

Electronic Supplementary Information

γ -Graphyne Nanotubes as Defect-Free Catalysts of Oxygen Reduction Reaction: A DFT Investigation

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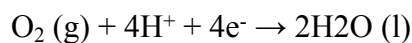
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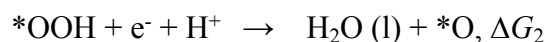
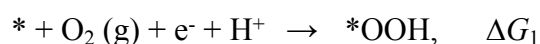
1. Detailed information about calculations on ORR energy profile.
2. Detailed information about calculations on hybridization state.
3. Pictorial representations of chiral vectors that define A- (n, n), Z- ($n, 0$), and C- (n, m)- γ GyNTs.
4. The optimized structures of all studied γ GyNTs.
5. Charge, curvature, diameter of different clear models and $\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4$ on different sites.
6. Q of C^{2-} and C^{2+} vs tube diameter.
7. Relationship among $\Delta G_{OH}, \Delta G_{OOH}$ and $\Delta G_O, \Delta G_{OOH}$ as a function of Q .
8. U_L as function of tube size (n).
9. Calculated energy profiles and structures of O_2 adsorption on selected systems.

Supplemental Note 1

The ORR process occurring on the cathode of a fuel cell or in discharge of an air battery can be described as:



It has been well studied that the ORR process takes place on graphyne materials via an efficient one-step four-electron mechanism. [1, 2] That is, in an acidic environment, the ORR occurred through four electron-proton coupling transfer reaction pathways as displayed below:



The free energy changes for each elementary step of the ORR process can be described as: $\Delta G_1 = \Delta G_{\text{OOH}} - 4.92$, $\Delta G_2 = \Delta G_{\text{O}} - \Delta G_{\text{OOH}}$, $\Delta G_3 = \Delta G_{\text{OH}} - \Delta G_{\text{O}}$, and $\Delta G_4 = -\Delta G_{\text{OH}}$. The Gibbs free energy difference in each step contains an electron transfer and can be obtained as bellow:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{\text{U}} + \Delta G_{\text{pH}}.$$

Here, ΔE , ΔZPE , and ΔS represent the energy difference of adsorption, zero-point energy, and entropy, respectively. ΔE is the electronic energy change upon intermediate adsorption, which can be computed as:

$$\Delta E_{\text{OOH}} = E_{*\text{OOH}} - E^* - [2E_{\text{H}_2\text{O}} - 3/2E_{\text{H}_2}],$$

$$\Delta E_{\text{O}} = E_{*\text{O}} - E^* - [E_{\text{H}_2\text{O}} - E_{\text{H}_2}],$$

$$\Delta E_{\text{OH}} = E_{*\text{OH}} - E^* - [E_{\text{H}_2\text{O}} - 1/2E_{\text{H}_2}],$$

where E^* , $E_{*\text{OOH}}$, $E_{*\text{O}}$ and $E_{*\text{OH}}$ are the electronic energies of substrates and intermediate OOH, O, OH adsorbed on substrates, E_{H_2} and $E_{\text{H}_2\text{O}}$ are the electronic energies of free H_2 and H_2O molecules, which were obtained from DFT calculations. The values for ΔZPE and $T\Delta S$ of adsorbates were obtained via DFT calculations, while those of gas molecules were obtained from standard thermodynamic data. [3] Note that the thermodynamic data of gas-phase H_2O at 0.035 bar was used as the reference state because at this pressure, gas-phase H_2O is in equilibrium with liquid water. [4] ΔG_{U} represents the effect of a bias on all states involving an electron in the electrode, $\Delta G_{\text{U}} = -eU$, where U refers to the electrode potential. ΔG_{pH} represents the correction of the free energy induced by a different H^+ concentration, $\Delta G_{\text{pH}} = 0.059 \times \text{pH}$. In the present work, $U = 0$, $\text{pH} = 1$, and $T = 298.15$ K.

