Electronic Supplementary Information for

DHQ-graphene: A novel two-dimensional defective-graphene for corrosion resistant coating

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Table S1. Comparison adsorption energy of a single O atom on bridge sites of some 2D carbon allotropes [18-20].

2D carbon structures	Bridge-sites	E_{PBE}(eV)	E_{DFT-D2}(eV)	E_{DFT-D3}(eV)
Perfect graphene	6-6	1.02	0.80	0.84
Net-τ	6-5	0.59	0.55	0.56
	6-8	0.22	0.17	0.20
	5-10	0.49	0.46	0.48
	6-10	0.02	-0.02	0.00
Biphenylene	4-6	0.02	-0.18	-0.17
	4-8	0.18	-0.04	-0.02
	6-8	0.12	-0.09	-0.07
	8-8	1.76	1.55	1.58
Phagraphene	5-6	0.40	0.27	0.29
	5-7	0.36	0.23	0.25
	6-6	0.60	0.46	0.48
	6-7(1)	0.76	0.62	0.65
	6-7(2)	0.71	0.57	0.61
DHQ-graphene	6-10(1)	-0.20	-0.29	-0.27
	6-4	0.38	0.31	0.32
	6-10(2)	-0.01	-0.10	-0.07
	4-10	0.43	0.32	0.36
	6-6	0.26	0.18	0.21

Text S1

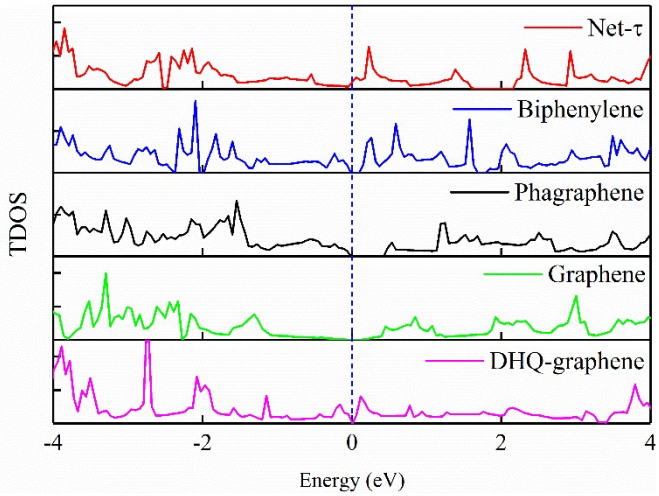


Fig. S1. The DOS of geometry structure after O adsorption.

The results implied that the structures of net-τ and DHQ-graphene after O adsorption maintained metallicity, whereas those of biphenylene, phagraphene, and graphene changed into those of semiconductors. Stronger covalent and ionic bonds, as indicated by the maintained metallicity following O-adsorption on the net-τ and DHQ-graphene structures, implied a weak van der Waals force.

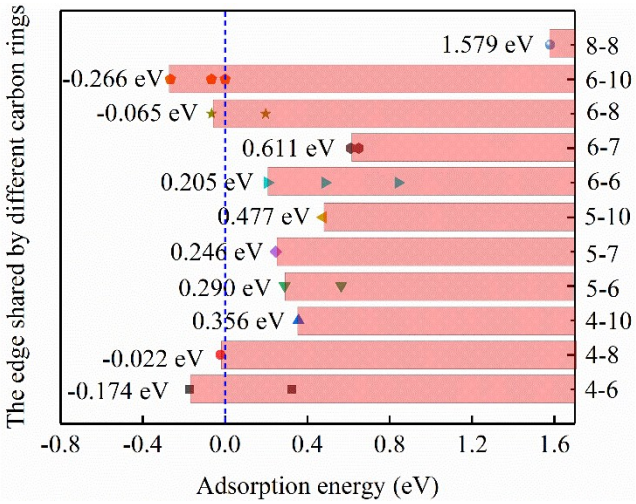


Fig. S2. Adsorption energies at junctures of different carbon rings.

Text S2. Comparison of the O adsorption energy of Net-τ, Biphenylene, Phagraphene, graphene and DHQ-graphene

The adsorption energy U of O on graphene was calculated according to $U = E_{slab/O} - E_{slab} - \mu_O$, where μ_O, E_{slab}, and $E_{slab/O}$ are the electronic energies per atom of the O_2 molecule, of the graphene sheet, and of the adsorption system, respectively. The adsorption energy represents the energy gained (or lost) by removing two O atoms from the surface and forming an O_2 molecule in the gas phase. Based on this definition, a more negative adsorption energy indicated a more favorable exothermic reaction between the graphene sheet and O atoms.

