Supporting Information

Metal-Free Graphdiyne Doped with sp-Hybridized Boron and Nitrogen Atom at Acetylenic Sites for High-Efficient Electroreduction of CO_2 to CH_4 and C_2H_4

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Table S1. The total electronic energies (E_{tot}, Ha), zero-point energies (ZPE, eV), and entropy at room-temperature (TS, eV) for small molecules, including H_2, H_2O, CO, CO_2 CH_4, C_2H_4.

	E_{tot}	ZPE		TS	
		our work	experimental value[1]	our work	experimental value[1]
H_2	-1.16	0.27	0.28	0.42	0.40
H_2O	-76.39	0.56	0.56	0.60	0.58
CO	-113.23	0.13	0.13	0.61	0.61
CO_2	-188.48	0.31	0.30	0.66	0.66
CH_4	-40.47	1.19	1.22	0.64	0.58
C_2H_4	-78.50	1.36	1.34	0.71	0.67

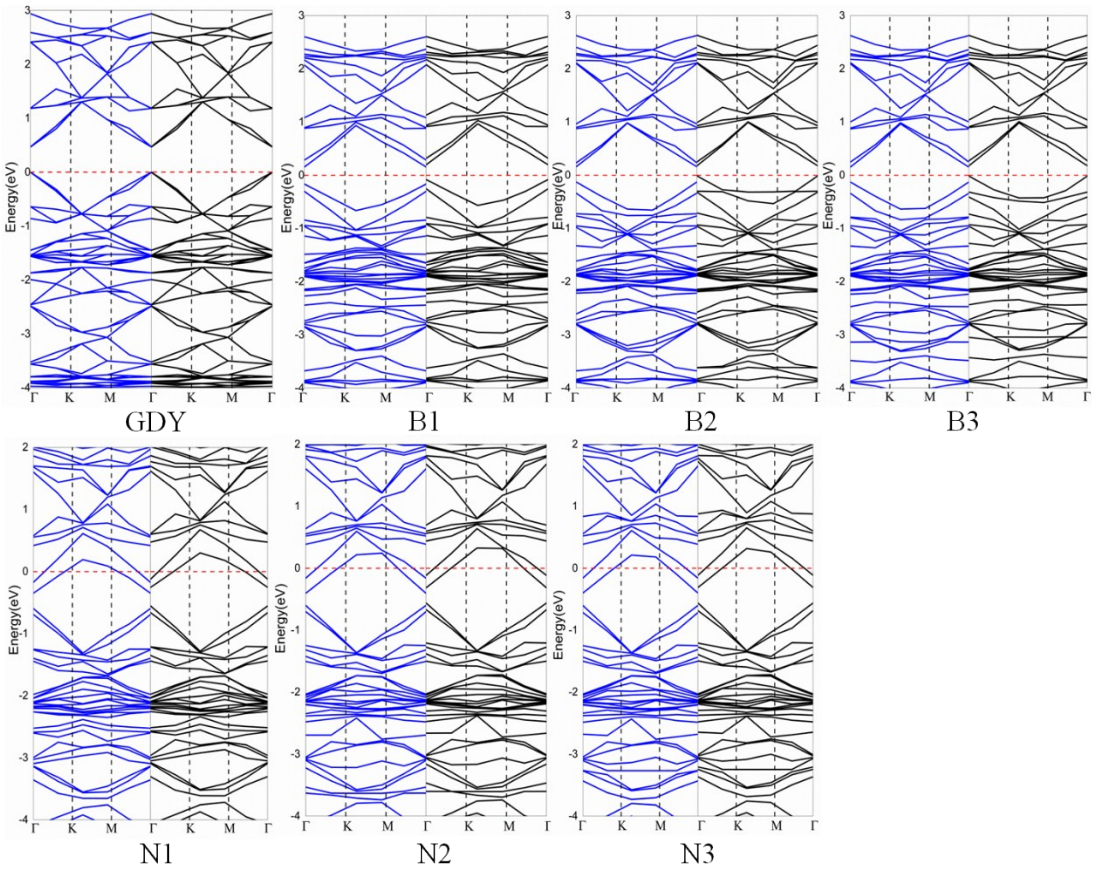


Figure S1. The computed band structures of pristine and various doped GDYs with B and N atom. The Fermi level is set as zero in red dotted line.

