Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

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Here, we make a detailed comparisons between calculated results with general gradient approximation (GGA)[1] and local density approximation (LDA)[2], remaining the same other parameters.

1. Binding energies of first O adatom with GGA

The binding energies under GGA of T-bond site and O-bond site without electric field are –4.82 eV and −3.50 eV respectively which are higher than LDA which are –5.79 eV and −4.46 eV respectively. Usually, LDA functional will overestimate the binding energy while GGA functional underestimate it.

The binding energies under GGA of five positions are shown in Fig. S1 after introducing the electric field. Comparing with the binding energies under LDA in Fig. 3, we can find that all the values of GGA are about 0.5~1.0 eV smaller than that under LDA. However, the tendencies of the curves are almost the same. It can be conclude that the physics will not be changed by changing functional and just the relative values are change. Namely, the initial aggressive O adatoms will trend to adsorb onto

positions V of T-bond site along one side of CNT, instead of random sites without electric field.

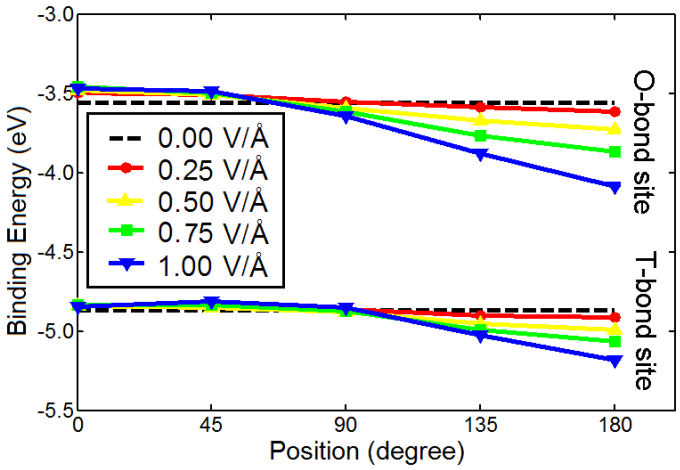

Fig. S1 The binding energies (GGA) of different positions under electric field and the schematic of electric dipole under electric field. The black and red balls are carbon and oxygen atoms, respectively.

2. Binding energies and diffusion barriers of second O adatom

The binding energies of second O adatom of different configurations under GGA and LDA are listed in table S1. For comparison, there are only quantitatively differences instead of qualitative changes on binding energies under different functional. Also the conclusion 'The second O adatom will prefer to adsorb onto B site of CNT, which is the adjacent position V near site A.' can be get.

And the total energies under GGA of these configurations are calculated to get the energy barriers, and the effect of electric field on the O adatom diffusion is shown in Fig. S2. The similar rules can be got comparing with Fig. 5 under LDA. electric field could well control the ease of O diffusion, obtaining unimpeded O diffusion on CNT

surface, which makes for epoxy regular arrangement to form more smooth edge of GNRs.

Table S1. Calculated binding energies (in eV) for second O adatoms in different configurations.

Electric Field	AB		AC		AD	
	LDA	GGA	LDA	GGA	LDA	GGA
0.00 V/Å	−6.12	−5.13	−4.42	−3.41	−4.48	−3.52
0.25 V/Å	−6.15	−5.12	−4.36	−3.17	−4.51	−3.53
0.50 V/Å	−6.20	−5.25	−4.24	−3.31	−4.59	−3.69
0.75 V/Å	−6.28	−5.43	−4.40	−3.51	−4.63	−3.96
1.00 V/Å	−6.43	−5.49	−4.53	−3.64	−4.86	−4.01