The ideal catalyst should be able to facilitate the ORR just above the equilibrium potential, which requires all four charge transfer steps to have reaction free energies of the same magnitude at zero potential ($-4.92 \text{ eV}/4 = -1.23 \text{ eV}$). The catalyst that fulfills this requirement is thermochemically ideal. Real catalysts do not display this behavior. If any imbalance may exist in the allocation of the given total Gibbs free energy difference among the four steps, the elementary step with the smallest $-\Delta G$ becomes the potential-determining step. Thus, the limiting potential (U_L) for each catalytic site is defined as:

$$U_L = \text{Min} [-\Delta G_i, i = 1 - 4]/e$$

The limiting potential is the highest potential where all of the ORR elementary steps are downhill in free energy, which can be compared with the half-wave potential measured on the RHE scale.[5]

Supplemental Note 2

The calculations of hybridization of active sites on γ GyNTs were carried out with the Gaussian 09 package [6]. The corresponding structures were directly abstracted from Material Studio's file and non-periodic condition was taken into account. The dangling bonds at the edge of each γ GyNT were passivated by H atom. The NBO analysis were performed by B3LYP [7] method conjugated with 6-31+G* basis set [8].

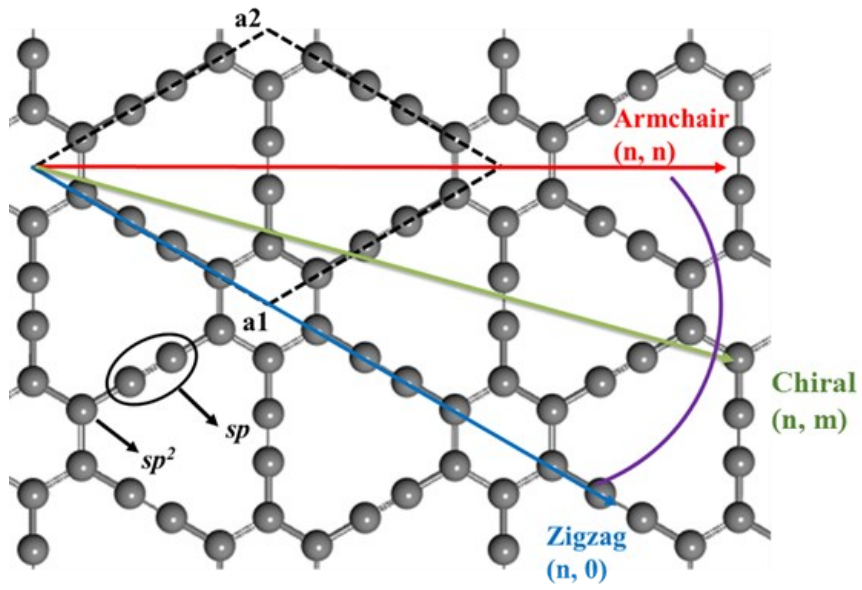


Figure S1 Pictorial representation of chiral vectors that define armchair, zigzag and chiral γ GyNTs.

