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Geometric and Electronic Properties of Graphene Modified by "External" N-Containingng Groups

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Using first-principles spin polarized density functional theory (DFT) calculations, we investigated structures and electronic properties of "external" nitrogen-containing groups (pyridine derivatives) modified graphene via single or double bonding mode. Our results show that, in the most stable structures, the bonding between pyridine derivatives and graphene are all involving with the ortho-carbon of pyridine derivatives, as confirmed by bader charge analysis. The enhanced stability of pyridine derivatives on graphene by [2+2] cycloaddition e.g., double bonding mode(DBPyNG), is caused by the matches between frontier orbitals of pyridine derivatives and those of graphene, which leads to the formation of stronger chemical bonds. Interestingly, electronic structure density of states (DOS) analysis of SBPyNG reveal that the spin-up and spin-down parts are clearly split while it is not case for the double bonding pyridine derivatives modified graphene (DBPyNG).

1. Introduction

The last decades have witnessed a surge of research activities for the investigation of synthesis and property of graphene, which is largely stimulated by their remarkable structure and unique physical properties [1-5] such as quantum hall effect, tunable band gap and high elasticity. However, in many practical applications, pristine graphene has to be modified due to its inert properties caused by the perfect crystal phase (e. g. *sp*^{2}–type aromatic carbon). These chemical modifications, including nitrogen [6-17], boron [18-22], sulfur [23-27]and other heteroatoms [28-36] doping or functionalized by containing nitrogen, oxygen species [37-41], which effectively manipulate electronic structure and thereby enhance the desired chemical reactivity and physical properties.

For chemical modification of graphene by nitrogen atoms or nitrogen species, most studies have been focused on the substitution of lattice carbon atoms with nitrogen atoms for potential catalysis applications of nitrogen-doped graphene. There are numerous studies have been devoted to investigate the synthesis, properties, and application of nitrogen-doped graphene. For instance, Ratso et al. obtained that N-doped graphene is obtained by pyrolysis method [42]. Ahmed et al. revealed a simple, eco-friendly and efficient harmless chemical method by reaction of NH_3 and graphene oxide [43]. Chen et al. proposed that the single N atom substitution makes the antiferromagnetic semiconducting zigzag graphene nanoribbons into spin gapless semiconductors, suggesting the potential applications of N-doped zigzag graphene nanoribbons in nanoelectronics [44]. Moreover, Fujimoto et al. investigated the relationship among atomic structures, energetics, and electronic properties of nitrogen defects in graphene using first-principles DFT electronic structure study [45]. However, these studies focused on the modification of crystalline carbon atoms in the surface of graphene. To the best of our knowledge, very little work on the external nitrogen-doped modification of graphene has been reported before.

Recently, we reported a novel and efficient strategy for fabricating "external" N-doped graphene sheets via pyridine alkyne cycloaddition, which can serve as oxygen reduction reaction (ORR) electrocatalysts [46, 47]. These materials can be prepared through a one-step mild (80°C) chemical modification process. Meanwhile, Giambastiani et al. obtained the N-decoration of multiwalled carbon nanotubes via the introduction of tailored pyridinic functionalities as N-containing edge-type group under mild conditions [48, 49]. It is found that the interaction between pyridinic functionalities and carbon materials (graphene or CNTs) via single [48, 49] or double [46, 47] bonding mode. These nano-carbon materials with "external" nitrogen have similar catalytic properties with nitrogen-doped one. High temperature is necessary in order to prepare nitrogen-doped graphene, in which the lattice carbon is substituted by nitrogen. Graphene with "external" nitrogen can be synthesized under much more mild conditions. Of course, the stability of nitrogen-doped graphene is superior than graphene with "external" nitrogen. Thus, a systematically theoretical study on the structures and properties of graphene with "external" nitrogen is essential.

In this study, the structures and properties of graphene with a series of "external" species containing nitrogen, including pyridine, pyrimidine, pyridazine, pyrazine and triazine have been investigate using DFT calculations. Firstly, the interaction between these species and graphene by either single bonding mode (SBPyNG) or cycloaddition (DBPyNG) were considered to identify the possible structures. Further, the electronic properties of the most stable structures including band structure, charge difference, bader charge and frontier orbital analysis have been studied in detail.