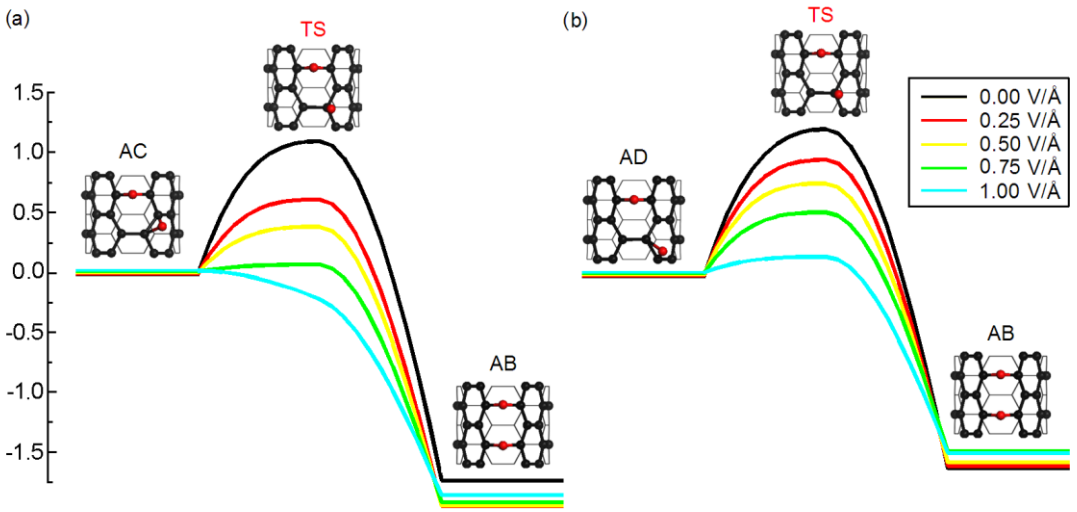

Fig. S2 The diffusion energy barriers (GGA, in eV) of the second O adatom from less stable sites to the most one. The black and red balls are carbon and oxygen atoms, respectively.

3. Binding energies and diffusion barriers of third O adatom

Similar phenomena and rules can be found about binding energies and diffusion barriers of the third adsorbed O atom, shown in table S2 and Fig. S3, respectively.

Table S2. Calculated binding energies (in eV) for third O adatoms in different configurations.

Electric Field	ABE		ABF		ABG	
	LDA	GGA	LDA	GGA	LDA	GGA
0.00 V/Å	−5.98	−4.96	−4.20	−3.17	−4.43	−3.48
0.25 V/Å	−5.98	−5.13	−4.24	−3.33	−4.44	−3.58
0.50 V/Å	−6.20	−5.20	−4.36	−3.42	−4.57	−3.69
0.75 V/Å	−6.28	−5.29	−4.40	−3.49	−4.79	−3.86
1.00 V/Å	−6.50	−5.51	−4.51	−3.58	−5.03	−4.17

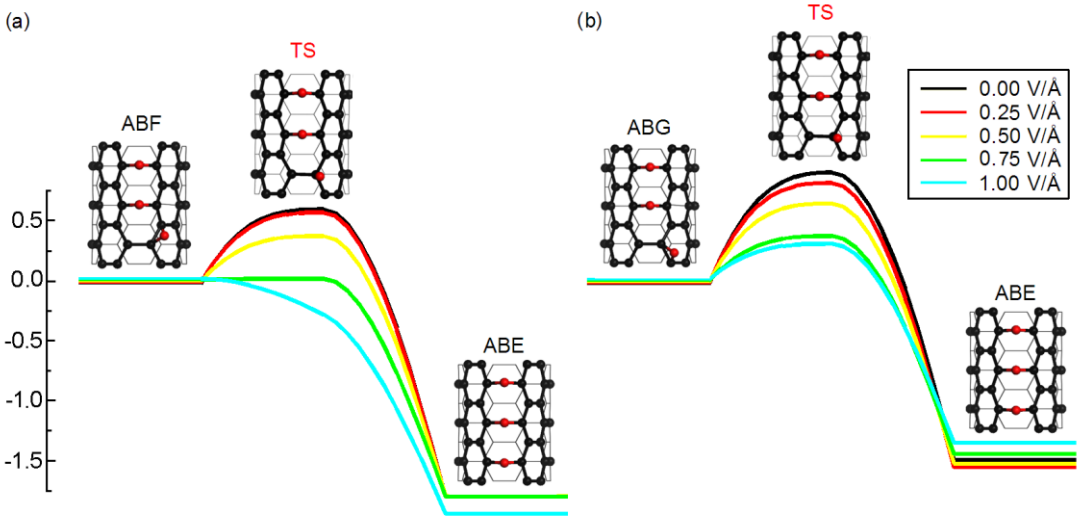

Fig. S3 The diffusion energy barriers (GGA, in eV) of the third O adatom from less stable configurations to the most stable configuration. The black and red balls are carbon and oxygen atoms, respectively.

4. Conclusions

The calculated binding energies with GGA are only quantitatively lower than that with LDA, while the qualitative rules are similar. It can be found that the physics is not modified for different functions, namely that the unzipping rules will not depend on the precise approximations adopted.

Reference

1. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. ReV. Lett.* 1996, **77**, 3865.

2. W. Kohn, L. Sham, *J. Phys. Rev.*, 1965, **137**, A1697–A1705.