Electronic Supplementary Information for

Electrochemical CO_2 reduction on graphdiyne: a DFT Study

Tianfu Liu,[a] Qi Wang,*[b] Guoxiong Wang*[a] and Xinhe Bao[a]

[a] State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China. Email: wanggx@dicp.ac.cn

[b] Liaoning Key Materials Laboratory for Railway, School of Materials and Engineering, Dalian Jiaotong University, Dalian 116028, China. Email: qiwang@djtu.edu.cn

Computation setup

The calculations presented in the paper were performed using the periodic, spin-polarized DFT as implemented in the Vienna ab initio simulation package (VASP).[1, 2] The electron-ion interactions were described by the projector augmented wave (PAW) method proposed by Blochl[3] and implemented by Kresse[4]. The Perdew-Burke-Ernzerhof functional was used as an exchanged-correlation functional approximation[5] and a plane wave basis set with an energy cutoff of 400 eV was used. Gamma point was used for Brillouin zone sampling. For all the calculations, the van der Waals contributions were evaluated with a semiempirical method, from Grimme.[6] To model the graphdiyne, a cluster composed of 72 carbon atoms is used in a cell with 19.6 Å × 19.6 Å × 14 Å, and $\alpha = \beta = 90^\circ$, $\gamma = 60^\circ$, as shown in Figure 1. The graphene model is composed of 180 carbon atoms as shown in the inset of Figure 3. All atoms in the cell were allowed to relax during the structural optimization, and the optimization was stopped when the force residue was smaller than 0.05 eV/Å. The zero-point energy, enthalpy, and entropy corrections of the adsorbates were calculated to convert electronic energy to free energy.

The Gibbs free energy (G) at 0 V is corrected by Equation S(1).

$$G = E_{total} + ZPE - TS + \int C_p dT \qquad \text{S(1)}$$

where, E_{total} is the total energy obtained by DFT optimization, ZPE, S and $\int C_p dT$ are zero-point vibrational energy, entropy and heat capacity at 298.15 K and 1 atm. The energy details of different adsorbates are listed as shown in Table S1.

Supplementary Figures

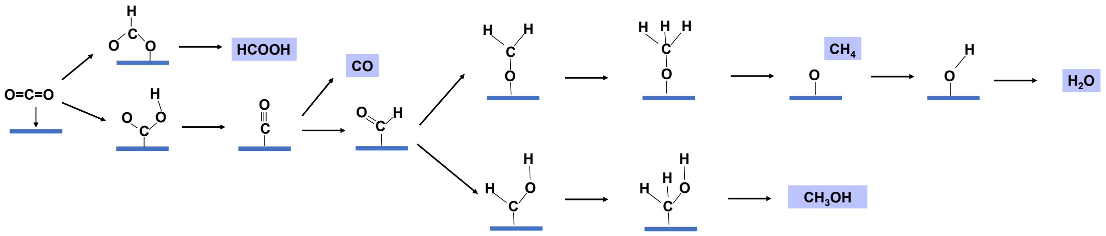

Figure S1. The CO$_2$RR reaction pathway for production of CO, HCOOH, CH$_3$OH and CH$_4$.

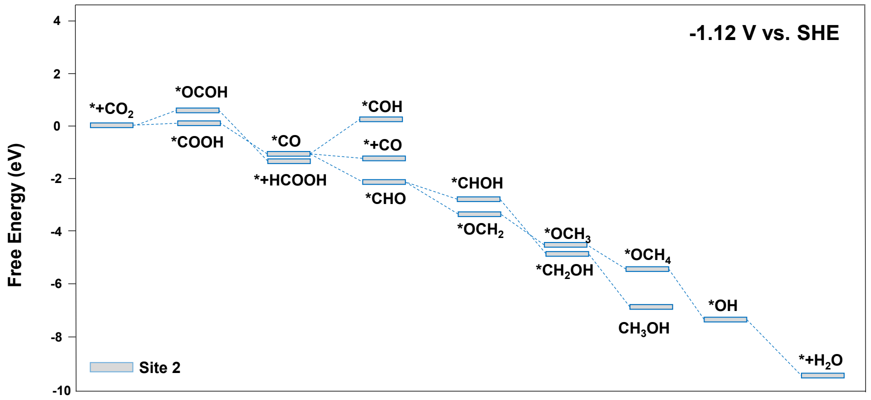

Figure S2. The free energy diagram of CO$_2$RR on Site 2 after applying -1.12 V vs. SHE.

