Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Identify the Trend of Reactivity for sp^2 Carbon Materials: Electron Delocalization Model from First Principles Calculations

Ziyun Wang,[ab] Bo Yang,[b] Yulong Wang,[b] Yifang Zhao,[b] X.-M. Cao*[a] and P. Hu*[ab]

[a] State Key Laboratory of Chemical Engineering, Center for Computational Chemistry and Research Institute of Industrial Catalysis , East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China

E-mail: p.hu@qub.ac.uk, E-mail: xmcao@ecust.edu.cn

b School of Chemistry and Chemical Engineering, The Queen's University of Belfast, Belfast BT9 5AG, U.K.

1. Calculation details

All the calculations were carried out using the Vienna Ab-initio Simulation Package (VASP)[1, 2] with the projector augmented wave method and a cutoff energy of 450 eV. The generalized gradient approximation method was chosen with Perdew-Burke-Ernzerhof (PBE) functional for the exchange-correlation term[3, 4].

For the armchair edge modelling, a unit cell of 10.00 Å ×12.82 Å ×23.00 Å was chosen with 5 benzene ring units in Y direction (zigzag) and 4 benzene ring units in Z direction (armchair), see Fig. S1. Vacuums above 10 Å in X and Z directions were used to avoid interactions, while the graphene was expanded in Y direction. For the zigzag edge, the unit cell was set to 12.33 Å ×10.00 Å ×24.11 Å, with 5 benzene ring units in both X and Z directions, shown in Fig. S2. Vacuums above 10 Å were also used in Y and Z directions, and graphene was expanded in X direction. All the edges were saturated with hydrogen atoms. For basal plane calculations, the graphene was expanded in X and Y directions with 4 benzene units (12.33 Å) in each direction (see Fig. S3) and 12.00 Å vacuum was set in Z directions. 1×3×1, 3×1×1 and 3×3×1 Monkhorst-Pack *k*-point sampling were used for the armchair, zigzag and basal plane,

respectively. All the atoms in the system were relaxed in the calculations, with 0.05 eV/Å convergence of forces.

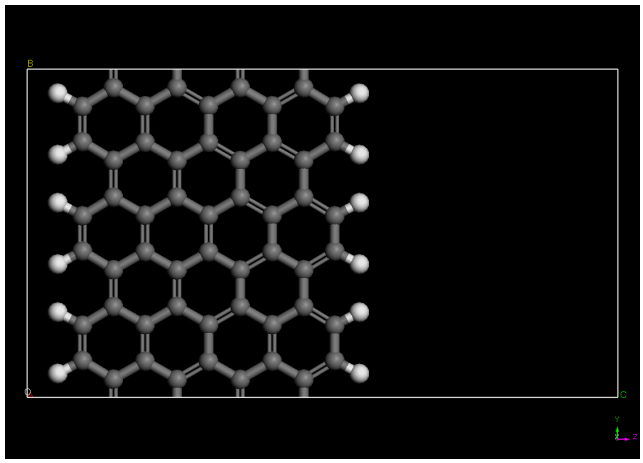


Fig. S1 The model of armchair edge of grapheme. Y direction is vertical and Z direction is horizontal. Grey balls stand for carbon atoms and white balls for hydrogen atoms and this notation is used throughout the paper.

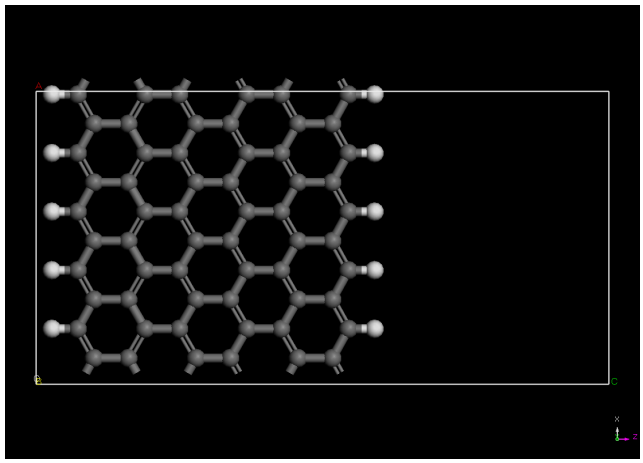


Fig. S2 The model of zigzag edge of grapheme. X direction is vertical and Z direction is horizontal.