2. Computational Detail

Geometry optimization and electronic structure were performed by using ab initio VASP program [50, 51]. The generalized gradient approximation (GGA) with Perdew Burke Ernzerhof (PBE) [52] formalism was used to treat the exchange-correlation (XC) effects. The valence electrons were described by plane wave basis sets with a cutoff energy of 400 eV, and the core electrons were replaced by the projector augmented wave pseudo potentials. For the Brillouin zone integration, the Γ centered 3×3×4 grid was adopted. One non-local correlation vdW-DF based on rPW86 functional was applied to correct the dispersion interaction. All internal structural parameters were relaxed until the Hellman-Feynman forces on each ion were lower than 0.01 eV/Å. For the optimized geometry of VASP, frontier orbital analysis was carried out by using DMol^3 program [53, 54], with the functional of GGA-PBE and DNP basic set. The adsorption energy is calculated as:

$$E\text{ads} = E(\text{graphene} + \text{adsorbate}) - E(\text{graphene}) - E(\text{adsorbate})$$

Where E(graphene + adsorbate), E(graphene) and E(adsorbate) are the total ground state energies of adsorbate on graphene, isolated graphene and adsorbate alone, respectively. For SBPyNG and DBPyNG, the most stable radical species and pyridine alkyne, pyrimidine alkyne, pyridazine alkyne, pyrazine alkyne and triazine alkyne were used to the reference system.

3. Results and discussion

3.1 Structures of SBPyNG

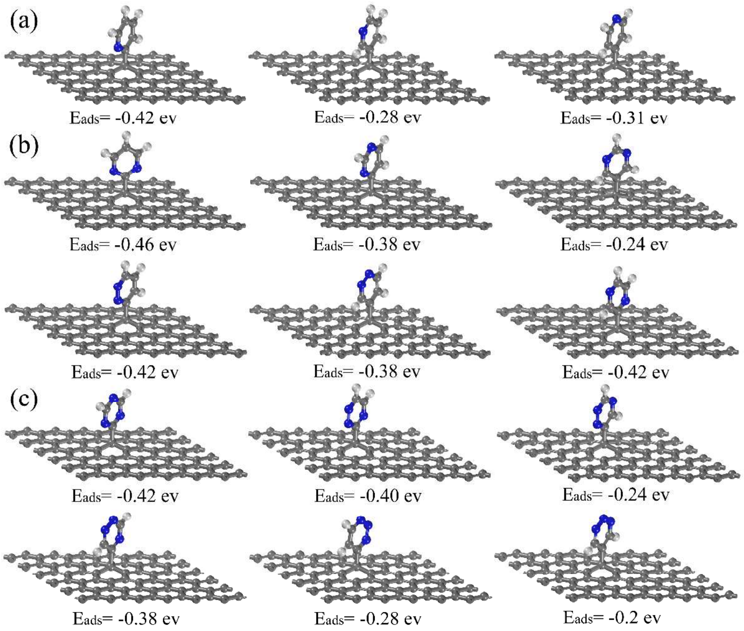


Fig. 1 Optimized structures and adsorption energy of (a) pyridine, (b) pyridazine, pyrimidine, pyrazine, (c) triazine on graphene via single bond

A series of pyridine derivatives (one, two and three nitrogen) modified graphene have been considered. The optimized structures and adsorption energy of pyridine derivatives on graphene are showed in Fig.1. It is found that ortho-carbon of pyridine radical is the most stable binding position, which indicates that ortho-carbon has unique electronic properties [6, 46].

The adsorption energy of pyridine radical on graphene via metal-, and para- carbon position are less stable about +0.14 and +0.11 eV than the most stable one (ortho-carbon position, −0.42eV). There are three kinds of pyridine derivatives containing two nitrogen atoms, pyrimidine, pyridazine and pyrazine. Similarly, the ortho-carbon is found to be the most stable adsorption C position of pyridine derivatives containing two nitrogen atoms on graphene. The meta-carbon of pyrimidine and pyridazine radical adsorption on graphene is slightly less stable than the ortho-carbon one. For pyrazine, there is only one possible adsorption site, in which the adsorption energy is −0.42 eV. Even though, the shared ortho-carbon of two interval nitrogen in pyrimidine radical is still the most stable binding position on graphene. Compared with other structures including pyridazine and pyrazine, synergistic effects of internal nitrogen contribute stronger adsorption to the shared ortho-carbon. The adsorption energy of triazine radical is −0.42 eV via ortho-carbon bonding on graphene. For all of adsorption of pyridine derivatives, it is clear that ortho-carbon is the most stable adsorption position on graphene.

In addition, external N-modification induces a slight deformation to the graphene sheet. Firstly, the carbon atoms linking with external-N are pulled out from the graphene sheet. Secondly, the C-C bond length in graphene involving the linking carbon atom for single N atom SBPyNG (1.538, 1.539, and 1.543 Å), two N atoms SBPyNG (1.541, 1.542 and 1.546 Å) and three N atoms SBPyNG (1.538, 1.540 and 1.546 Å) are longer than the normal C-C bond length (1.432 Å) in pristine graphene.