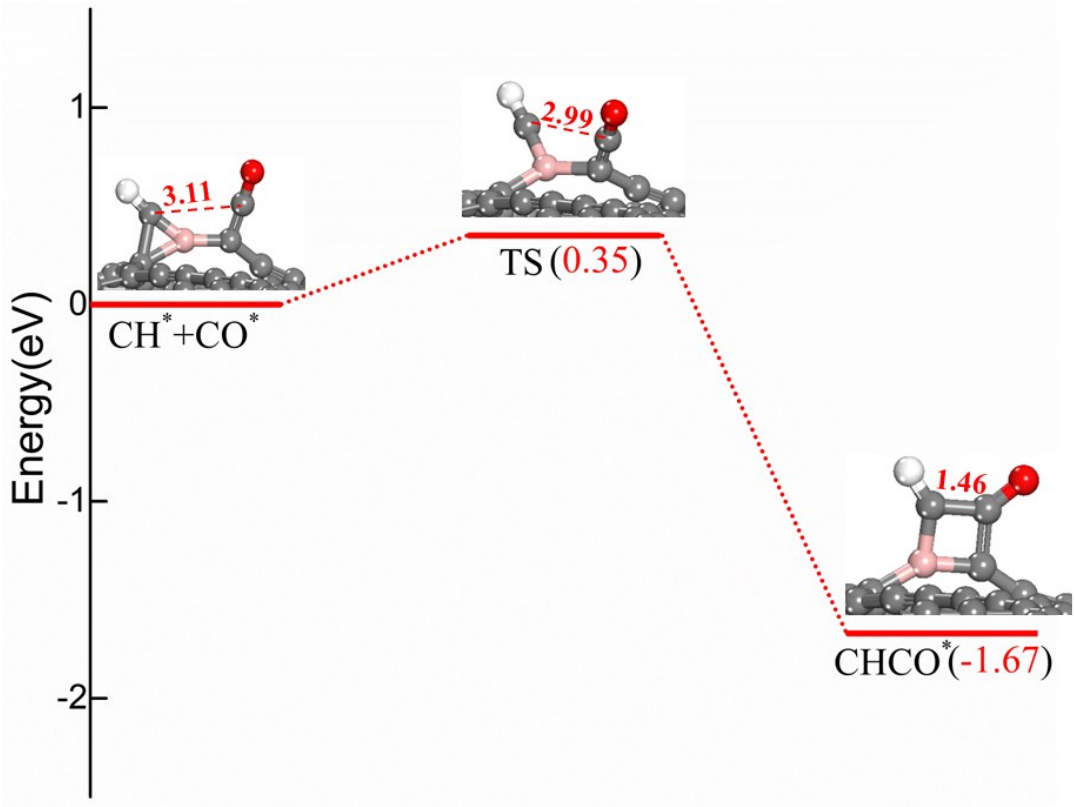
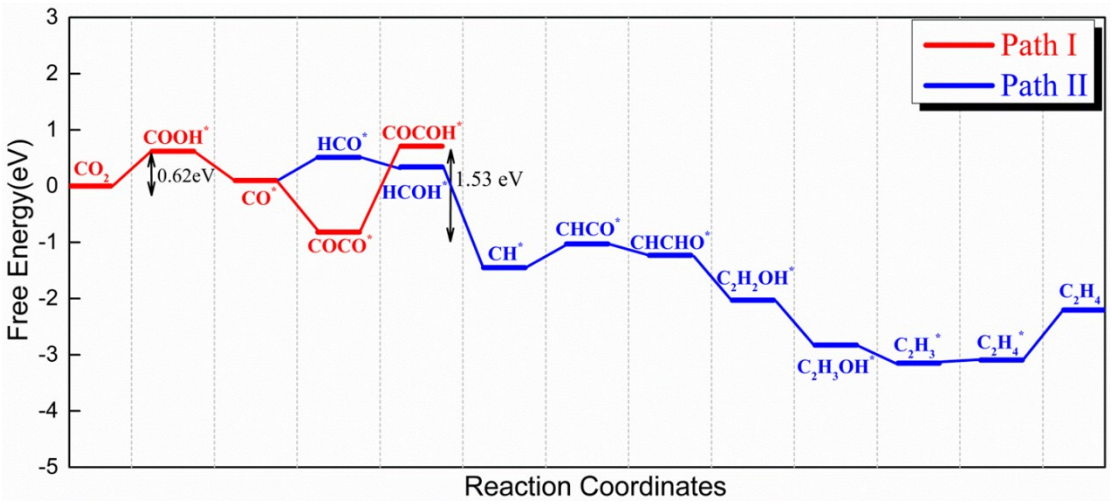
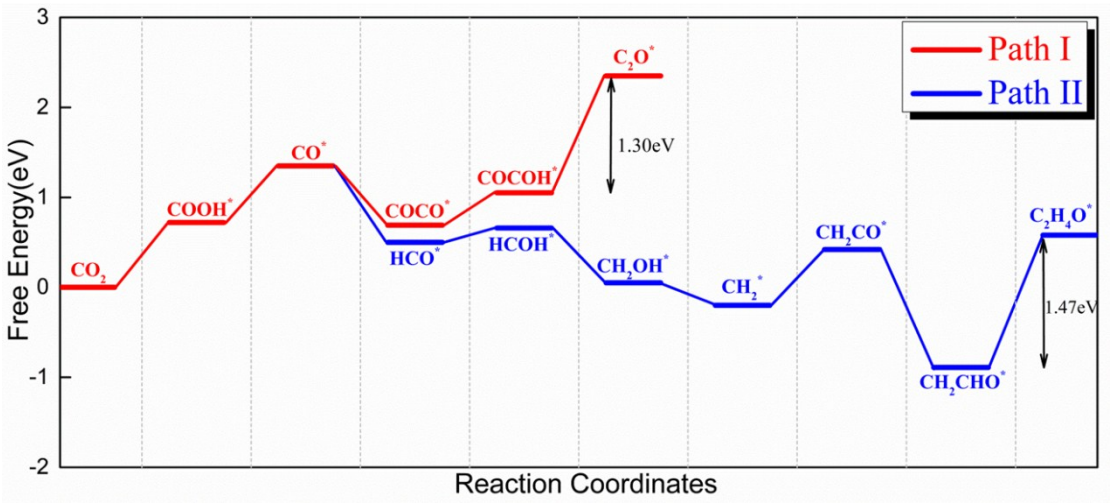