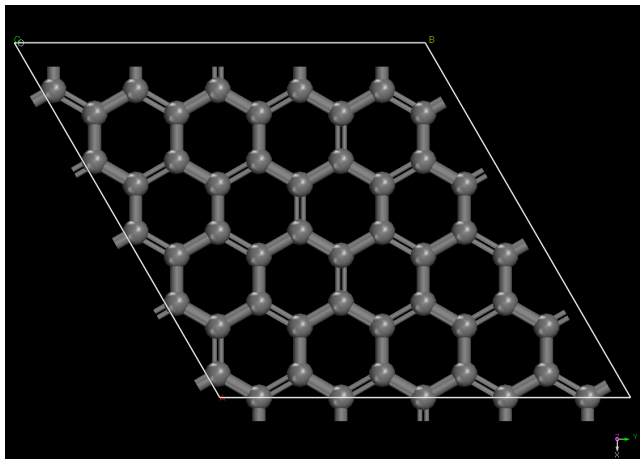
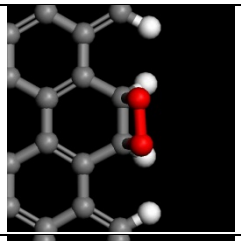
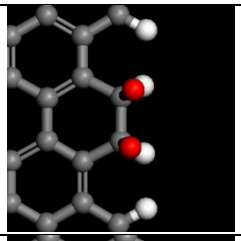
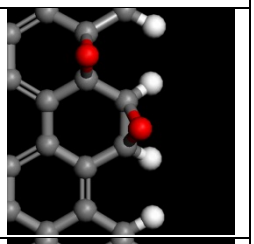
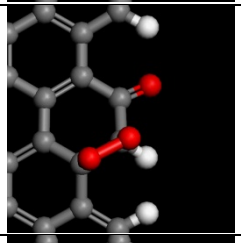
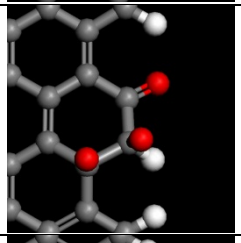
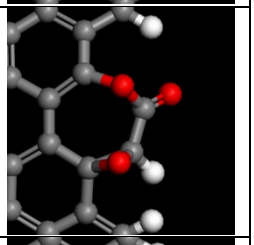
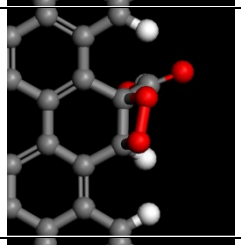
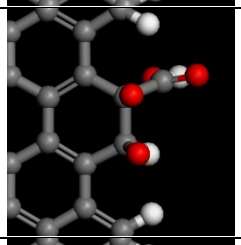
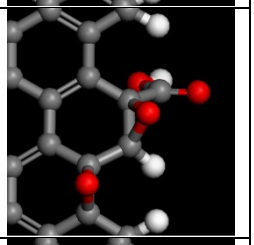
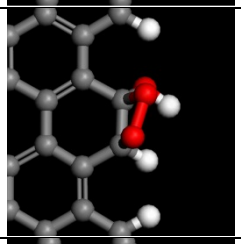
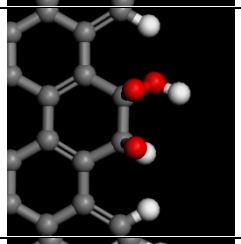
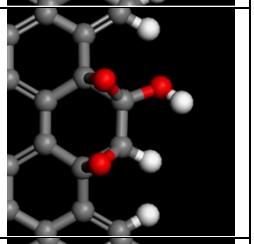
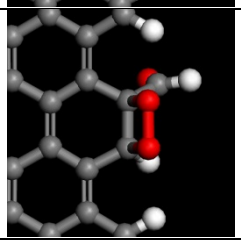
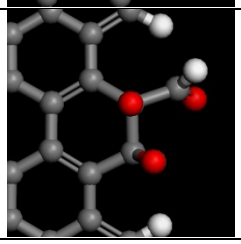
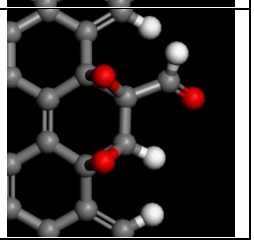


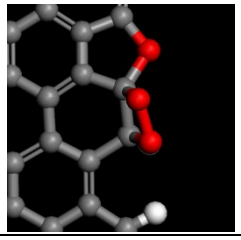
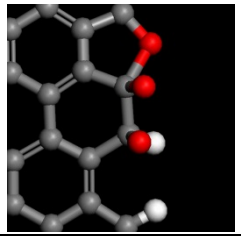
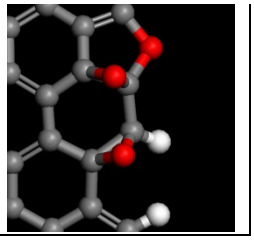
Fig. S3 The model of basal plane of grapheme. X direction is vertical and Y direction is horizontal.

