

Interaction of Rhodamine 6G molecule with graphene: A combined theoretical and experimental approach

Kan Zhang, Shansheng Yu,* Baoming Jv and Weitao Zheng

Department of Materials Science, Key Laboratory of Mobile Materials, Ministry of
Education, and State Key Laboratory of Automotive Simulation and Control, Jilin University,
Changchun, 130012, China.

Experimental details

Preparation of GO.

GO is synthesized by a modified Hummer's method.¹ Typically, 2.0 g of graphite powder is dissolved in a mixture of concentrated H₂SO₄ (98 wt%, 67.5 mL) and NaNO₃ (1.5 g) under stirring. KMnO₄ is gradually added into the reaction container under stirring in an ice bath for 2 h. The reaction is kept for 5 days at room temperature with modest stirring. The graphite oxide dispersion is treated ultrasonically (at 40 Hz with power of 320 W) for about 2 h to ensure that most graphite oxide is exfoliated into single layer GO. The supernatant liquor is collected for the next procedure. The intrinsic graphene was obtained via the CVD method and transferred onto an Au film.

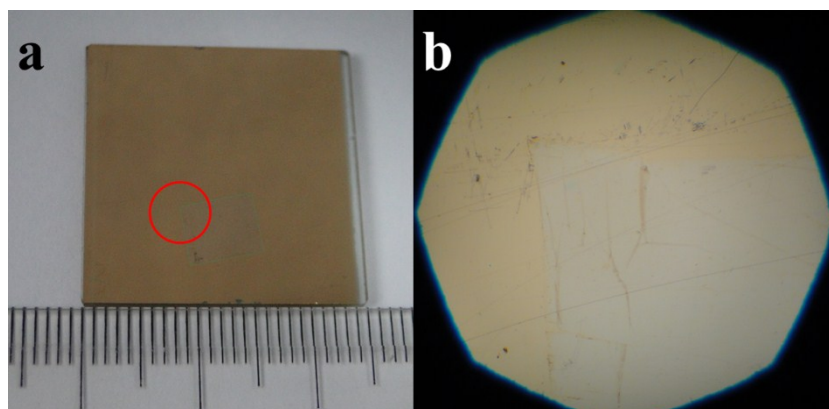


Fig. S1. Photograph (a) and optical micrograph (b) of the graphene film transferred onto an Au substrate.

Assembly and electrochemical reduction of GO.

GO modified sensor chip surface was prepared by injecting GO aqueous solution (1 mg mL⁻¹) and incubating for 2 hours over gold surface. The sensor chip surface was then rinsed with water and dried under N₂ flow. GO is electrochemically reduced by cyclic voltammetry with a potential range from 1.6 – 0.0 V in PBS (pH = 7.4) with a CHI650D electrochemical workstation. Figure S2 shows the morphological changes of an SPR sensor chip surface during the assembly and in situ electrochemical reduction of GO. Analysis of the topographic

data from at least three AFM images resulted in GO and ERGO coverages of 72.6 % and 69.1 %, respectively. This result supports the conclusion that the graphene oxide adsorbs flat onto the gold surface and was reduced by electrochemical method.

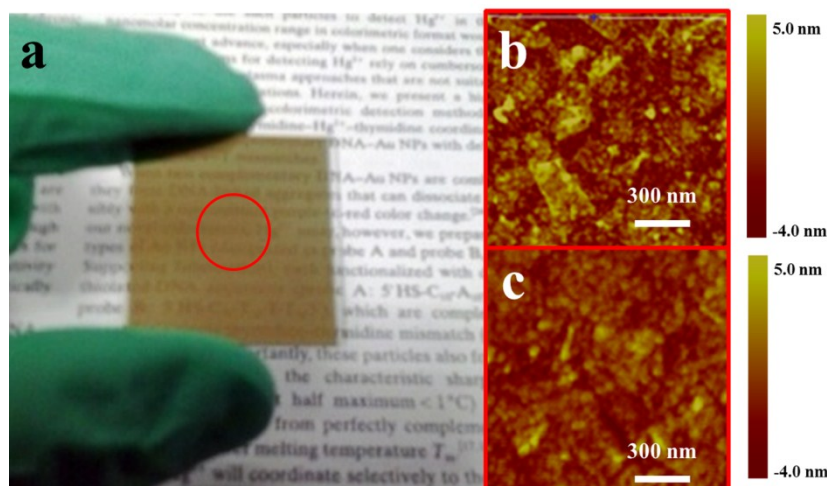


Fig. S2. Photograph (a) and AFM images of GO assembled on Au film (b), and (c) ERGO on Au film

