

Supporting information

# A Study on the Absorption Coefficient of Reduced Graphene Oxide Dispersion

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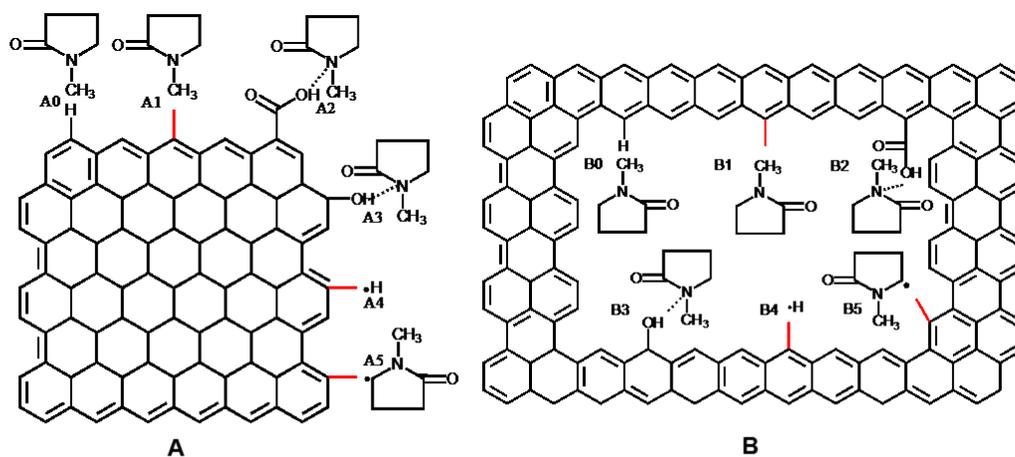
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## **1. How NMP molecules are introduced to RGO flake.**

NMP molecules will be introduced to the RGO flakes during the ball-milling. We use the Density Functional Theory (DFT) calculations to explain the type of interactions between NMP and RGO flakes. The results of DFT calculations show the interactions are including physisorption, H-bonding, and chemical bonds. The details are shown in scheme 1. NMP molecules can be dissociated into two isolated free radicals during the ball-milling, hydrogen free radical ( $\text{H}\cdot$ ) and NMP free radical ( $\text{NMP}\cdot$ ). The adsorption energies of these two free radicals at the edge are up to 4.896 and 3.898 eV, illustrating the formation of strong chemical bonds between  $\text{NMP}\cdot$  (or  $\text{H}\cdot$ ) and carbon dangling bonds. Moreover, a hydrogen bond forms between NMP molecules and oxygen-containing groups ( $-\text{COOH}$  or  $-\text{OH}$ ). The corresponding adsorption energies at the edge are 0.617 and 0.493 eV. In addition, a weak

physisorption exists between NMP molecule and hydrogen-terminated carbon bond or dangling carbon bond at the edge due to the corresponding adsorption energy is 0.048 or 0.126 eV. It is worth to note the defects are not restricted to edge, but exist in surface as well.



	0	1	2	3	4	5
	NMP/H-C-	NMP/-C-	NMP/HOOC-C-	NMP/HO-C-	H/-C-	NMP/-C-
A	0.048	0.126	0.617	0.493	4.896	3.898
B	0.042	0.110	0.579	0.672	2.741	3.423

**Scheme 1.** Schematic representation of adsorption of NMP molecule, H $\cdot$  and NMP $\cdot$  on two types of graphene defect. **A** and **B** represent graphene with defects on the edge and on basal plane, respectively. The red line represents carbon dangling bond. The bottom table is the corresponding adsorption energies for NMP, H $\cdot$  and NMP $\cdot$  absorbed on two types of graphene surface (eV).