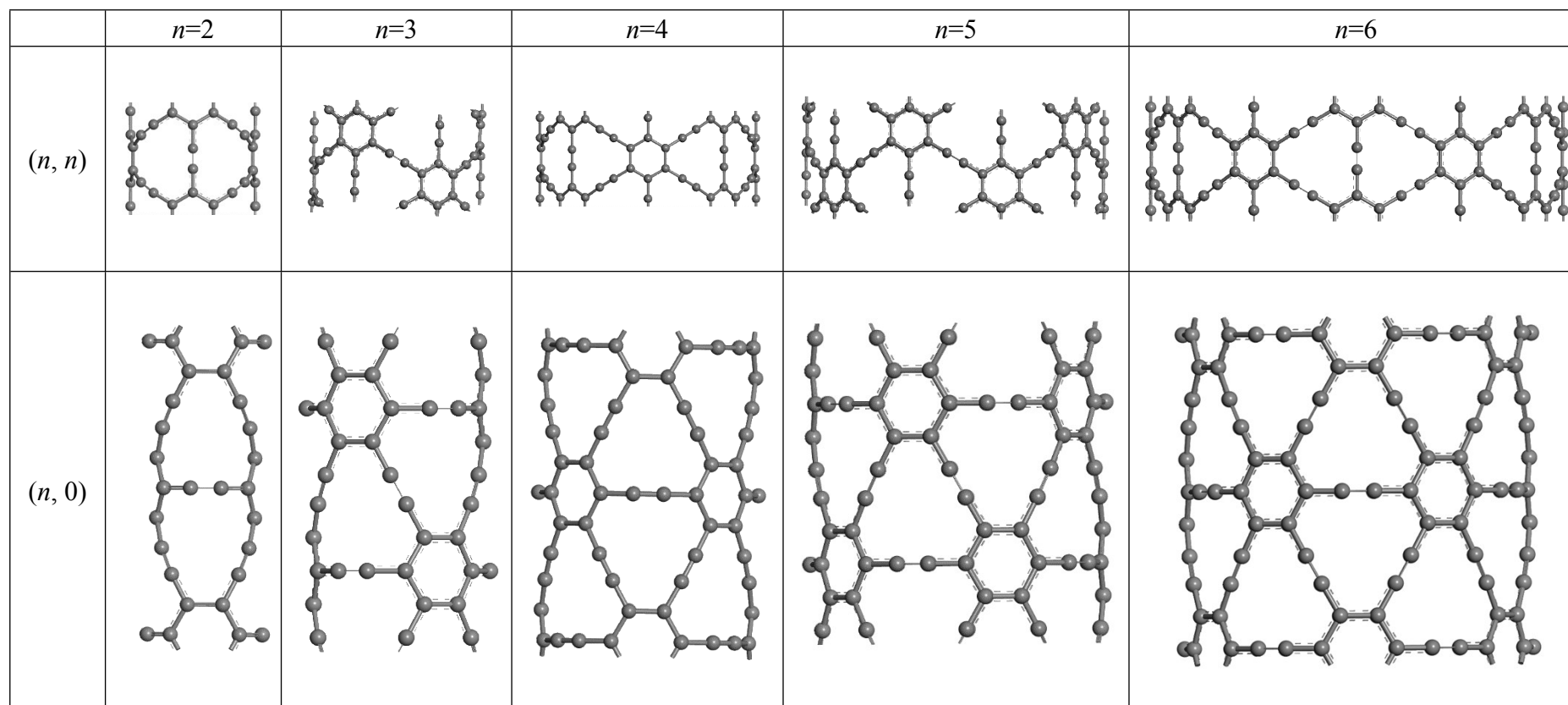


Figure S2 Optimized structures of all studied γ GyNTs.

Table S1 Charge (Q), hybridization (n), diameter (D) and ΔG_1 , ΔG_2 , ΔG_3 , ΔG_4 of different sites for studied γ GyNTs.