2. Geometries of each state

2.1 Geometries of armchair edge

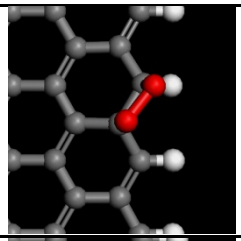
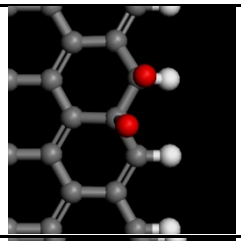
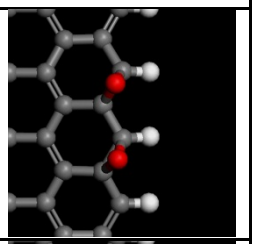
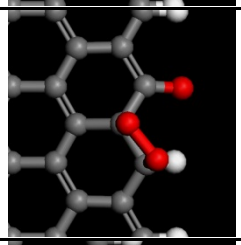
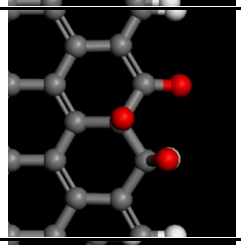
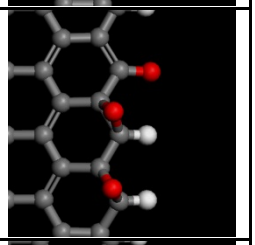
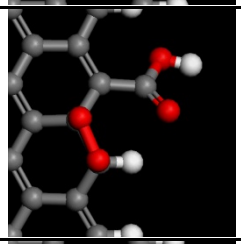
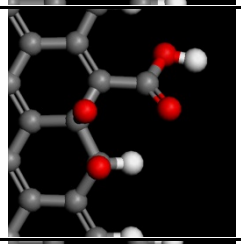
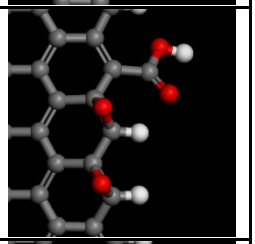
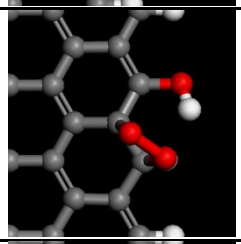
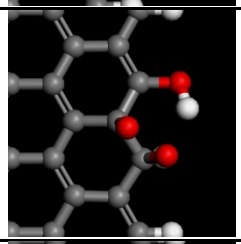
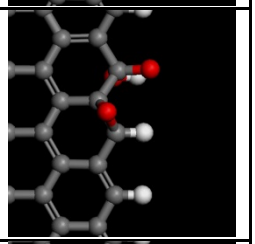
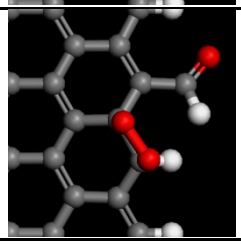
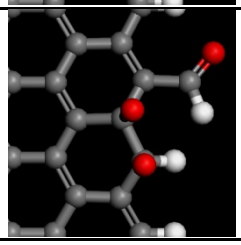
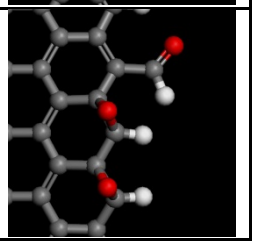
Table 1 Geometries of the initial states (ISs), transition states (TSs) and final states (FSs) for O_2 dissociation on armchair edges of graphene and graphene oxide (GO) with different oxygen-containing groups. Red balls stand for oxygen atoms and this notation is used throughout the paper.

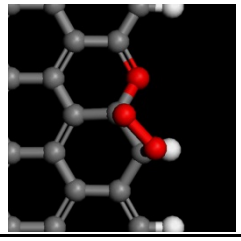
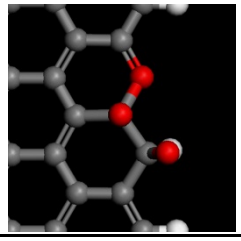
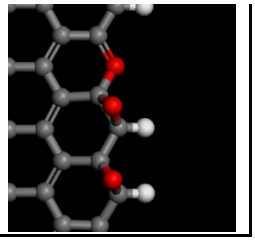
		IS	TS	FS
armchair	graphene			
	ketone			
	carboxyl			
	hydroxyl			
	aldehyde			

