Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for "Contrasting diffusion behaviors of O and F atoms on graphene and within bilayer graphene"

Seho Yi[a], Jin-Ho Choi[b,a*] Hyun-Jung Kim[c], Chul Hong Park[d], and Jun-Hyung Cho[a*]

[a] *Department of Physics and Research Institute for Natural Sciences, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 04763, Korea*

[b] *Research Institute of Mechanical Technology, Pusan National University, 2 Pusandaehak-ro 63 beon-gil, Geumjeoung-gu, Busan 46241, Korea*

[c] *Korea Institute for Advanced Study, 85 Hoegiro, Dongdaemun-gu, Seoul 02455, Korea*

[d] *Department of Physics Education, Pusan National University, 2 Pusandaehak-ro 63 beon-gil, Geumjeoung-gu, Busan 46241, Korea*

1. Convergence of binding energies with respect to the number of k-point

Our DFT calculations were carried out with a 12×12 uniform mesh in the two-dimensional Brillouin zone. In Fig.S1, it is seen that the 12×12 mesh gives sufficiently converged binding energies in these systems.

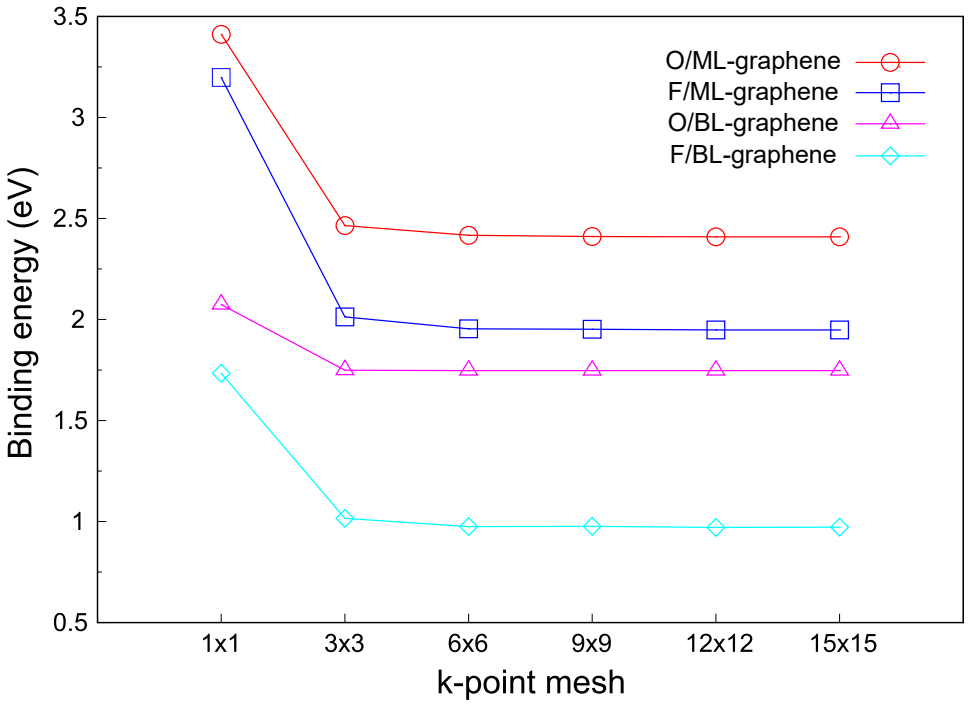

FIG. S1: Binding energies of O/graphene and F/graphene systems with different k-point meshes

2. Geometries of O/graphene and F/graphene for the transition states

The geometry of the transition state T of O/ML-graphene is displayed in the Fig. S2(a). In the inset of Fig. S2(a), the bond angles of the C−C−O bonds are 101.5°, 102.5°, and 106.3°, close to those 99.9°, 101.0°, and 108.1° of a previous DFT calculation [Suarez, A. M.; et al. *Phys. Rev. Lett.* **2011**, 106, 146802]. Here, the slight disagreement of bond angles may be caused by the different calculation schemes employed in present and previous calculations: i.e., PBE+vdW vs PBE.

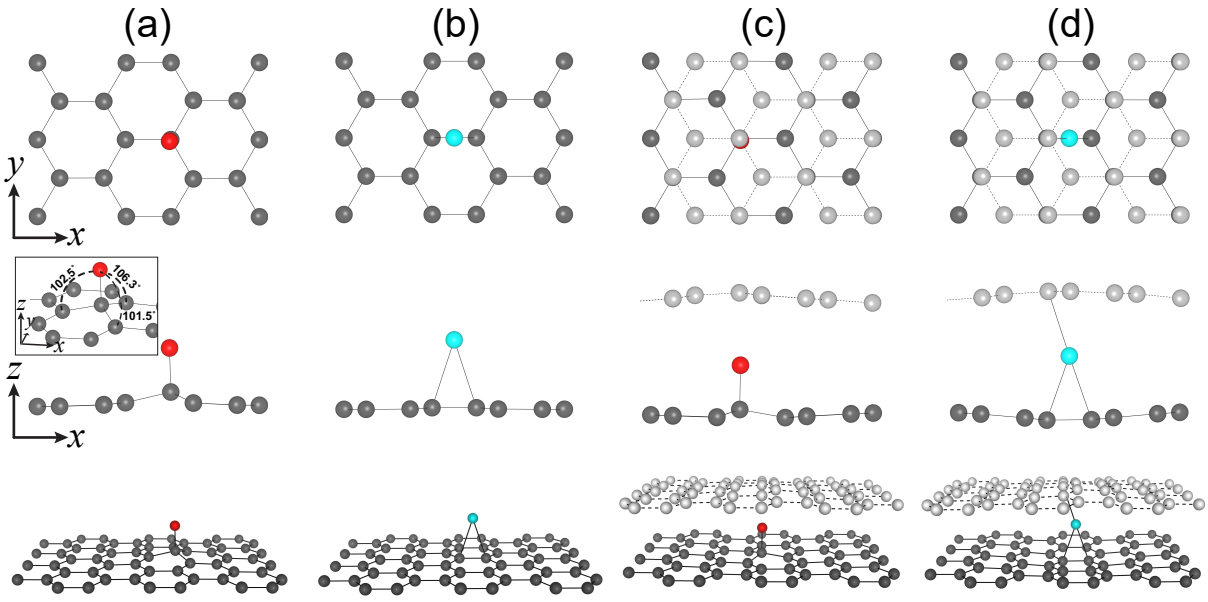

FIG. S2: Orthogonal top, side views and perspective side views of the O/graphene and F/graphene transition states. In the inset of (a), three different C−C−O angles are given.