Supplementary Material (ESI) for Nanoscale

Supporting Information

Twist-Boat Conformation in Graphene Oxides

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Structural Details

We depict in Figure S1 the various fully-oxidized structures. The geometry details are listed in Table S1. Included epoxy-pair (strips) structure has the same structure as Figure S1.c, but with alternating pairs of sp^2 and sp^3 stripes, respectively. The calculated binding energy and gap are shown in Table S2. The calculated band gap for the twist-boat structure using the B3LYP functional is 6.42 eV.

Table S1: Fractional coordinates of various GO structures. All the structures are of D_{2h} symmetry. The coordinates of the other atoms can be determined by the symmetry operations.

Structure	Symmetry	Element	Fractional coordinates of atoms		
			x	*y*	*z*
Boat (*zigzag*)	*Pmmn*	C O	0.6692 0.5000	0.0000 0.0000	0.4887 0.4055
Twiste-boat (*armchair*)	*Pcca*	C O	0.5840 1.0000	-0.0087 -0.0773	0.6246 0.2500
Epoxy-pair (*zigzag*)	*Pmmm*	C C O	0.7053 -0.1418 0.5000	0.0000 0.5000 0.0000	0.5000 0.5000 0.4263
Epoxy-pair (*alternating*)	*Pbam*	C C O	0.5476 0.8751 0.5000	-0.1163 -0.1506 0.5000	-0.5000 -0.5000 -0.5724
Twist-boat chair	*P2/c*	C C O O H	0.1505 0.6684 0.0752 0.5000 0.2619	-0.0216 -0.0101 0.1074 -0.0877 0.1379	0.1433 0.9167 0.5527 0.7500 0.7853
Epoxy-pair (*armchair*)	*Pmma*	C C O O	0.0000 0.0000 0.9407 0.9407	0.3342 0.1039 0.5000 0.5000	-0.0825 0.0907 0.0000 0.5000

Table S2: Calculated binding energies per oxygen atom for various GO structures. For boat (zigzag), Γ = (0, 0), W= (π /2a_1, π/2b_1), L= (π /2a_1, 0), where a_1=2.52 Å, b_1 =4.49 Å, respectively. For twist-boat (armchair), Γ = (0, 0), S= (π /2a_2, π/2b_2), D= (π /2a_2, 0), where a_2=5.10 Å, b_2 =4.28 Å, respectively. For epoxy-pair, T= (π /2a_3, 0), where a_3=4.50 Å, b_3 =2.52 Å, respectively; R= (π /2a_4, π/2b_4), where a_4=4.60 Å b_4 =5.47 Å, respectively; and Q= (π /2a_5, 0), a_5=5.10 Å b_5 =4.48 Å.

Structure	C/O ratio and number of atoms per unit cell	Binding Energy (eV)	Gap (eV)	Unit Cell (Å^2)
Boat (*zigzag*)	2 (C4, O2)	-23.39	2.95 direct at Γ	2.52×4.49
Twiste-boat (*armchair*)	2 (C8, O4)	-23.65	4.40 direct at Γ	5.10×4.28
Epoxy-pair (*zigzag*)	2 (C4, O2)	-23.06	0.40 direct at T	2.52×4.50
Epoxy-pair (*alternating*)	2 (C8, O4)	-23.54	1.85 direct at R	5.47×4.60
Twist-boat chair	4/3 (C8, O6, H4)	-20.13	3.22 direct at Γ	6.51×4.80
Epoxy-pair (*armchair*)	2 (C8, O4)	-22.89	0.45 direct at Q	5.10×4.49
Epoxy-pair (strips)	2 (C8, O4)	-23.82	metallic	2.51×10.14

Density-Functional Tight-binding Calculations

In order to characterize the randomly distributed carbonyl and hydroxyl functional groups on graphene, we have employed density-functional tight-binding approach on a large sample consisting of 84 carbon atoms. The large rectangular unit cell allows us to systematically investigate the corrugated patterns of fully oxidized GO.