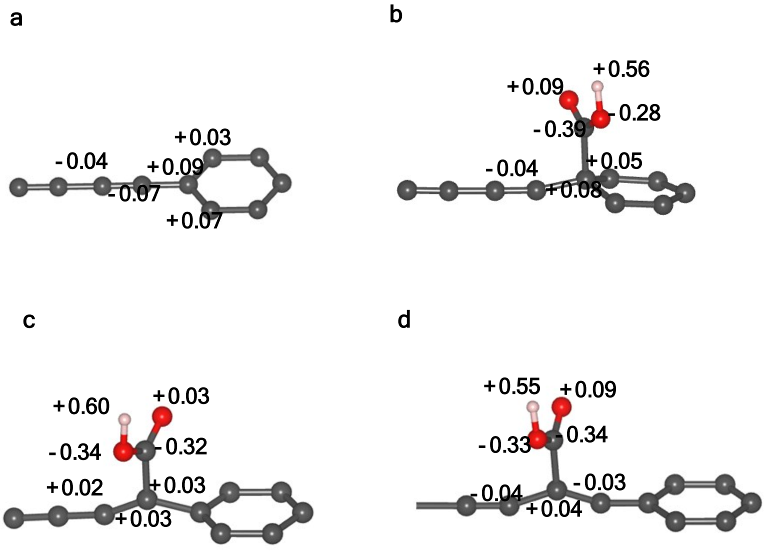

Figure S3. Bader charge analysis of (a) pristine graphdiyne, and *COOH adsorption on (b) site 1, (c) site 2, (d) site 3

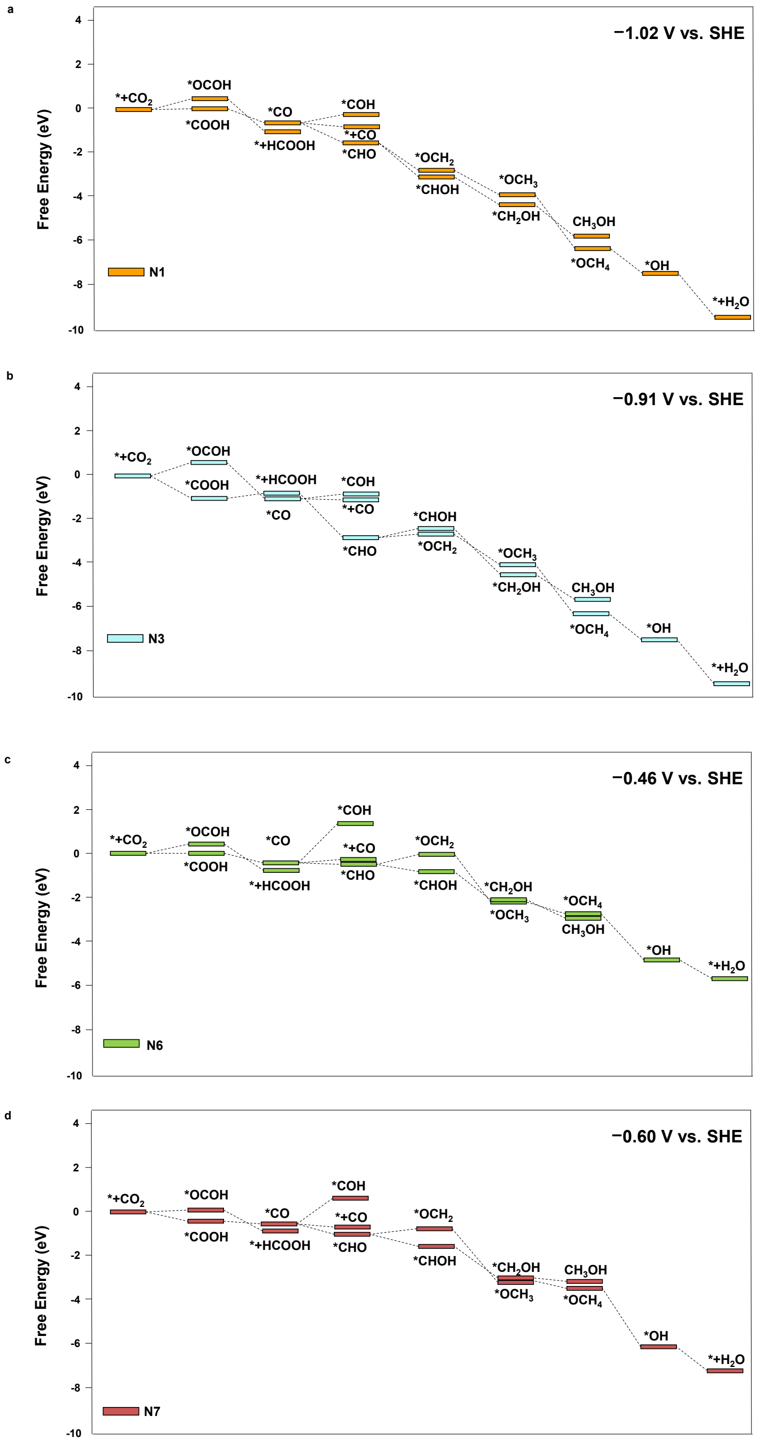

Figure S4. The free energy diagram of CO_2RR on N1, N3, N6, and N7 after applying −1.02 V, −0.91 V, −0.46 V, −0.60 V vs. SHE.