The characterization of assembly and electrochemical reduction of GO was described in our previous reports in detail.^{2,3}

References:

1. W. S. Hummers, and R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339.
2. T. Y. Xue, X. Q. Cui, J. L. Chen, C. Liu, Q. Y. Wang, H. Wang, W. T. Zheng, *ACS Appl. Mater. Interfaces* 2013, **5**, 2096.
3. T. Y. Xue, X. Q. Cui, W. Guan, Q. Y. Wang, C. Liu, H. Wang, K. Qi, D. J. Singh, and W.T. Zheng, *Biosens. Bioelectron.* 2014, **58**, 374.

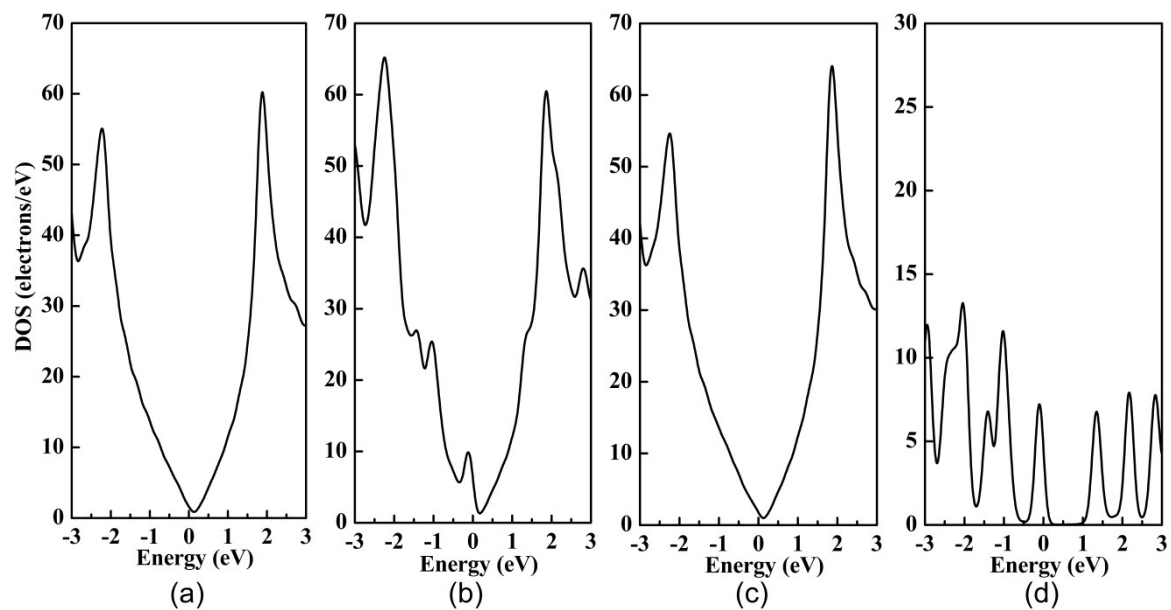


Fig. S3. (a) DOS of perfect graphene, (b) DOS of perfect graphene adsorbed with R6G molecule, DOS of (c) graphene substrate and (d) R6G adsorbate in graphene-R6G complex. The Fermi level is set as 0 eV