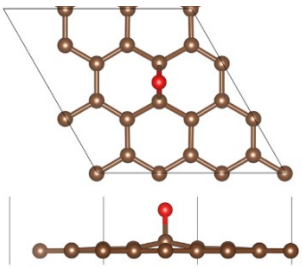
The O adsorption energies with PBE, DFT-D2 and DFT-D3 are shown in Figure 1, and the detail values are presented in Table S1. The adsorption energies of Net-τ and DHQ-graphene with the vdW corrected approaches is similar to the predictions from PBE. It may be related to the fact that the C-O bond involves significant charge transfer and is substantially ionic, rendering weak dispersion interactions less significant. It is worth to note that after consideration of van der Waals attraction based on DFT–D2 and DFT–D3 method, the adsorption of O atom is strengthened by 0.1–0.3 eV, while the trend of U is agreement with that based on DFT.

The calculated U values with DFT-D3 dispersion correction for a single O atom at the bridge sites on the edges shared by the 6-5, 6-8, 5-10, and 6-10 carbon rings of net-τ were 0.56, 0.20, 0.48, and 0.00 eV, respectively; the adsorption energies at bridge sites on the edges shared by the 4-6, 4-8, 6-8, and 8-8 carbon rings of biphenylene -0.17, -0.02, -0.07, and 1.58 eV, respectively; the adsorption energies at bridge sites on the

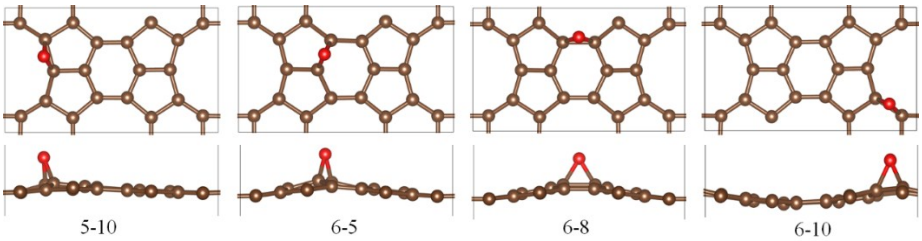
edges shared by the 5-6, 5-7, 6-6, 6-7(1), and 6-7(2) carbon rings of phagraphene were 0.29, 0.25, 0.48, 0.65, and 0.61 eV, respectively; the adsorption energies at bridge sites on the edges shared by the 6-10(1), 6-4, 6-10(2), 4-10, and 6-6 carbon rings of DHQ-graphene were -0.27, 0.32, -0.07, 0.36, and 0.21 eV, respectively. All of these adsorption sites showed stronger O adsorption than that on perfect graphene (0.84 eV), implying that O atoms were more easily adsorbed on defective graphene, consistent with the experimental finding of low surface activity for traditional perfect graphene [12].

Adsorption energies at bridge sites on edges shared by different rings are compared in Figure1. The results indicated that the bridge site on the edge shared by six- and ten-membered rings had stronger adsorption energy for an O atom (-0.27 eV) than sites at other carbon ring combinations (-0.17 to 1.58 eV). It is noteworthy that the adsorption structure with 6-10 carbon rings had a negative adsorption energy when applying dispersion correction (DFT-D3), indicating that adsorption at this site should be exothermic and energetically favorable.

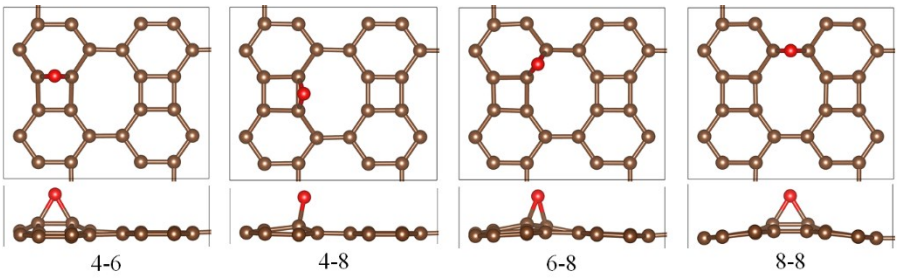
(a) Perfect graphene



(b) Net-τ



(c) Biphenylene



(d) Phagraphene

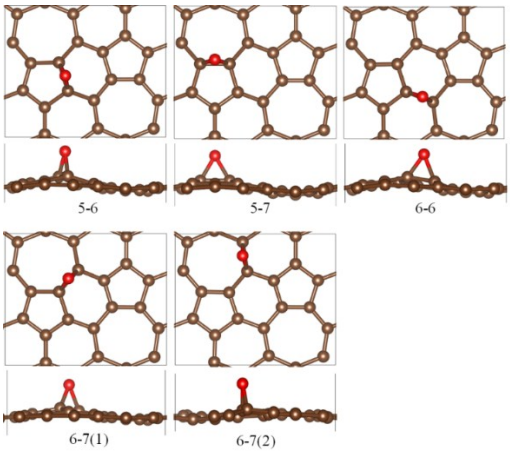


Fig. S3. The adsorption structure of a single O atom on bridge sites of some 2D carbon allotropes, (a) perfect graphene. (b) Net-τ. (c) Biphenylene. (d) Phagraphene.

