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Research paper

Adsorption of chloroform on N-doped and Al-doped graphene: A first-principle study

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ABSTRACT

Adsorption properties of chloroform ($CHCl_3$) on pristine graphene, N-doped graphene and Al-doped graphene are studied by using density functional theory (DFT) calculations. Our calculations reveal that there are higher charge transfer and smaller adsorption distance and bigger adsorption energy when $CHCl_3$ is adsorbed on Al-doped graphene comparing with adsorptions on pristine graphene and N-doped graphene. The *p-p* orbital coupling between Al and Cl is stronger than those of C—Cl and N—Cl, which suggests that Al-doped graphene is more sensitive to the adsorption of $CHCl_3$. Al-doped graphene can be a good candidate for sensors or catalyst to detect and adsorb $CHCl_3$.

1. Introduction

Chloroform ($CHCl_3$) is one of the chlorinated organic compounds, it has strong volatile and is a kind of pollution which could cause cancer. What's more it's well known that trace amounts of $CHCl_3$ are contained in water. Production of $CHCl_3$ in trap water is caused by reaction between residual chlorine and organic compound [1]. The quality of water sources has deteriorated in recent times, leading to an increase in the amount of chlorine added to trap water at filtration plants. These chlorinated organic compounds must be removed because of their carcinogenicity. One possible removal method is adsorption by using carbons. Carbon based materials engrossed greatly concentration because of their low density, high stability, appropriateness for bulky scale production, diversity of structural shapes, and the capability to change the pore structures. As a novel member of carbon structures, graphene has attracted intense attention since its first discovery in experiments in 2004 [2–4]. Graphene has more superior performance in addition to its unique two-dimensional structure, it also has unique chemical properties, such as excellent electrical, optical and mechanical properties, Because of its excellent properties, graphene has been widely applied in various aspects, such as electronic circuitry elements, energy production, spintronic devices, and field-effect transistors, [2–5]. Graphene has also been experimentally and theoretically proved to have potential applications in detecting various molecules. Owing to its low dimensions and great surface area, graphene could be selected as a novel material toward adsorption and desorption processes [6]. Based on its adsorption aptitude to some chemicals via physical π-π interaction, graphene also can be considered as a good candidate material for sensors or catalyst [7].

There appear changes of the graphene structure and the physical and chemical properties when molecules are adsorbed on graphene sheet [8–10]. The local carrier concentrations will be changed by the adsorption, and then the conductivity properties of the system presents remarkable fluctuations, so it is possible for graphene to be a solid-state sensor to detect particular molecule from others. One of the major difficulties in applying the pristine graphene directly on molecules sensing is the low adsorption energy, which could lead to unstable and inconspicuous detecting signals [8]. It also should be noticed that because of the 2D structure (sp^2 hybridizing of carbon atoms) of graphene, there is a space limitation to adsorb large molecules on its surface [11]. As a result, it may not be the best choice to use pristine graphene to adsorb large molecules. Doped graphene will be one of the best ways to solve the above problems because doping can significantly changes the electronic structure of graphene [12–15]. In recent years, doped graphene acted as adsorbent to adsorb different molecules has attracted many researchers' interests and it also has been recognized that higher sensitivity of graphene toward different chemicals could be mainly enhanced by doping. For example, the applications of graphene as sensors to detect NO_2, NO, NH_3, CO, N_2O have been researched and reported [16–22]. The detections of hydrogen cyanide, formaldehyde molecule, and methylated

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arsenic pollutants by using doped graphene also have been studied [12,23–26]. In other word, doped graphene could be more effective as a sensor or catalyst to detect and adsorb different molecules.

It is good to improve the interactions between $CHCl_3$ and graphene by using dopant atoms in graphene. In this article, we report that the sensitivity of graphene system to adsorb $CHCl_3$ could be enhanced to a higher level through N-doping and Al-doping based on density functional theory calculations (DFT). We hope our results provide a new idea for graphene to build solid-state sensors to detect molecule or as catalyst for molecular adsorptions.

2. Models and computational details

All DFT calculations are performed by using VASP with the projector augmented wave (PAW) basis sets and periodic boundary conditions [27,28]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is used [29], and the plane-wave cutoff energy is set to 500 eV throughout the calculations. Each simulated system consists of a 4×4 graphene supercell (32 C atoms) with one doped atom substitutes a C atom. A single $CHCl_3$ is adsorbed on the graphene surface. In the direction perpendicular to the graphene surface, the supercell is extended to 20 Å in order to avoid the interference. The Monkhorst-Pack k-point grid of $5 \times 5 \times 1$ is adopted for the Brillouin zone integration [30]. All atoms are allowed to relax during the structural optimizations and the convergence criteria for the total energy and the force are 10^{-4} eV and 0.02 eV/Å, respectively. The van der Waals interactions with DFT + D2 method are included in the calculations.