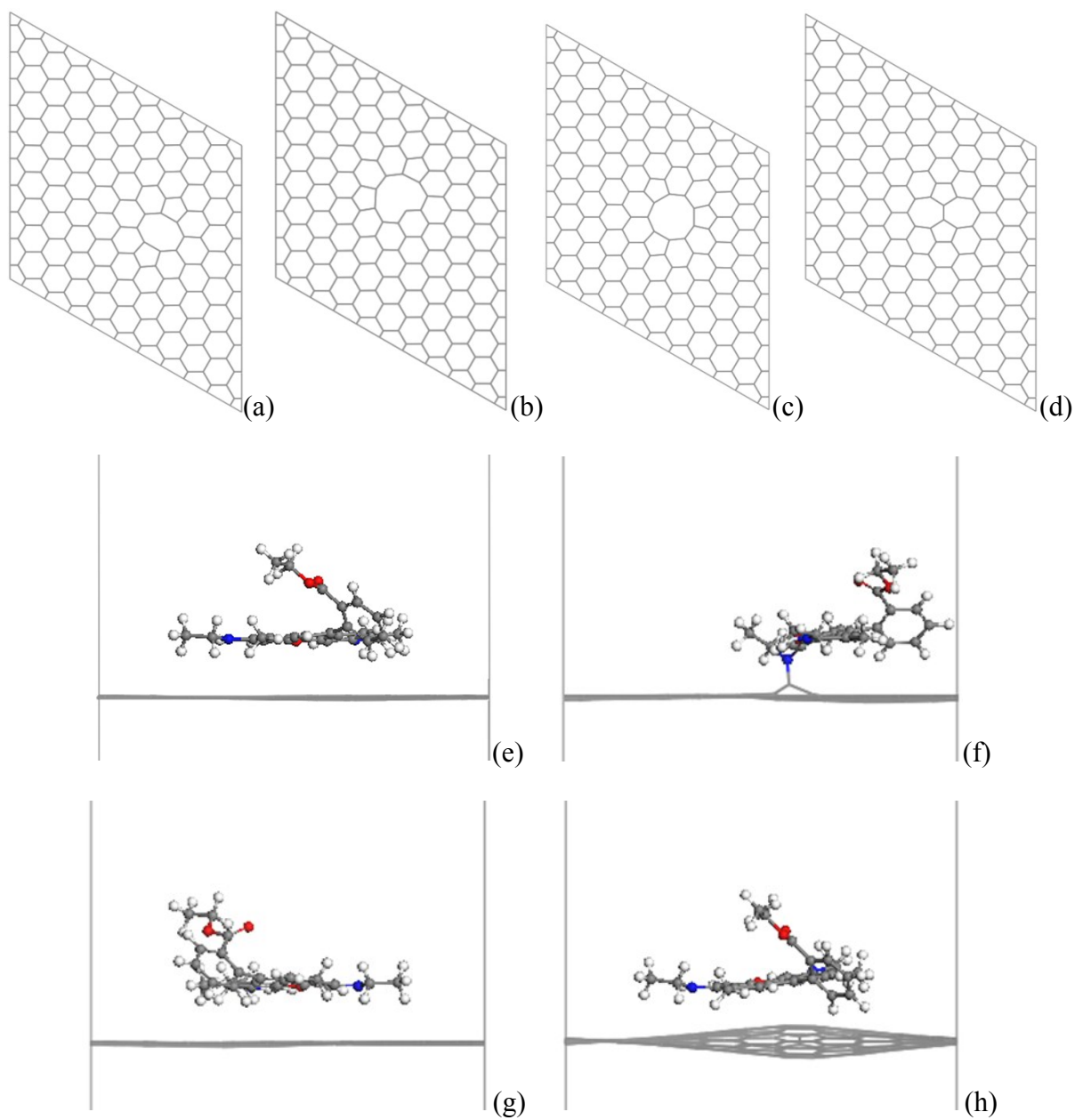


Fig. S4. Geometric structures of (a) divacancy, (b) trivacancy, (c) tetravacancy, and (d) Stone-Wales defect in graphene sheet, and corresponding to R6G adsorption system (e)~(h) are shown.