The unit cell was constructed through randomly deposited hydroxyl and carbonyl groups on graphene. While for hydrogenated graphene one can employ a classical Tersoff potential to simulate the absorption, the corresponding approach with use of DFTB method remains elusive due to computational costs. To circumstance this problem, we started from the fully hydrogenated graphene samples and connect the nearest-neighbor pairs to epoxy oxidization pattern, whereas the remaining to hydroxyl onsite functional groups. The resultant configuration reasonably reproduces results from previous studies in that there is the aggregation of the functional groups and the chain-like configurations of hydroxyl patterns.

It is worth noting that such generated random samples preclude epoxy pairs as the formation of an epoxy pair needs to accompany a nearly “hollow” site. This

approximation is, however, justified from energy calculations of various ordered configurations.

The configurations with randomly distributed functional groups were subsequently relaxed with use of conjugate-gradient method. One of the optimized configurations is shown in Figure 2.

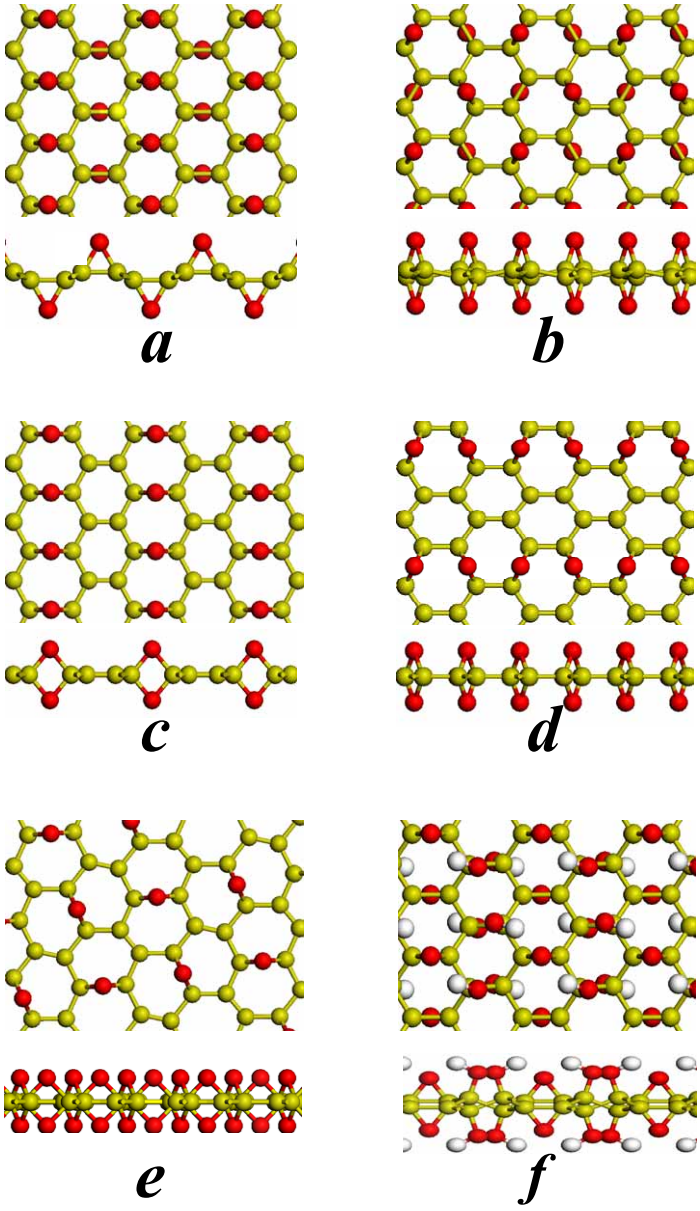

Figure S1: Top (and side) views of GO atomic structures for selected conformations: (a) Fully-oxidized epoxide-only boat phase C_2O with oxygen rows on both sides of the plane along the zigzag direction; (b) Fully-oxidized epoxide-only twist-boat C_2O phase along armchair; (c), (d), and (e) Epoxy-pair structures along zigzag, armchair, and alternating

directions, respectively; (f) Twist-boat-chair structure with hydroxyl-epoxide strips separated by epoxide chain. Carbon, oxygen, and hydrogen atoms are colored with gold, red, and white, respectively.