	Q	n	D (Å)	ΔG_1	ΔG_2	ΔG_3	ΔG_4
γ Gy	0.090	1.078	-	-0.251	-2.167	-1.066	-1.434
22-C ¹⁻	0.110	1.08	7.47	-0.057	-2.439	-0.793	-1.631
22-C ^{1⊥}	0.070	1.07	7.47	-0.711	-2.278	-1.015	-0.917
33-C ¹⁻	0.103	1.11	11.712	-0.140	-2.217	-0.936	-1.627
33-C ^{1⊥}	0.083	1.08	11.712	-0.660	-2.197	-1.043	-1.020
44-C ¹⁻	0.101	1.08	15.265	-0.163	-2.199	-0.944	-1.613
44-C ^{1⊥}	0.087	1.065	15.265	-0.620	-2.150	-1.043	-1.106
55-C ¹⁻	0.100	1.11	18.856	-0.111	-2.216	-0.981	-1.612
55-C ^{1⊥}	0.090	1.074	18.856	-0.488	-2.183	-1.077	-1.172
66-C ¹⁻	0.099	1.07	22.729	-0.292	-2.173	-0.974	-1.481
66-C ^{1⊥}	0.092	1.07	22.729	-0.543	-2.168	-1.024	-1.185
20-C ¹⁻	0.103	1.08	4.400	-0.558	-2.389	-1.064	-0.910
20-C ^{1⊥}	0.028	1.07	4.400	-1.485	-2.304	-0.925	-0.206
30-C ¹⁻	0.099	1.08	6.513	-0.374	-2.289	-1.082	-1.175
30-C ^{1⊥}	0.048	1.07	6.513	-1.103	-2.097	-1.224	-0.496
40-C ¹⁻	0.099	1.08	8.772	-0.313	-2.262	-1.100	-1.244
40-C ^{1⊥}	0.061	1.07	8.772	-0.936	-2.125	-1.185	-0.675
50-C ¹⁻	0.098	1.08	10.959	-0.413	-2.175	-1.087	-1.245
50-C ^{1⊥}	0.072	1.07	10.959	-0.801	-2.127	-1.166	-0.826
60-C ¹⁻	0.098	1.08	13.177	-0.408	-2.153	-1.003	-1.356
60-C ^{1⊥}	0.078	1.08	13.177	-0.711	-2.134	-1.171	-0.904

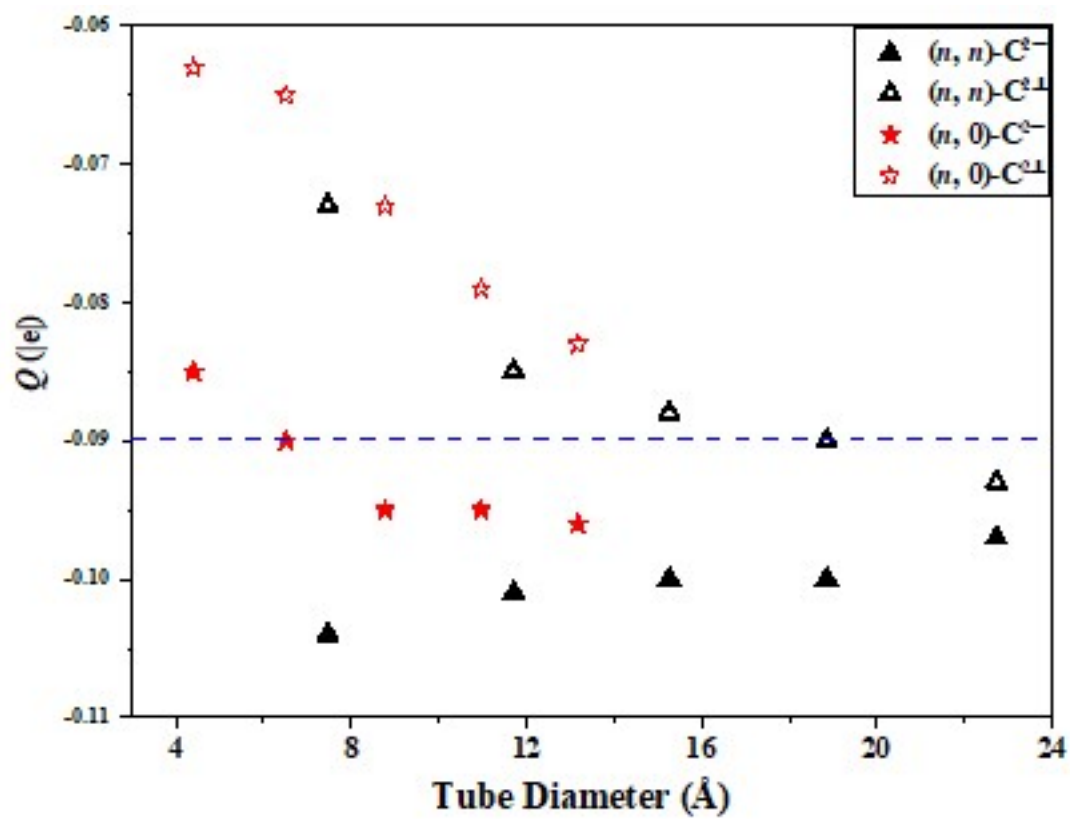


Figure S3 Q of C^{2-} and C^{2+} vs tube diameter.