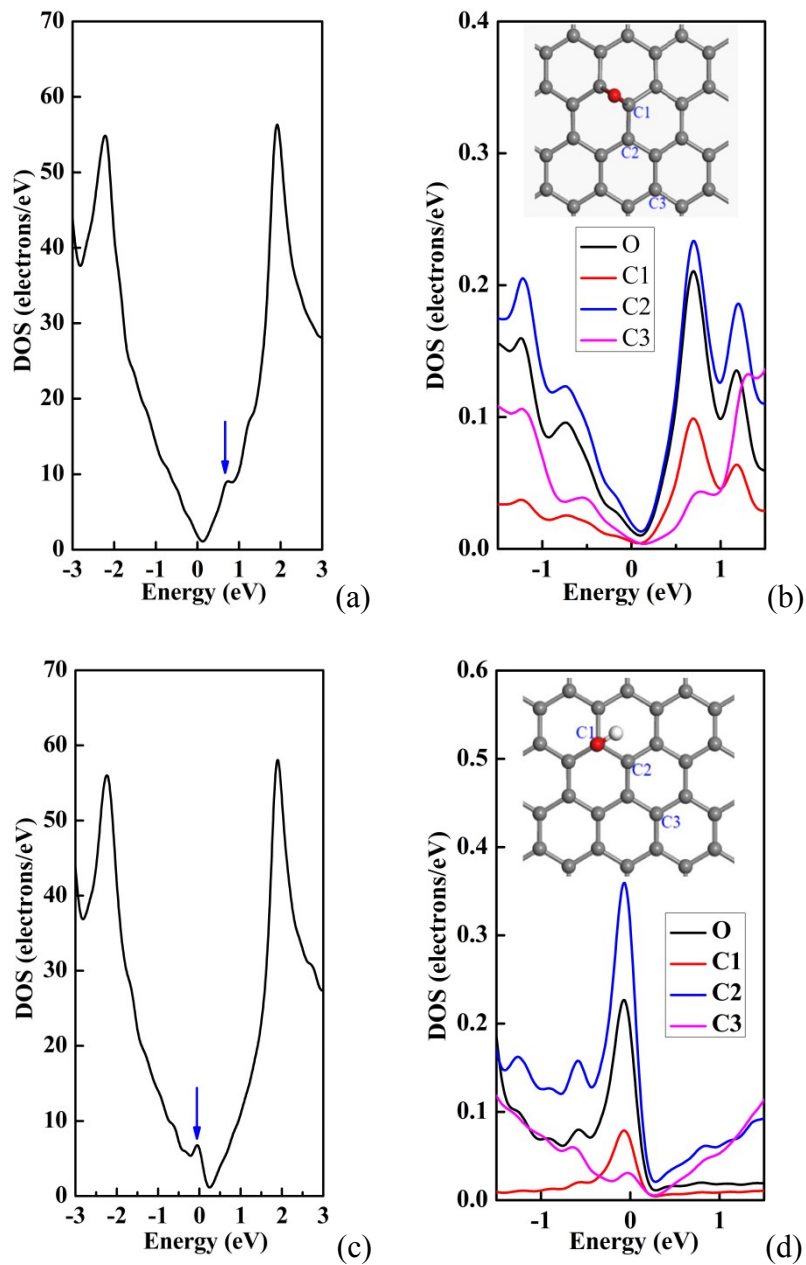


Fig. S5. The calculated electronic structures of (a) (b) *O and (c) (d) *OH attaching perfect graphene sheets are shown. The Fermi level is set as 0 eV

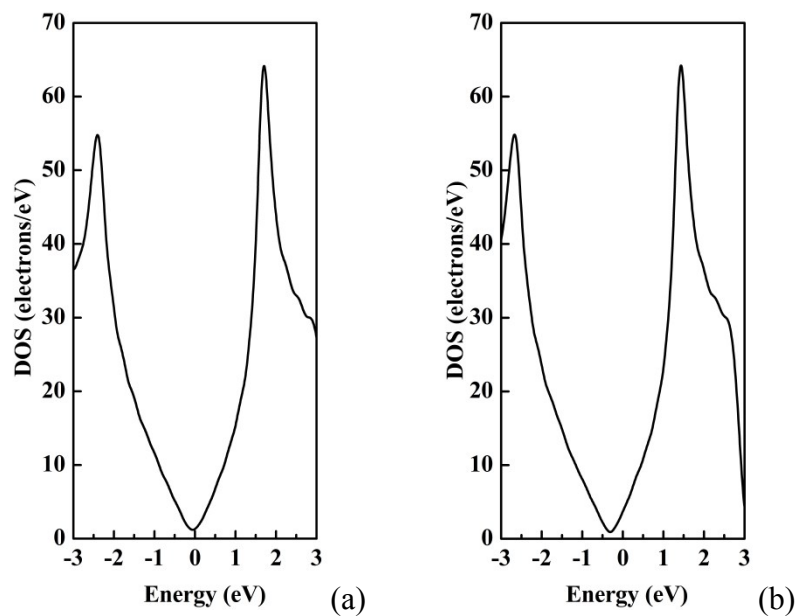


Fig. S6. The calculated DOS of perfect graphene substrates after removal of (a) *O and (b) *OH species are shown. The Fermi level is set as 0 eV