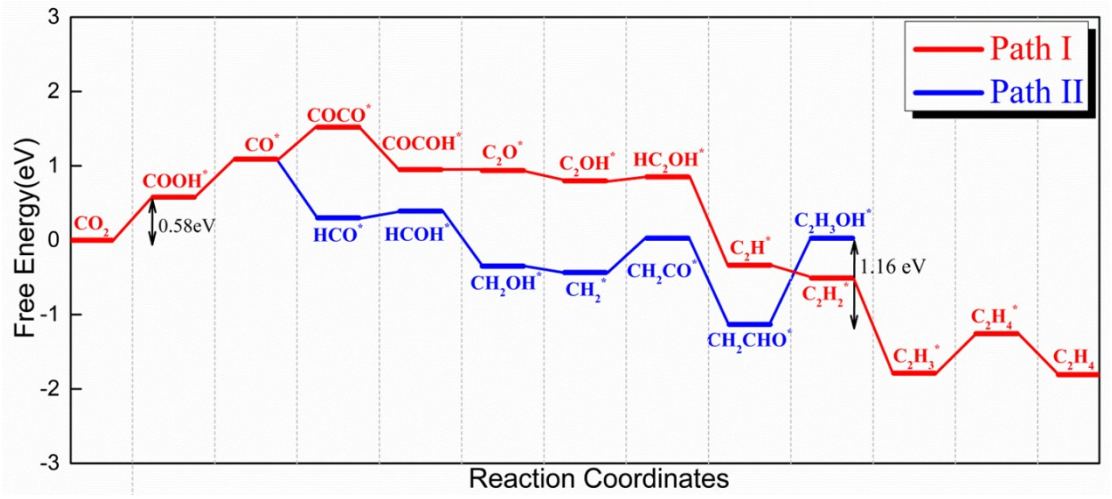
Figure S2. The obtained minimum reaction pathway for the C-C coupling of CH^* species with CO with LST/QST method.[2]



(a)



(b)



(c)

Figure S3. The computed free energy profiles of CO_2ER to C_2H_4 along path I and II on

B3, N1, and N2 surfaces.

References :

1. Computational Chemistry Comparison and Benchmark Database. http://cccbdb.nist.gov/.

2. N. Govind, M. Petersen, G. Gitzgerald, D. King-Smith and J. Andzelm, *J. Comput. Mater. Sci.*, 2003, **28**, 250