After full relaxation, it is found that both N-doped and Al-doped graphene are all retain the planar form. The C—N atom distance is found to be 1.41 Å and the C—Al atom distance is 1.70 Å, which are consistent with previous theoretical works in Al-doped single wall carbon nanotubes and Al-doped graphene [31,32]. For the adsorption systems, the possible adsorption sites of $CHCl_3$ on graphene are top, hollow, and bridge, namely, the tops of a carbon atom, the center of a carbon hexagon, and the center of a carbon-carbon bond, respectively. There are three different adsorption ways of $CHCl_3$ on graphene for each adsorption position above, i.e., three Cl atoms are parallel to the graphene sheet, H atom downward perpendicular to the graphene sheet, and one Cl atom downward perpendicular to the graphene sheet, respectively. These three different adsorption configurations are all calculated and it is found that the total energy will be the lowest when one Cl atom is downward adsorbed on the top site of Al atom, so we adapt this adsorption configurations in the following calculations. Fig. 1 gives the relaxed configurations when $CHCl_3$ is adsorbed on pristine graphene, N-doped graphene and Al-doped graphene, respectively.

3. Results and discussions

It can be found from Fig. 1(a) and (b) that the pristine graphene and N-doped graphene have almost no change after $CHCl_3$ is adsorbed. While in Fig. 1(c), the adsorption of $CHCl_3$ causes a structure change in Al-doped graphene dramatically, where the Al atom protrudes out of the graphene plane. The adjacent C atoms also protrude in varying degrees. The distance between the C and Cl atoms is 3.14 Å, which means one Cl atom is divorced from the molecule. That is to say the reaction between $CHCl_3$ and Al-doped graphene is stronger. More calculation results of the adsorption systems were given in Table 1. Adsorption energy is a physical quantity reflecting the adsorption strength. The adsorption energy E_{ad} of $CHCl_3$ on graphene is calculated from the equation $E_{ad} = E_{tot} - E_{sheet} - E_{chl}$, where E_{tot}, E_{sheet} and E_{chl} are the total energies of the adsorbed system, graphene sheet and isolated $CHCl_3$, respectively. Based on the definition of adsorption energy, it is generally negative, and the adsorption is unstable if we get positive values. The greater the absolute value of adsorption energy is, the more stable the system will be [33,34]. Charge transfer ΔQ between $CHCl_3$ and graphene are calculated based on the Bader charge analysis [35]. By using this method, the charge of each atom in the simulated system can be calculated, and the total system charge can also be gotten through charge accumulation. For the system of molecules adsorbed on graphene sheet, ΔQ can be calculated as the charge variation of molecules before and after

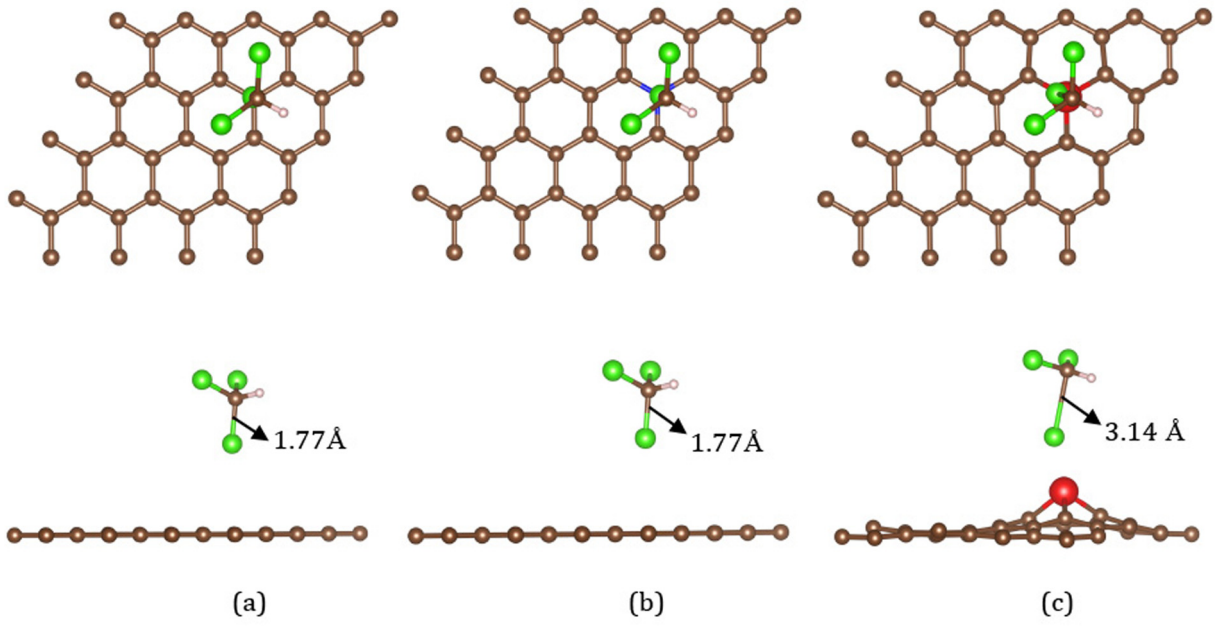

Fig. 1. Top and side views of top-site adsorption configurations for (a) pristine graphene; (b) N-doped graphene; and (c) Al-doped graphene. The brown, pink, blue, green and red spheres are denoted as C, H, N, Cl and Al atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)