3.2 Structures of DBPyNG

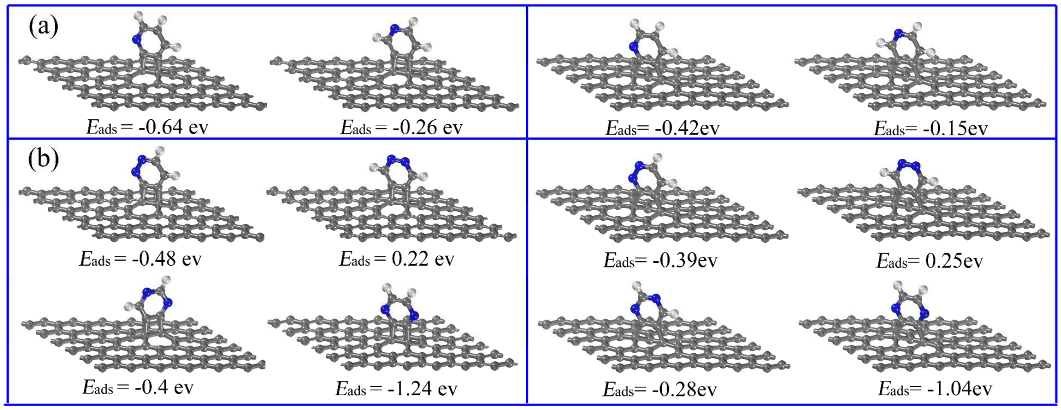
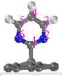
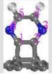


Fig.2 Optimized structures and adsorption energy of (a) pyridine, (b) pyridazine, pyrimidine cycloaddition with graphene either in [4+2] (left panel) and [2+2] (left panel) modes

Since the pyridine derivatives containing three nitrogen atoms could not bond with graphene by cycloaddition, in this section, we only investigated the derivatives containing one and two nitrogen cycloaddition with graphene either in the [2+2] or the [4+2] mode. The optimized structures and adsorption energies are shown in Fig. 2. For each cycloaddition mode, two kinds of adsorption sites have been considered by either ortho-, meta-position (termed as 2-3) or meta-, para-position (termed as 3-4). It is found that the adsorption of pyridine alkyne in 2-3 mode is much more stable than in 3-4 mode for both the [2+2] and the [4+2] cycloaddition, in which the ortho-position is serving as one adsorption position. Furthermore, we also note that the adsorption energy via the 2-3 adsorption sites is about −0.22 eV more stable than the 3-4 one. In term of adsorption energy, pyrazine alkyne adsorption structures in both [2+2] and [4+2] modes are extremely stable than others, where the E_{ads} values (−1.24 and −1.04 eV) are much larger than other adsorptions (see Fig. 2).

3.3 Electronic structure

Table 1 The Bader charge analysis of nitrogen, carbon in different positions of adsorbed pyridine derivatives

	1	2	3	4	5	6
	+0.4704	−0.0228	−0.0228	−0.0609	+0.5	−1.1313
	+1.087	−1.1836	+0.5685	−0.0848	+0.4938	−1.1193
	+1.0568	−1.1486	+1.0482	−1.1618	+1.1359	−1.1906
	+0.5747	−0.0493	−0.0622	−0.0504	+0.4501	−1.1643
	+0.6018	+0.5115	−1.1342	+0.5118	+0.4332	−1.1549
	+0.5905	−0.0567	+0.0393	−0.0391	+0.4343	−1.1724
	+0.516	+0.6486	−1.1676	+0.4231	+0.4751	−1.1583

The present work shows that the ortho-position carbon is the most favorable adsorption site of pyridine derivatives on graphene and another ortho-position carbon is the possible catalytic active site [6, 46]. The Bader charge analysis of nitrogen, carbon at different positions in pyridine derivatives were performed and summarized in table 1. The charge of nitrogen is negative (~ −1.1 |e|). Only the ortho-carbon has about +0.5 |e| charge, while the meta- and the para-position carbon possess very little charge as low as ±0.05 |e|. And the shared ortho-carbon of two internal nitrogen atoms is ~ +1.0 |e|. These charge results clearly indicate the electron transfer mainly from the ortho-carbon to the neighbouring nitrogen.

