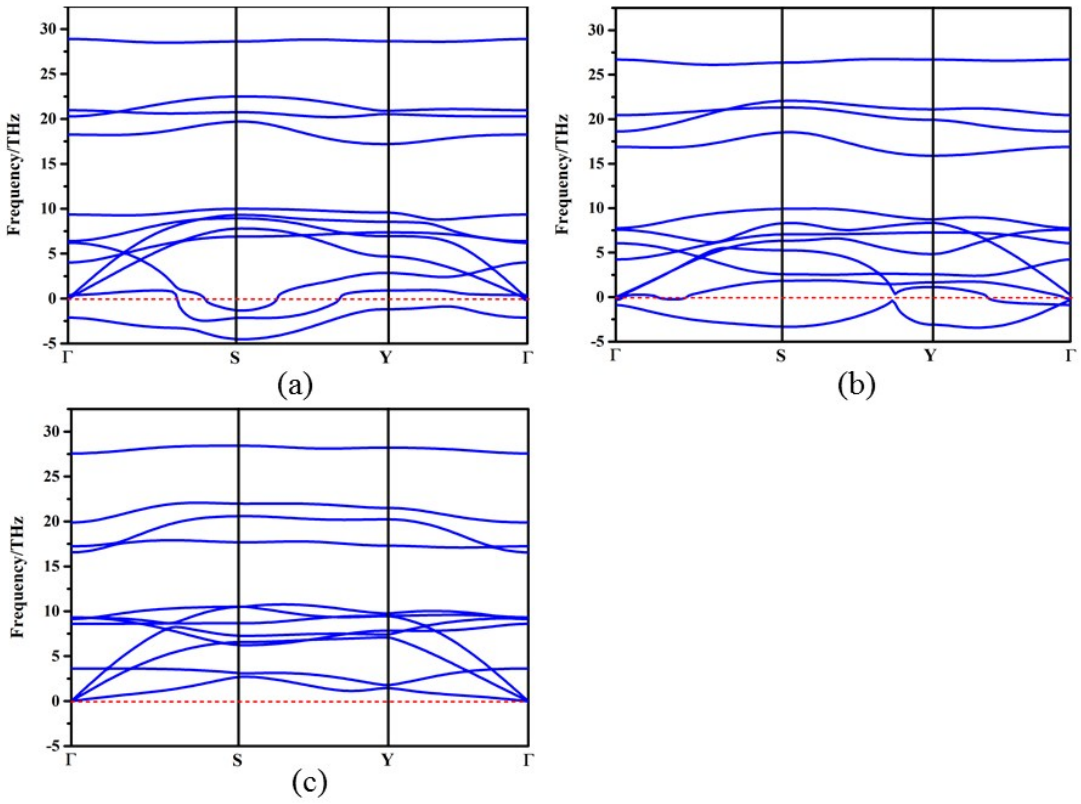

Figure S5. The computed phonon dispersion spectra of the predicted (a) Fe_2B_2, (b) Co_2B_2, and (c) Ni_2B_2 monolayers.

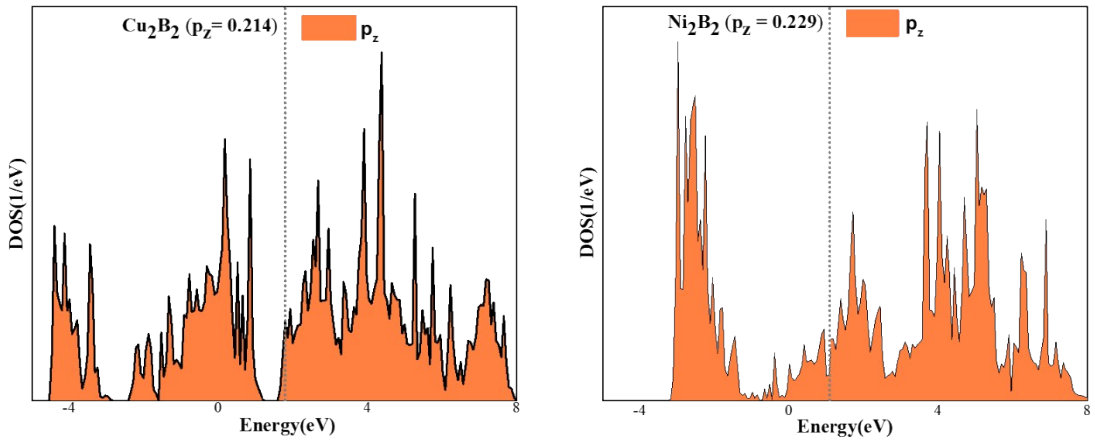

Figure S6. Density of states (DOS) of B-2p_z orbitals for (a) Cu_2B_2 and (b) Ni_2B_2 monolayers. The dashed lines indicate the Fermi level.