## 2. Details of (DFT) calculation

All the DFT calculations are carried out using DMol3 code for two types but similarly-sized single layer graphene surfaces ( $5\times 5$  or  $6\times 6$ ), in which the dangling carbon bonds are saturated with hydrogen atoms, hydroxyl or carboxyl group, etc. Prior to geometry optimization, the total charge of the system was set to 0. During this optimization, the generalized gradient approximation (GGA) scheme and Perdew-Burke-Ernzerh (PBE) were employed as exchange correlation functional. Spin unrestricted geometry optimization calculations were performed using double numerical plus polarization (DNP) basis set to expand the wave functions. DFT semicore pseudopotential core treatment was used to include some degree of relativistic effects and reduce the computational cost. All the atoms were allowed to relax to their ground state configuration with the convergence criteria of  $1\times 10^{-5}$  Ha, 0.002 Ha/Å and 0.005 Å for the total energy, forces and maximum displacement, respectively.

Adsorption energy is calculated by [1]

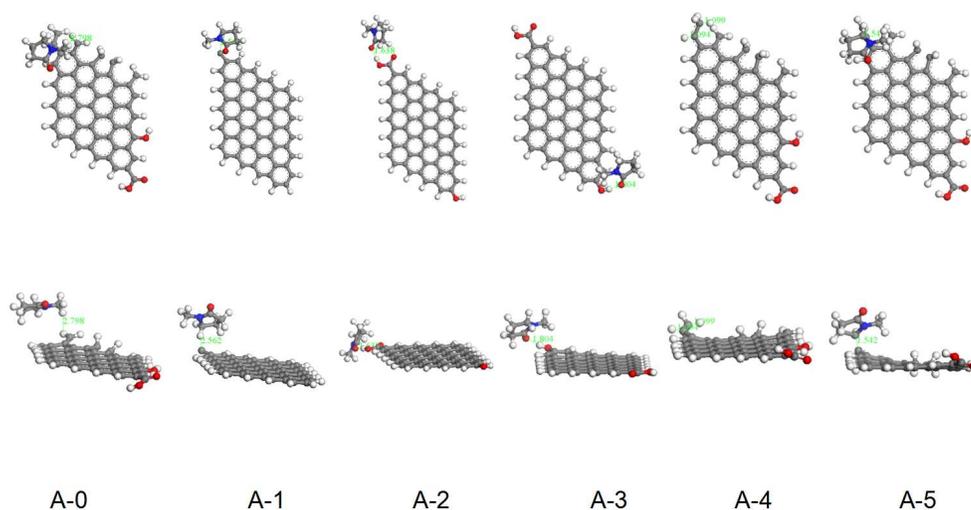
$$\Delta E_{\text{abs}} = E_{\text{A+B}} - E_{\text{A}} - E_{\text{B}}$$

where  $E_{\text{A+B}}$  is the energy of adsorbate (e.g., NMP, H· or NMP·) and the hydroxyl, carboxyl or hydrogen-terminated graphene surface,  $E_{\text{A}}$  and  $E_{\text{B}}$  are the energies of the graphene surface and adsorbate, respectively.

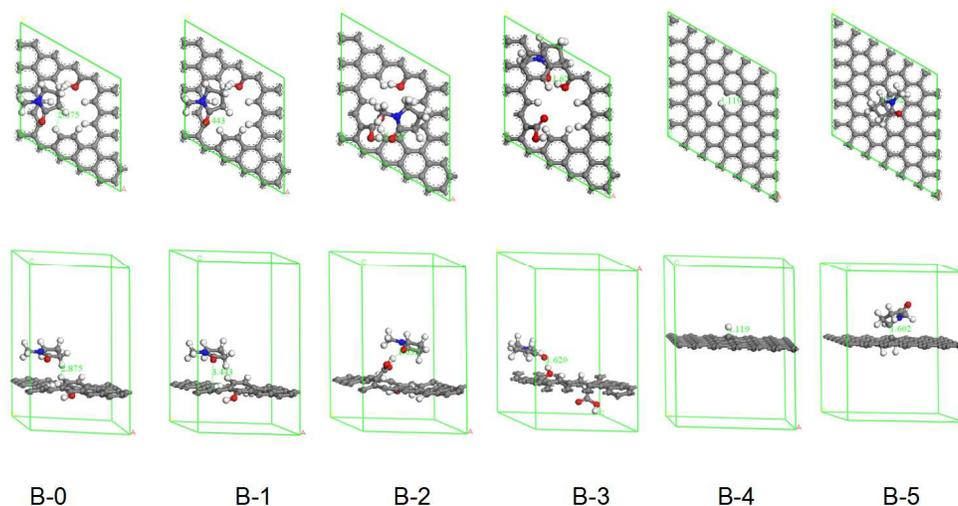
It is clear from Scheme 1 that the adsorption energy between NMP molecule and hydrogen-terminated carbon bond or between NMP molecule and dangling carbon bond of in-plane defected graphene is, respectively, 0.042 or 0.110 eV only, indicating that only a weak physisorption exists and there is no bond formed. But NMP molecules can form a relatively weak chemical bond, i.e., hydrogen bond, with the functional groups (-COOH or -OH) on the in-plane defected graphene surface. Furthermore, NMP molecules can be dissociated into isolated hydrogen free radical (H·) and NMP free radical (NMP·) and their adsorption energies are up to 2.741 and 3.423 eV, respectively, indicating that both of them can form strong chemical bonds