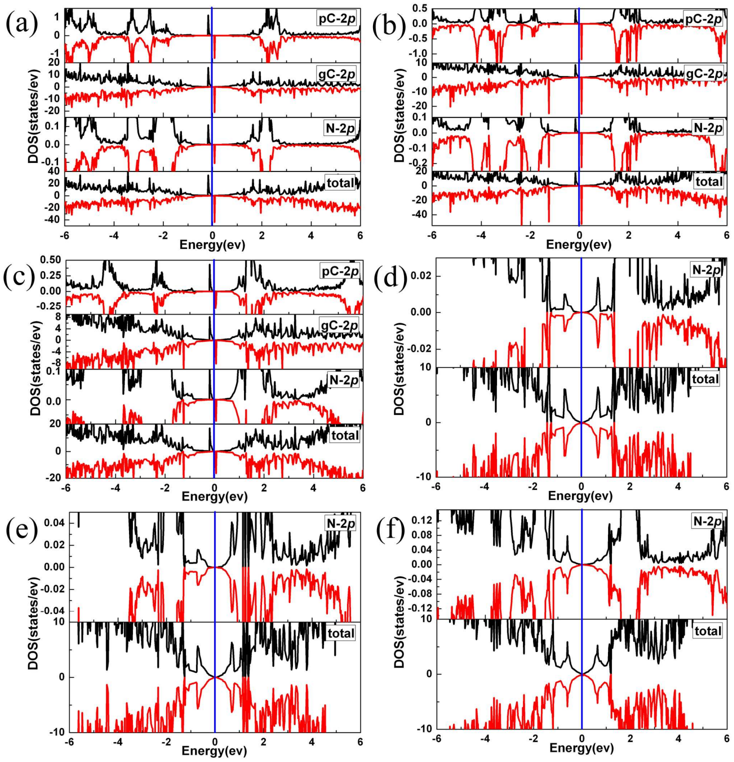


Fig. 3 Total DOS and PDOS of the most stable geometry of one (a), two (b) and three (c) nitrogen atoms-doped pyridine in single bond adsorption, single N- [2+2] (d), double N-[2+2] (e) and [4+2] (f) cycloaddition.

In order to identify the effect of adsorbed N-containing groups on the electronic properties of graphene, the calculations of electronic structures were carried out in this work. As shown in Fig. 3. In the case of SBPyNG, pyridine and its derivatives exhibit similar electronic characteristics. The total density of states (TDOS) of graphene overlap with those of adsorbates, suggesting the interaction exists between them. Interestingly, the spin-up and the spin-down parts of DOS obviously split in the vicinity of Fermi level. With further inspecting the PDOS, we find that the total DOS in the vicinity of Fermi level mainly originates from the 2*p* states of three carbon atoms of graphene around the ortho-carbon atom bonding with adsorbate and 2*p* states of carbon atoms in pyridine derivatives. Therefore, it is found that the adsorption of pyridine derivative induces the split of DOS peaks. Moreover, the band gap has kept the same characteristic with that of graphene. However, the phenomenon is different in the adsorption of DBPyNG. In the case of the most stable [2+2] and [4+2] cycloaddition either by single N or double N species, spin-up and spin-down PDOS peaks never split at the position of nearby Fermi level. Similarly, 2*p* states of N atoms play an important role in the TDOS and overlap with 2*p* states of C atoms. That is one major factor of stronger adsorption in [4+2] and [2+2] modes. However, their corresponding band gaps are always zero.

