Fluorine adsorption on the graphene films: From metal to insulator

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ABSTRACT

Electronic structures of fluorinated graphene are investigated by calculations using first-principle density functional theory (DFT). Our results suggest that the average charges on carbons reduce and the adsorption energies increase along with increasing coverages, this agrees with other theoretical/experimental works which show that F adsorption causes p-doping to the graphene. All of the stable configurations with different coverages have a band gap except for the case with one atom adsorption which is metallic. There is a magnetic moment when the number of F adatoms in a supercell on graphene sheet is odd. The magnetism comes from the distortion caused by the interaction between F atom and graphene, which was also manifested in the experimental works of Nair et al. (2012). The band gap range implies that fluorinated graphene, at certain coverage levels, might be useful for solar applications.

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1. Introduction

Graphene unique electronic properties and linear dispersion relation are beneficial for electron transfer. The practical applications are usually due to the ability to achieve stable n- and p-type doping by functionalization methods. Experimental and theoretical results have revealed excellent properties by functionalizing graphene with atoms, compounds or defects [2–23]. Modulating gaps in the band structures is a significant way to remove limitations in its usage in electronic instruments of graphene-based system. In many works, the functionalization of graphene with a full coverage of H or F shows admirable large gaps in graphene's energy spectrum [8–10,12,24]. One of graphene researches recently has reported the midgap states in some special configurations [25]. In the following, we have studied the band gap variations for different coverages and configurations, in order to make clear the influences of the gap caused by fluorine adatoms.

Adatoms and vacancies can induce the controllable paramagnetism. Palacios and Ynduráin [26] have reported that only when it has a high concentration of ordered vacancies on the same sublattices, the π magnetic moments can be sustained and lead to a ferromagnetically ordered state. The hydrogen-induced magnetism can survive only at very low concentrations (single-atom regime)

[12] and this magnetism can be stabilized on a distorted graphene with some bonds being strained and some being compressed [11]. It is commonly accepted that the chemisorption of single hydrogen atom on graphene leads to appearance of magnetic moments in the system [12]. Unlike H adatom, F adatom on one-side leads to notable spin-half paramagnetism at low temperature [1]. F adatoms in graphene have been reported from theory [10–12,27–29] and experiments [9,10,1,30–34]. It is still a controversial topic about its magnetic properties. Experimental results [1,33] depict the magnetic properties, but one existing report from DFT calculations emphasized the absence of magnetism [24]. In this paper, we calculated the electronic and magnetic properties of chemical fluorination of graphene. No magnetic phenomena were discovered for fluorographene with even number F adatoms. The magnetic properties are obtained for systems with odd number F adatoms when the coverage is larger than a critical value.

2. Methods

Making use of first principles methods, we performed spin-polarized density functional calculations within the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) [35] to describe fluorine adsorption on graphenes. The Vienna Ab initio Simulation Package (VASP) [36,37] with the projector augmented wave (PAW) basis sets has been used for solving the resulting Kohn–Sham equations. Employing the above methods, we obtained the relaxed structures for fluorographene, and computed

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their total energies, magnetic moments, and band structures. An $11 \times 11 \times 1$ k-mesh sampling of the supercell Brillouin zone is chosen in the structure relaxation calculations and a $13 \times 13 \times 1$ k-mesh is chosen for total energy calculations. The kinetic-energy cutoff of plane wave is set to 400 eV, the energy convergence is selected to 1×10^{-5} eV/atom, and the forces between atoms are less than 0.03 eV/Å. In order to calculate a two dimensional graphene by the VASP, we intentionally enlarge the vertical distance between graphene sheets to 10 Å in vacuum, so that the interactions between sheets reduce to a negligible value.

We calculate the magnetic moments and explore its relations on various F coverages. Three supercell models containing 8, 18, and 32 C atoms are used. The F atoms on one- or two-side of graphene plane are depicted in Fig. 1. Although we consider very small supercells, that is not a very realistic periodic arrangement of adatoms, at present stage, a systematic study of the electronic structure as a function of the coverage is very interesting.

Fluorine adatoms are on the top of carbon atoms. They saturate the σ bonds of the sp^3 configuration. Taking one fluorine adatom as an example, it only adheres to one carbon atom (C_0) it adsorbed. The other three nearest neighboring carbon atoms undergo a Jahn–Teller distortion. The hybridization type is changed. In order to describe sp characters, a quantitative analysis of distortion is used. Following Ref. [38], the angles between the bonds having sp character of C_0 orbitals are related on its s and p_z atomic orbitals. A is the hybridization parameter, which is used to characterize sp^2 and sp^3 hybridization. $A = \sqrt{2} \times \cot\theta$, where θ is the angle between the new σ orbitals and the direction normal to the graphene plane (z axis). Hybridization parameter $A = 0$ and $A = \frac{1}{2}$ correspond to the sp^2 and sp^3 configurations, respectively.