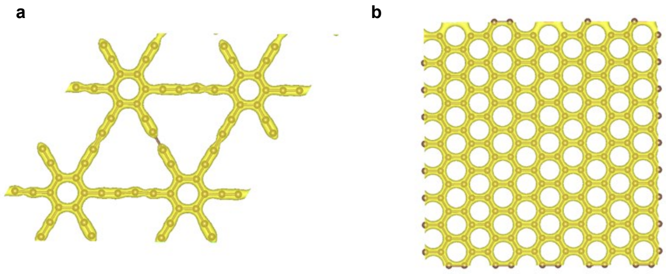

Figure S5. The charge density distribution of (a) graphdiyne, (b) graphene. The isosurface value is 0.002 e/bhor^3.

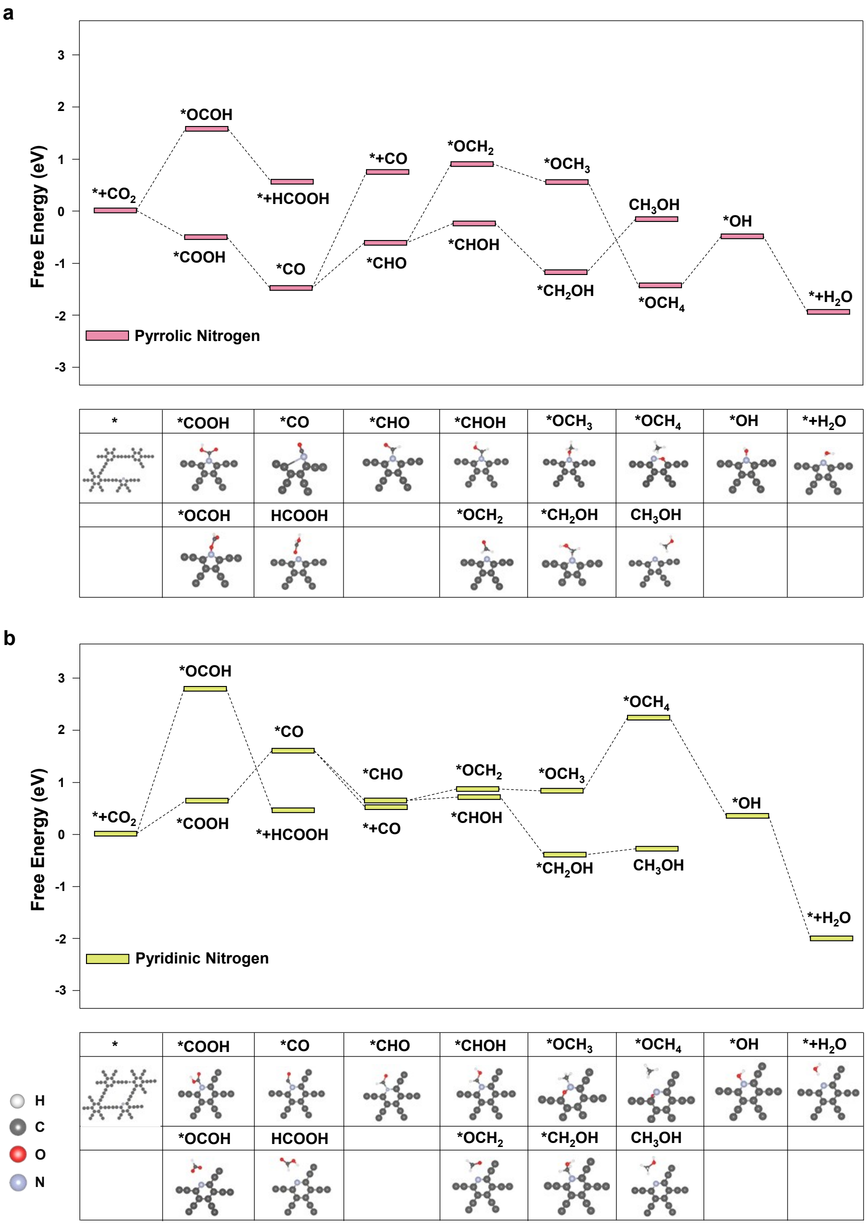

Figure S6. The free energy diagram of CO_2RR on pyrrolic and pyridinic nitrogen defects.