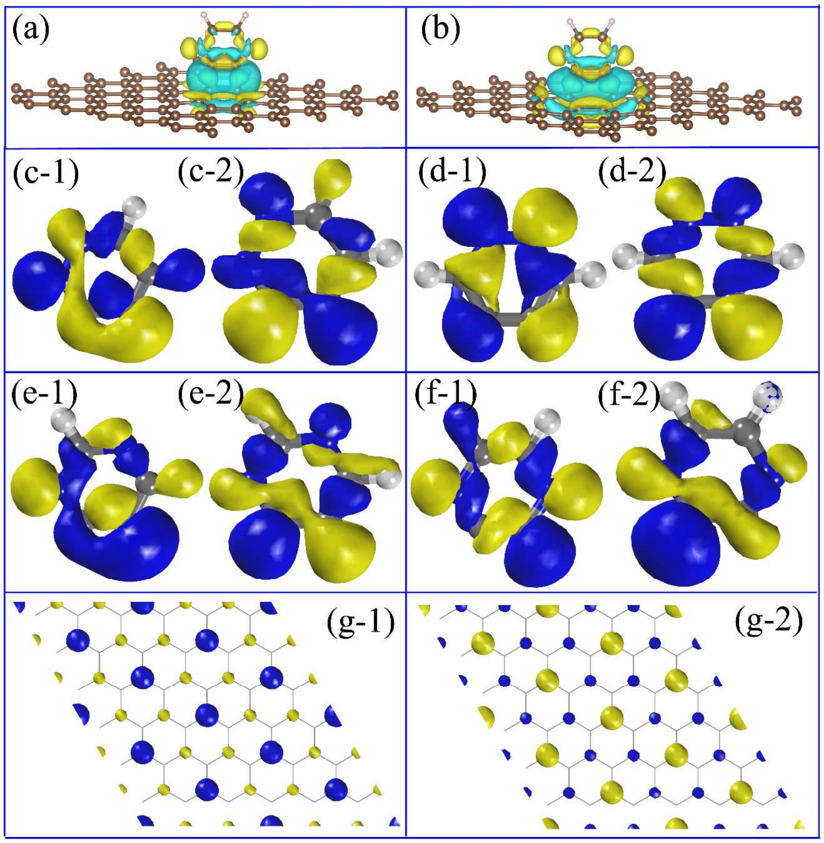


Fig.4 charge density difference of adsorption of pyrazine alkyne on graphene either [2+2] (a) or [2+4](b), Blue(yellow) isosurfaces indicate a depletion(addition) of 0.014e/A^{-3}; HOMO(1) and LUMO(2) of 3, 4-pyridazine alkyne(c), 4, 5-pyridazine alkyne(d), pyrimidine alkyne(e), pyrazine(f) and graphene.

Furthermore, charge density difference for the most stable configuration of the [4+2] and the [2+2] cycloaddition were conducted, as shown in Fig. 4(a-b). Clearly, charge transferred parts locate at the linking bond either [2+2] or [4+2] cycloaddition cases. Therefore, we conclude that stronger chemical bonds are generated between pyridine alkyne derivatives and graphene. Further comparison of frontier orbitals between them sheds light on three important aspects as follows: (1) As shown in Fig. 4(c-e), HOMO and LUMO of three pyridine alkyne derivatives (3, 4-pyridazine alkyne), 4, 5-pyridazine alkyne, pyrimidine alkyne) show similar characteristic, where 2p_x or 2p_y dangling orbitals of two carbon atom in alkyne are included; (2) However, for the cases of pyrazine alkyne (see Fig. 4f)**,** only one dangling orbital of 2p_x or 2p_y is effectively salient in one carbon atom of alkyne either HOMO or LUMO, which is different from those of other pyrazine alkyne derivatives; (3) On the graphene, both positive and negative 2p_z orbitals orderly appear each atom. Thus, frontier orbitals of pyrazine alkyne match well with those of graphene, resulting in the formation of stronger chemical bond. That also verifies the adsorption of pyrazine alkyne is more stable than others.

4. Conclusion

In summary, we employed DFT calculations to investigate the stable configurations and corresponding electronic structures of SBPyNG and DBPyNG. For the most stable structures, it is identified that the bonding between pyridine derivatives and graphene are all involving with the ortho-carbon of pyridine derivatives due to the unique electronic properties of ortho-carbon. Furthermore, it is found that SBPyNG has different electronic structures from those of DBPyNG. The present study helps to understand geometries of external-N modified graphene and promotes studies of structure-function relationship.

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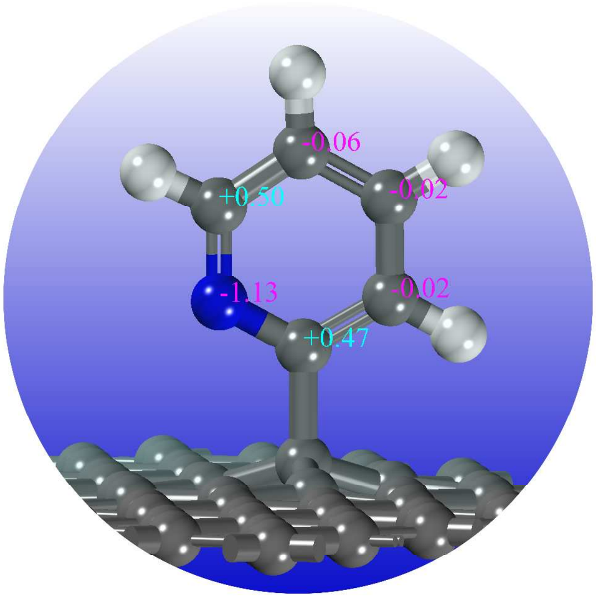

Due to electron from ortho-carbon to nitrogen, the ortho-carbon is the most stable binding site between pyridine derivatives and graphene or the catalytic site for a lot of reactions