	epoxy			

2.2 Geometries of zigzag edge

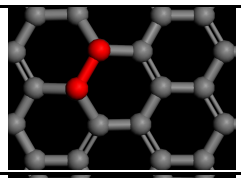
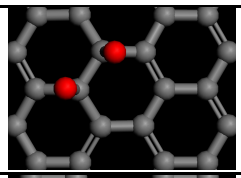
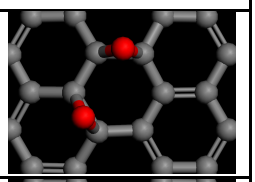
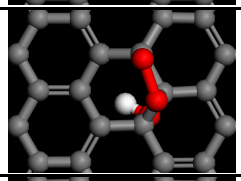
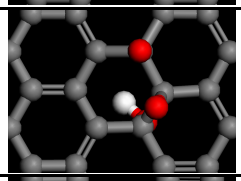
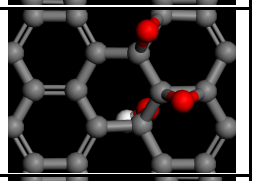
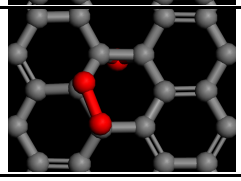
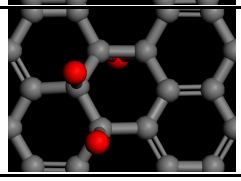
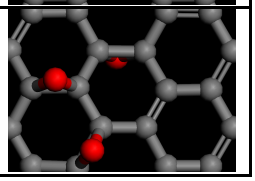
Table 2 Geometries of the ISs, TSs and FSs for O_2 dissociation on zigzag edges of graphene and GO with different oxygen-containing groups.

		IS	TS	FS
zigzag	graphene			
	ketone			
	carboxyl			
	hydroxyl			
	aldehyde			

	epoxy			

2.3 Geometries of basal plane

Table 3 Geometries of the ISs, TSs and FSs for O_2 dissociation on the basal plane of graphene and GO with different oxygen-containing groups.

		IS	TS	FS
basal plane	graphene			
	hydroxyl			
	epoxy			

3. HOMO calculations

We performed geometry optimizations and NBO analyses at the B3LYP/6-311++G(d) level of theory using Gaussian Package[5] on the molecules listed below:

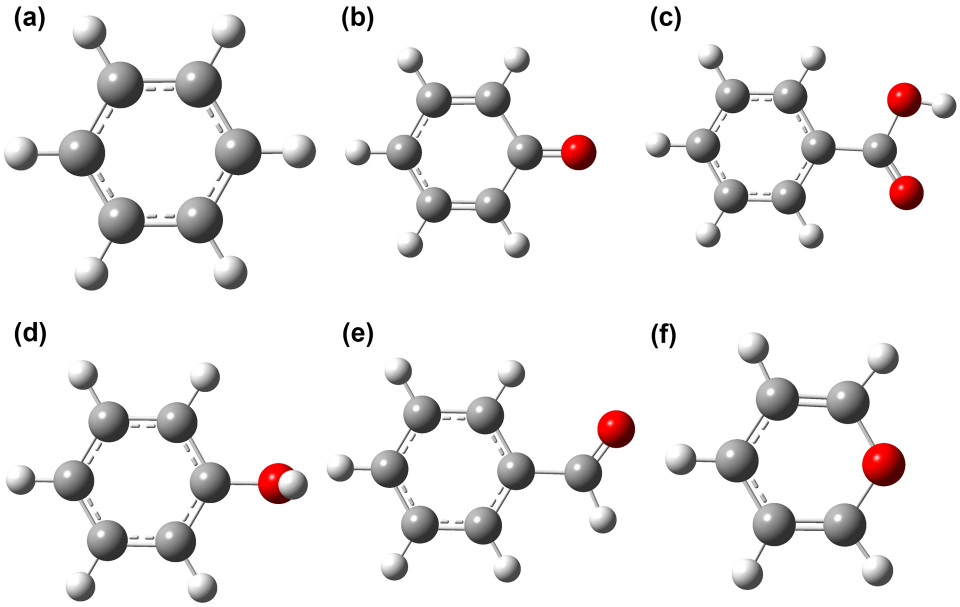


Fig. S1 Benzene molecules (a) with no oxygen-containing group, (b) with ketone group, (c) with carboxyl group, (d) with hydroxyl group, (e) with aldehyde group and (f) with epoxy group.

References:

1. G. Kresse and J. Furthmuller, *Comp Mater Sci*, 1996, **6**, 15-50.
2. G. Kresse and J. Hafner, *Phys Rev B*, 1994, **49**, 14251-14269.
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