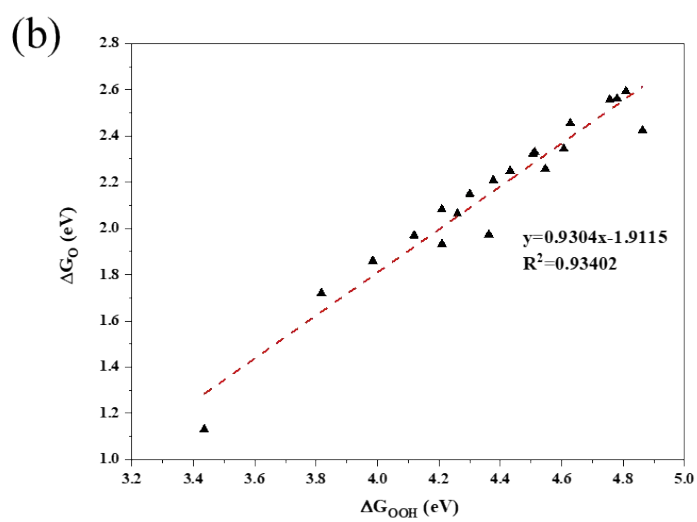
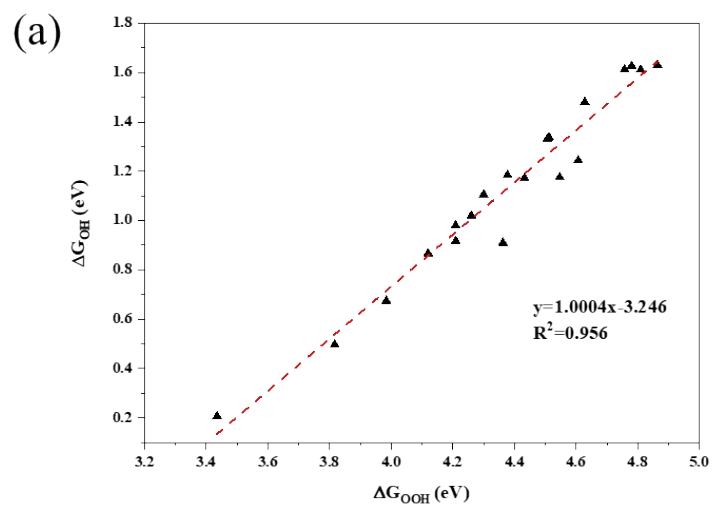


Figure S4 ΔG_{OH} as a function of ΔG_{OOH} , (b) ΔG_O as a function of ΔG_{OOH} .