The structure of DHQ-graphene

1. POSCAR of DHQ-graphene (unit cell)

DHQ-graphene-unit

1.0

8.9839000702	0.0000000000	0.0000000000
0.0000000000	6.6900000572	0.0000000000
0.0000000000	0.0000000000	20.0000000000

C

20

Direct

0.283100009	0.897199988	0.500000000
0.716899991	0.102800012	0.500000000
0.716899991	0.897199988	0.500000000
0.283100009	0.102800012	0.500000000
0.783100009	0.397199988	0.500000000
0.216899991	0.602800012	0.500000000
0.216899991	0.397199988	0.500000000
0.783100009	0.602800012	0.500000000
0.639490008	0.705810010	0.500000000
0.360509992	0.294189990	0.500000000
0.360509992	0.705810010	0.500000000
0.639490008	0.294189990	0.500000000
0.139490008	0.205810010	0.500000000
0.860509992	0.794189990	0.500000000
0.860509992	0.205810010	0.500000000
0.139490008	0.794189990	0.500000000
0.500000000	0.612640023	0.500000000
0.500000000	0.387359977	0.500000000
0.000000000	0.112640023	0.500000000
0.000000000	0.887359977	0.500000000

2. POSCAR of DHQ-graphene (primitive cell)

DHQ-graphene-primitive

1.0

5.6005997658	0.0000000000	0.0000000000
-1.6049338365	5.3657157134	0.0000000000
0.0000000000	0.0000000000	20.0000000000

C

10

Direct

0.180299997	0.614099979	0.500000000
0.819700003	0.385900021	0.500000000
0.614099979	0.180299997	0.500000000
0.385900021	0.819700003	0.500000000
0.345299959	0.066320002	0.500000000
0.654700041	0.933679998	0.500000000
0.066320002	0.345299959	0.500000000
0.933679998	0.654700041	0.500000000
0.112640023	0.112640001	0.500000000
0.887359977	0.887359977	0.500000000

3. 3D stacked DHQ-graphene

3D-stacked-structure

1.0

9.3447999954	0.0000000000	0.0000000000
0.0000000000	6.7697000504	0.0000000000
0.0000000000	0.0000000000	4.9805998802

C

40

Direct

0.209050000	0.613070011	0.841620028
0.790950000	0.386929989	0.158379972
0.790950000	0.386929989	0.841620028
0.209050000	0.613070011	0.158379972
0.790950000	0.613070011	0.158379972
0.209050000	0.386929989	0.841620028
0.209050000	0.386929989	0.158379972
0.790950000	0.613070011	0.841620028
0.709050000	0.113070011	0.341620028
0.290950000	0.886929989	0.658379972
0.290950000	0.886929989	0.341620028
0.709050000	0.113070011	0.658379972
0.290950000	0.113070011	0.658379972
0.709050000	0.886929989	0.341620028
0.709050000	0.886929989	0.658379972
0.290950000	0.113070011	0.341620028
0.856899977	0.770290017	0.660099983
0.143100023	0.229709983	0.339900017
0.143100023	0.229709983	0.660099983
0.856899977	0.770290017	0.339900017
0.143100023	0.770290017	0.339900017
0.856899977	0.229709983	0.660099983
0.856899977	0.229709983	0.339900017
0.143100023	0.770290017	0.660099983
0.356899977	0.270290017	0.160099983
0.643100023	0.729709983	0.839900017
0.643100023	0.729709983	0.160099983
0.356899977	0.270290017	0.839900017
0.643100023	0.270290017	0.839900017
0.356899977	0.729709983	0.160099983
0.356899977	0.729709983	0.839900017
0.643100023	0.270290017	0.160099983
0.000000000	0.882179976	0.658200026
0.000000000	0.117820024	0.341799974
0.000000000	0.117820024	0.658200026

0.000000000	0.882179976	0.341799974
0.500000000	0.382179976	0.158200026
0.500000000	0.617820024	0.841799974
0.500000000	0.617820024	0.158200026
0.500000000	0.382179976	0.841799974