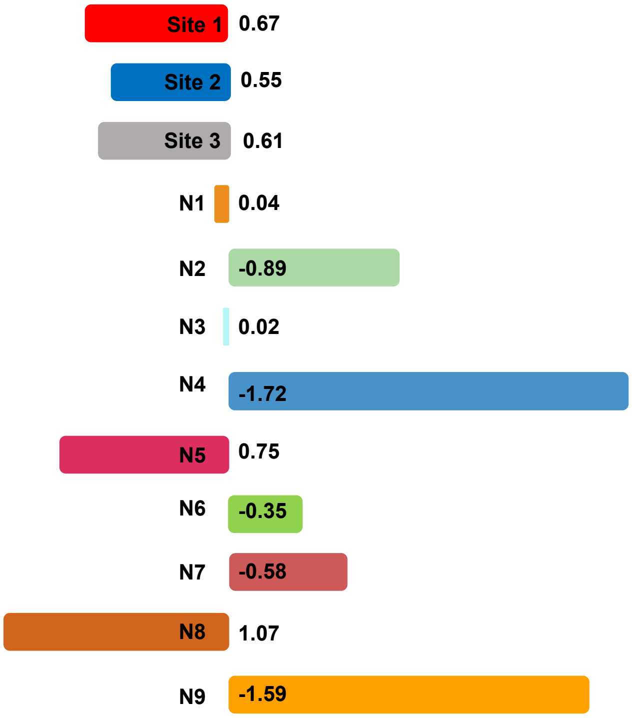

Figure S7. The adsorption free energy of *H adsorption on sites 1, 2, 3, and N1-N9.

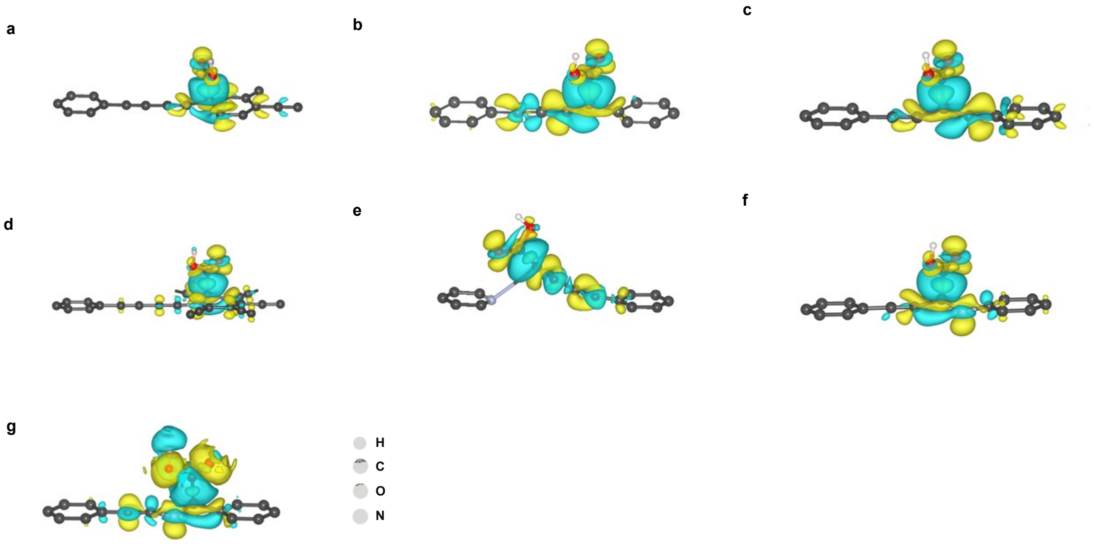

Figure S8. The charge density difference of *COOH adsorption on (a) Site 1, (b) Site 2, and (c) Site 3 of pristine graphdiyne, and (d) N1, (e) N3, (f) N6, and (g) N7 of nitrogen-doped graphdiyne, respectively. The isosurface value is 0.002 e/bhor^3. Yellow area represents charge accumulation, and cyan one represents charge depletion.

Table S1. The calculated free energy corrections for adsorbates. All values are given in eV

Adsorbate	Zero Point Energy	$\int C_p dT$	TS
*COOH	0.65	0.10	0.24
*OCOH	0.63	0.10	0.20
*CHO	0.51	0.07	0.15
*COH	0.50	0.05	0.09
*CHOH	0.85	0.07	0.15
*OCH_2	0.73	0.11	0.26
*CH	0.23	0.03	0.25
*CH_2OH	1.12	0.07	0.15
*OCH_3	1.12	0.09	0.19
*OH	0.39	0.04	0.07
*OCH_4	1.29	0.13	0.32

References:

1. G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15-50.
2. G. Kresse and J. Furthmüller, *Physical Review B*, 1996, **54**, 11169-11186.
3. P. E. Blöchl, *Physical Review B*, 1994, **50**, 17953-17979.
4. G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758-1775.
5. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys Rev Lett*, 1996, **77**, 3865-3868.
6. S. Grimme, *Journal of Computational Chemistry*, 2006, **27**, 1787-1799.