3. Results and discussion

3.1. Structural stability

In this subsection, we use a 2×2 supercell to find out a stable configuration. The supercell contains 8 carbon atoms. We study the stable configurations for various F atoms coverages. Although a molecular dynamic simulation carried out by Paupitz et al. presents the fluorine adsorption mechanism in graphene and exhibits different F configurations in the structures [39], we still need to find the structural stability with different F configurations at the zero temperature. In the following calculations with DFT, all the temperatures are assumed the same. Adsorption is a spontaneous exothermic process. The value of the adsorption energy (E_{ad}) reveals the degree of difficulty in forming an adsorptive system.

We define the adsorption energy of per fluorine adatom in a system

$$E_{ad} = -\frac{1}{N}(E_{GF} - E_G - NE_F) \qquad (1)$$

where N is the number of F atoms. E_X is the total energy of system, where X represents GF (fluorinated graphene), G (pure graphene) or F (fluorine adatom) system respectively. It should be pointed out that E_F we take in this equation is the energy of a single F atom. Accordingly, Fig. 2(a) shows the calculated E_{ad} values as a function of coverage (F/C), the ratio of numbers of F and C, for both one-side and two-side adsorptions. It's an exothermic reaction if the value of E_{ad} is positive, and the interactions between F and C atoms become stronger as the value is increased. The larger E_{ad}, the easier the accomplishment of adsorption process is. From this picture, we can see the most stable structures are 25% coverage (C_8F_2 (abbreviated as $(C_4F)_n$)) for one-side adsorption and 100% coverage (C_8F_8 (abbreviated as $(CF)_n$)) for two-side adsorption, respectively. The most stable adsorption configuration for one-side is composed by one fluorinated site plus its third nearest neighbor fluorinated site in a para position of a 2×2 system, the configuration in Fig. 1(a). For two-side case, the most stable one is the fully fluorinated states, which depicts that F adatoms bonded with carbon atoms in ortho positions (one plus its first nearest neighbor) are in different sides of graphene sheet. Furthermore, in the same coverage, the configuration for two-side is more favorably formed than that for one-side (Fig. 2(a)). These configurations are in good agreement with the preferred ones from molecular dynamic simulations reported by Paupitz et al. [39], their simulation has more authenticity in structural calculations because its fluorination occurs in a random way.

3.2. Magnetic properties

In this section, we only calculate the total energies and magnetic moments for three supercells, where case α, case β and case γ is a 2×2, a 3×3 and a 4×4 cell, respectively. All the three cases have only one adsorbed F atom in each supercell. The various values of energy cut-off from 300 to 500 eV, and different k-point sampling from $9 \times 9 \times 1$ to $23 \times 23 \times 1$ are applied to these three cases during the calculations. We have found that the emergence of the magnetic solutions does not depend on the k-points sampling and the energy cut-off, although the magnetic value may be affected. And the value is nearly unchanged when the k-grid is larger than $11 \times 11 \times 1$.

Case α always has a magnetic moment, while no magnetism appears for cases β and γ, which implies that there is no
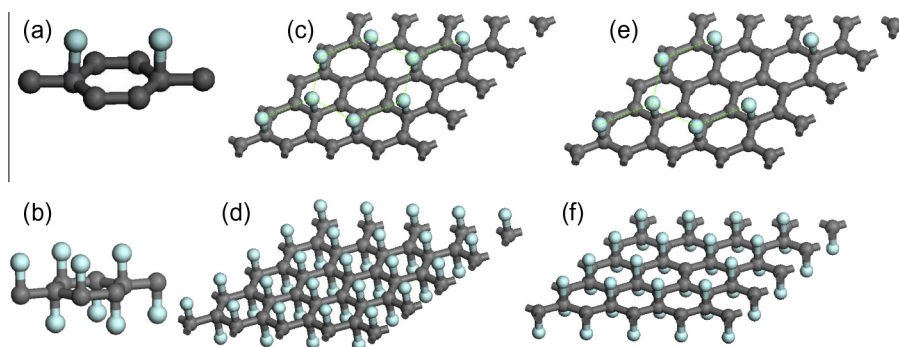

Fig. 1. The F atoms on one-side of plane are depicted in (a), (c), and (e), and on two-side of plane in (b), (d), and (f). (a) and (c) are the saturated states for one-side adsorption of 2×2 and 4×4 supercell, (b) and (d) are the saturated states for two-side adsorption of 2×2 and 4×4 supercell, (e) and (f) are the one defect states for saturated fluorinated 4×4 graphene. Carbon is in gray color, and fluorine in cyan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)