with the carbon dangling bonds.

In contrast, the adsorption energy between NMP molecule and hydrogen-terminated carbon bond or between NMP molecule and dangling carbon bond on the edge-defected graphene is, respectively, 0.048 or 0.126 eV only, which is slightly higher than 0.042 and 0.110 eV. And a similar hydrogen bond can be formed between NMP molecules and functional groups (-COOH or -OH) at the edge and the corresponding adsorption energies are 0.617 and 0.493 eV. Chemisorptions also happen to the dissociated free radicals  $\text{H}\cdot$  and  $\text{NMP}\cdot$  and the corresponding adsorption energies are 4.896 and 3.898 eV. In most cases, the adsorption energies on the defects at the edge are higher than those on the defects within in-plane graphene surface.



**Fig. S1** Configurations of NMP molecule interacting with (A-0): hydrogen-terminated carbon on the edge-defected graphene, (A-1): dangling carbon bond on the edge-defected graphene, (A-2): -COOH-decorated graphene, and (A-3): -OH-decorated graphene;  $\text{H}\cdot$  (A-4) and  $\text{NMP}\cdot$  (A-5) interacting with in-plane defected graphene. Top row corresponds to top view while the bottom corresponds to side view. The grey, red and white colors represent carbon, oxygen and hydrogen atoms, respectively.



**Fig. S2** Configurations of NMP molecule interacting with (B-0): hydrogen-terminated carbon on the in-plane defected graphene, (B-1): dangling carbon bond on the in-plane defected graphene, (B-2): -COOH-decorated graphene, and (B-3): -OH-decorated graphene; H· (B-4) and NMP· (B-5) interacting with in-plane defected graphene. Top row corresponds to top view while the bottom corresponds to side view. The grey, red and white colors represent carbon, oxygen and hydrogen atoms, respectively.

As observed from Fig. S6-(B-2) and (B-3), the two closest atoms from NMP molecule and graphene are oxygen and hydrogen atoms. The distances between them are 1.632 and 1.620 Å, respectively. This implies that H-bonding can be formed and the corresponding adsorption energies are 0.579 and 0.672 eV, respectively. Likewise, the distance between the two closest atoms in Fig. S6-(B-4) is about 1.119 Å while the distance between two closest atoms of NMP free radical and graphene is about 1.602 Å (Fig. S6-(B-5)).

Similarly, as observed from Fig. S5-(A-2) and (A-3), the two closest atoms from NMP molecule and graphene are oxygen and hydrogen atoms. The distances between them are 1.638 and 1.804 Å, respectively. This implies that H-bonding can be formed and the corresponding adsorption energies are 0.617 and 0.493 eV, respectively. Likewise, the distance between the two closest atoms in Fig. S5-(A-4) is about 1.099

Å while the distance between two closest atoms of NMP free radical and graphene is about 1.542 Å (Fig. S5-(A-5)).

[1] K. Wong, Q.H. Zeng and A.B. Yu, *J. Phys. Chem. C*, 2011, **115**, 4656.