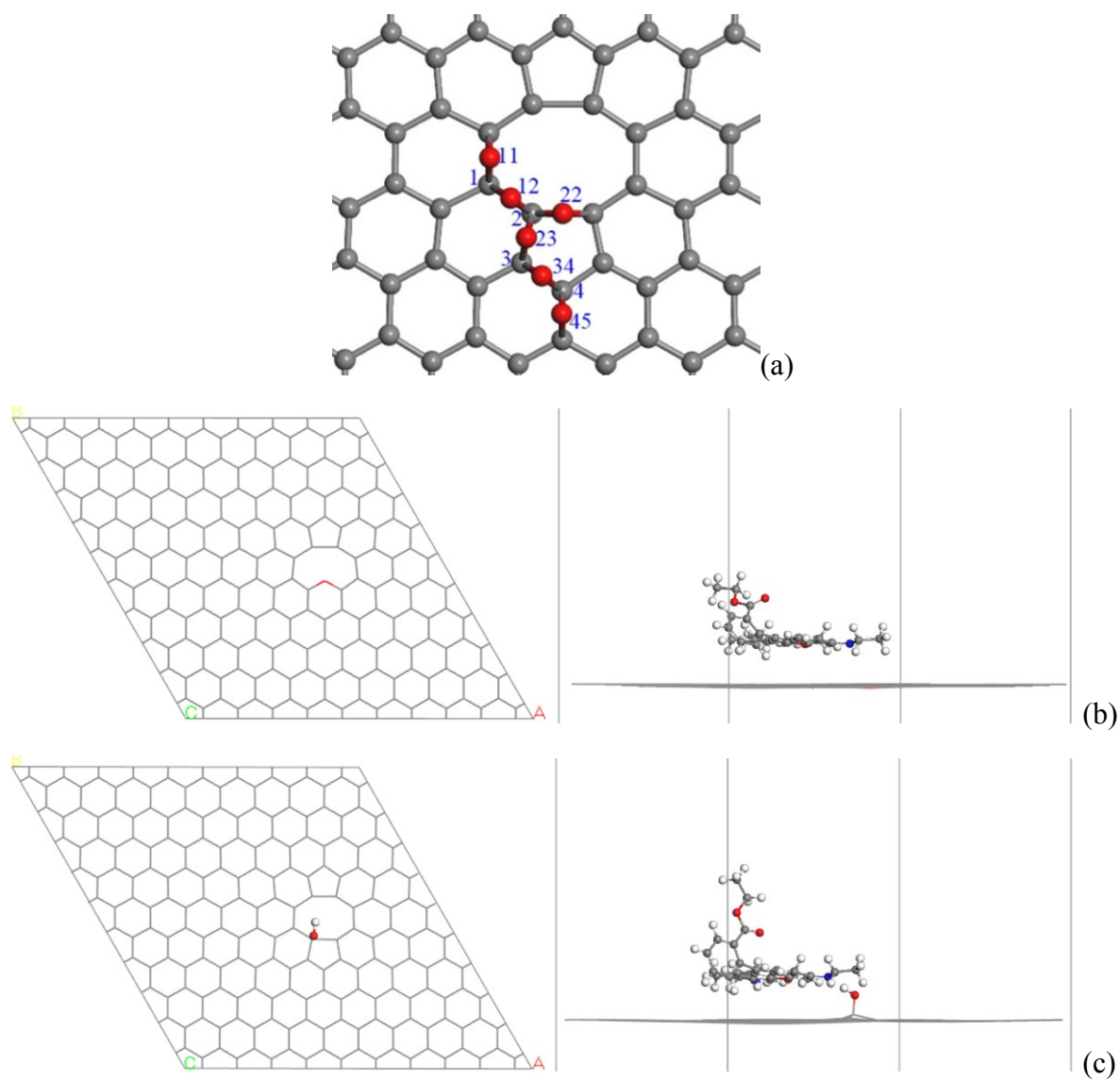


Fig. S7. (a) The possible adsorption sites are considered around a divacancy. The optimized structures of graphene substrate for *O attaching a divacancy and corresponding to graphene-R6G (b), and the counterparts for *OH (c) are shown.