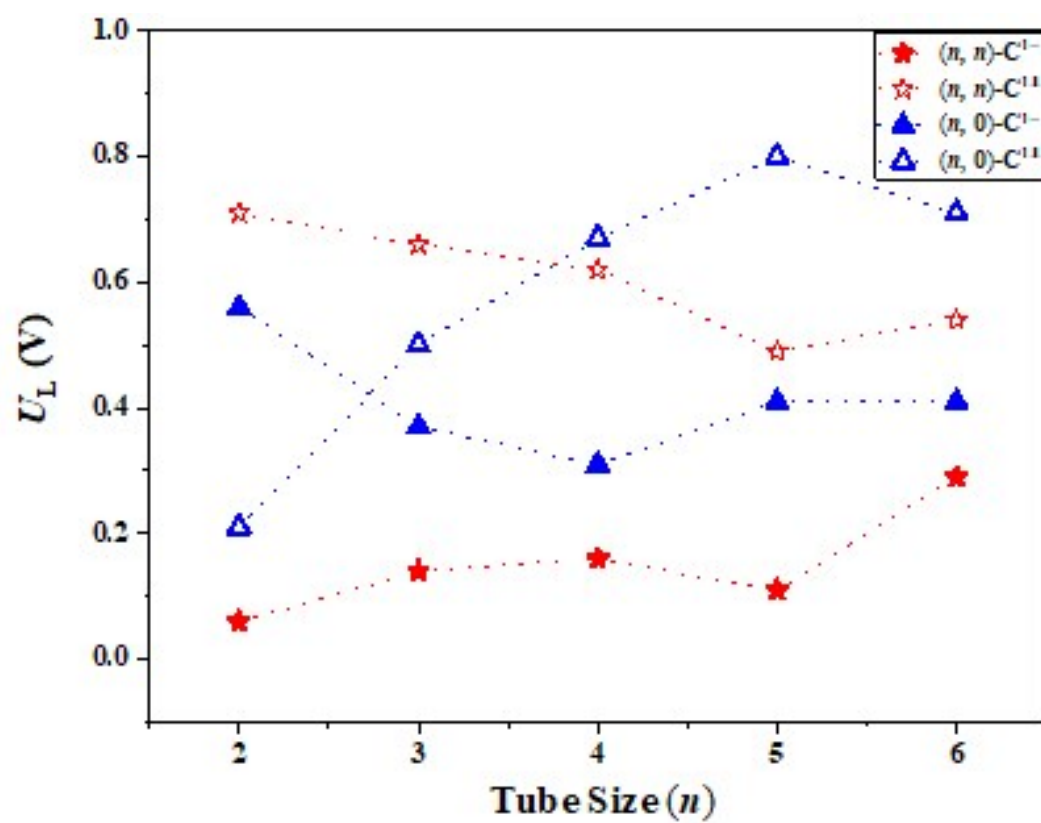


Figure S5 U_L as function of tube size (n).

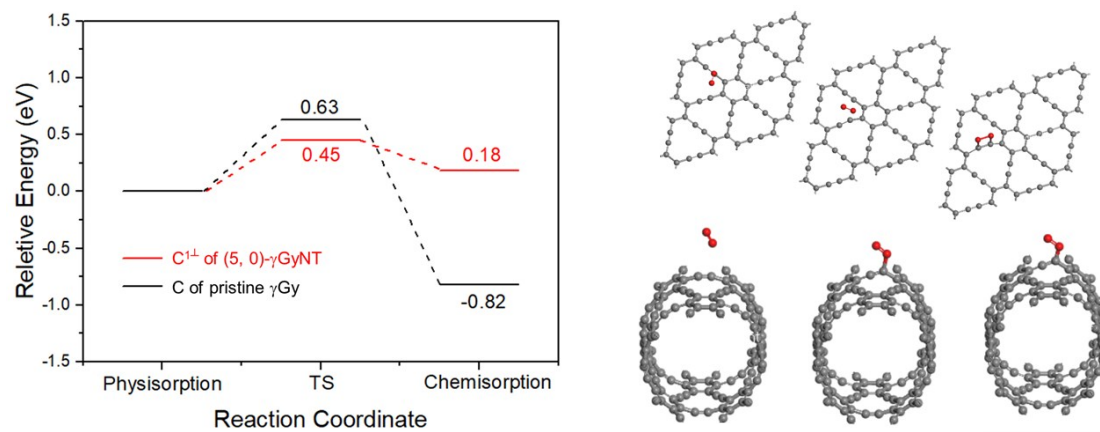


Figure S6 Calculated energy profiles and structures of O₂ adsorption on C¹⁺ of (5, 0)- γ GyNT and C¹ of pristine γ Gy.

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