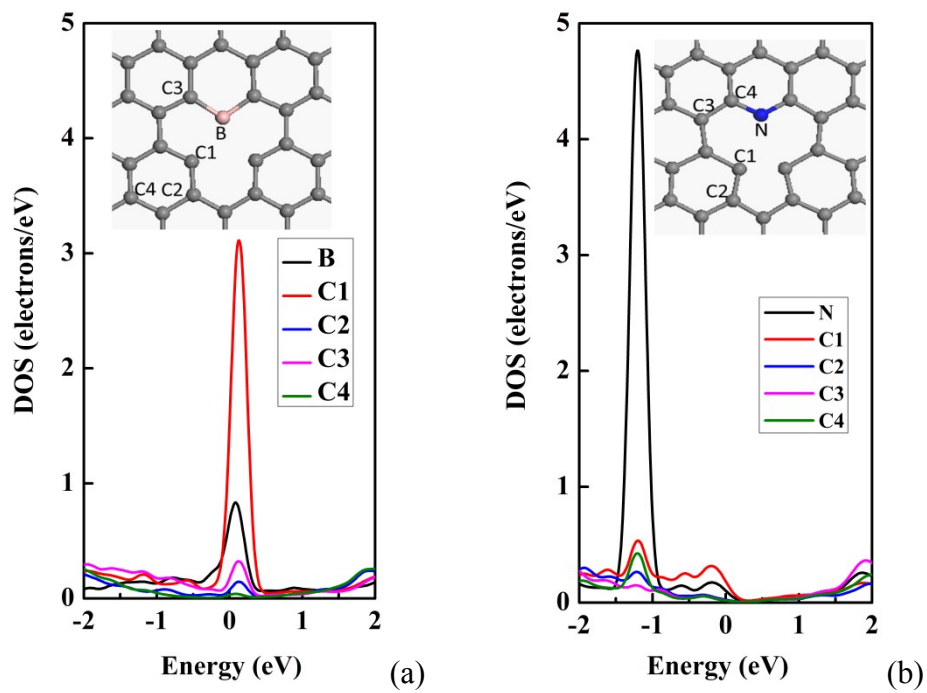


Fig. S8. The local DOS around MV for (a) B doping and (b) N doping cases are shown. The Fermi level is set as 0 eV.

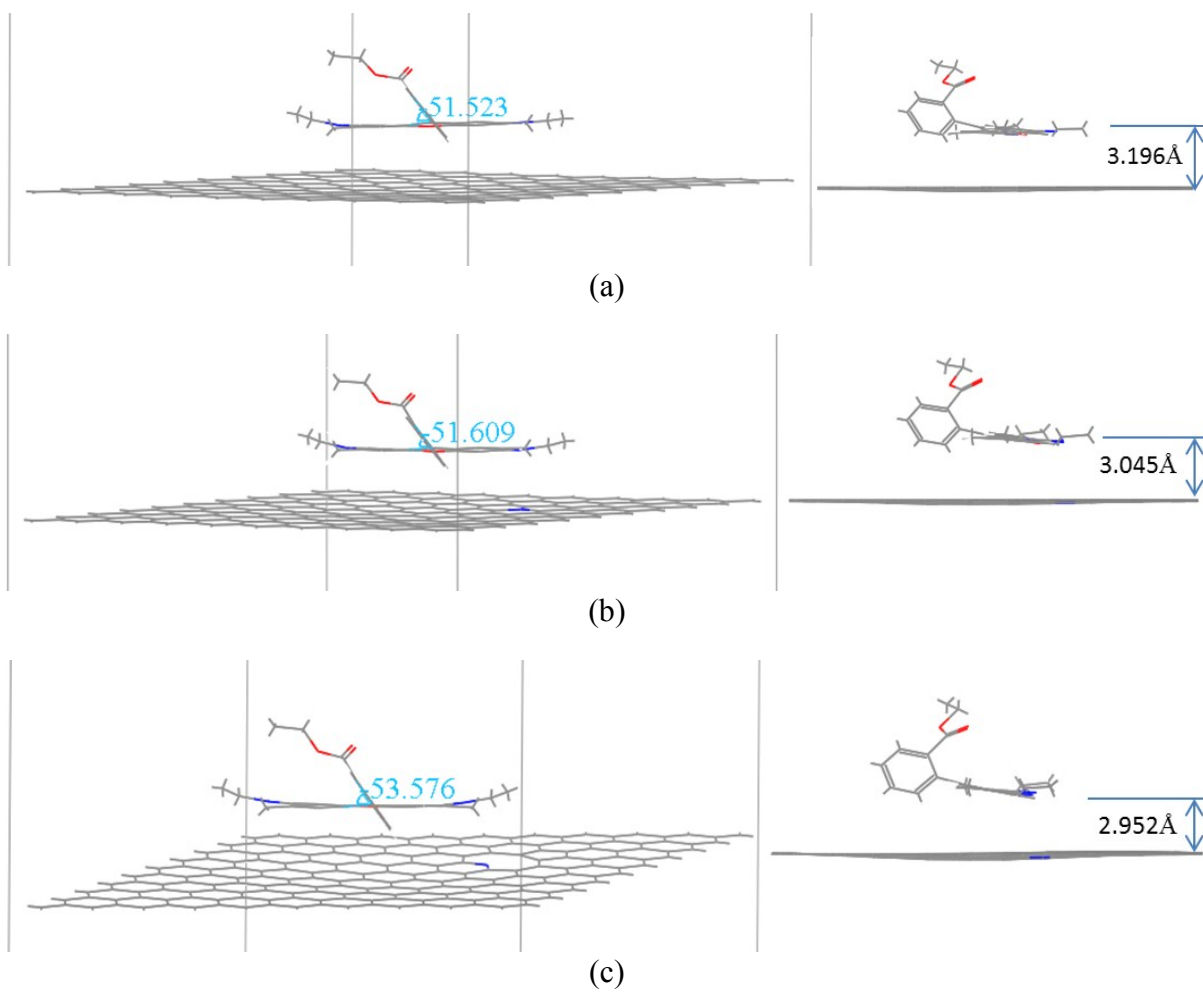


Fig. S9. The optimized structures of R6G molecule on (a) perfect graphene, (b) graphitic N doping graphene, and (c) pyridine N doping graphene are shown.

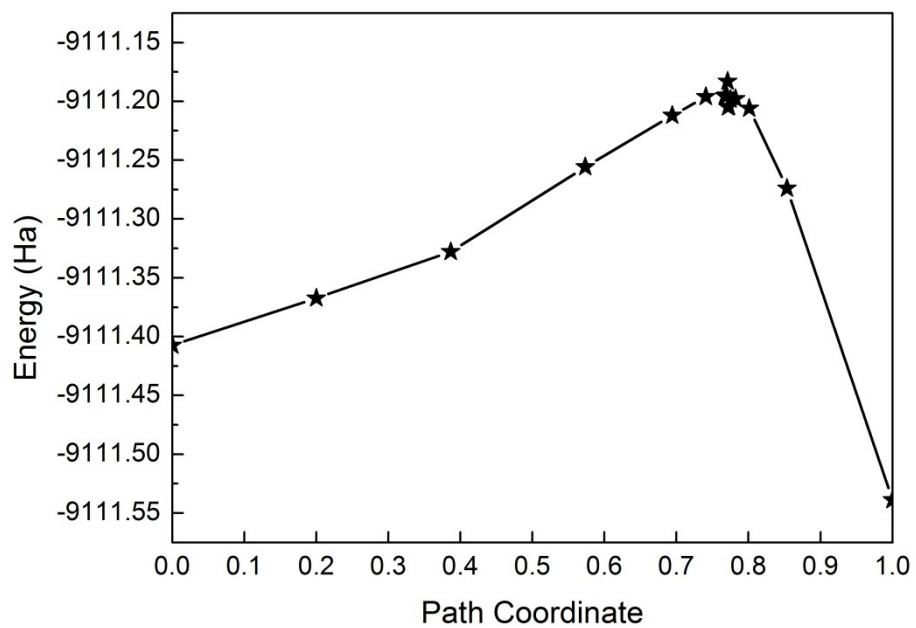


Fig. S10. The plots of energy variation for the removal of *O from perfect graphene is exhibited. The energy of reaction is -82.508 kcal/mol and energy of barrier is 140.773 kcal/mol.