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Density functional theory calculations on the adsorption of formaldehyde and other harmful gases on pure, Ti-doped, or N-doped graphene sheets

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ABSTRACT

Understanding the interaction mechanisms of CO, NO, SO_2, and HCHO with graphene are important in developing graphene-based sensors for gas detection and removal. In this study, the effects of doped Ti or N atom on the interaction of these gases with graphene were investigated by density functional theory calculations. Analyses of adsorption energy, electron density difference, and density of states indicated that the doped Ti atom could greatly improve the interaction of gas molecules with graphene. The Ti-doped graphene sheet demonstrated selective gas absorption. The order of interaction between the gas molecules and the Ti-doped graphene sheet was as follows: SO_2 > NO > HCHO > CO. By contrast, the N-doped graphene sheet did not exhibit apparent selective gas absorption. These results imply that the Ti-doped graphene sheet is more effective than the N-doped graphene sheet in detecting and removing gas molecules because of its high selectivity.

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1. Introduction

Graphene is a well-known two-dimensional (2-D) material that is chemically inert. This material has become popular because of its excellent electronic properties [1–3]. The 2-D crystal structure of graphene causes electrons to behave like massless fermions, with the speed of light being replaced by a Fermi velocity of approximately 106 m/s. Electrons in graphene show high charge-carrier mobility. Owing to its excellent properties, graphene is regarded as a promising functional material in many applications, such as ultra-high frequency transistors, gas sensors, and potential electrode materials. The potential application of graphene as a gas sensor has been extensively studied [4–7]. Recently, graphene sheets have been proven to have more effective sorbency than activated carbon.

Formaldehyde (HCHO) has attracted considerable attention as a dominant indoor pollutant that poses harmful effects on human health [8]. At low concentrations, airborne HCHO mainly causes irritation of the eyes, nose, and mucous membrane. Its carcinogenic risk increases with increasing concentrations. HCHO is widely used as an important industrial precursor of many chemical compounds. However, given its toxicity, monitoring and controlling the exposure of HCHO in both residential and industrial environments have been given much focus in the past decades [9–10]. Therefore, effective materials for detecting HCHO are needed. Several approaches for formaldehyde removal have been studied, including chemi-sorption, photocatalytic oxidization, and biological degradation. Chemi-sorption is considered the most effective and practical method of HCHO removal, and chemically modified activated carbon appears to be the most promising adsorbent. We considered graphene as a new chemi-adsorbent for HCHO removal because of its many specific properties. In this study, the ability of graphene to detect other harmful gases, such as CO, NO, and SO_2, was evaluated. In the past years, doping in graphene-related systems has attracted considerable interest from researchers [11–16]. The adsorption of gas molecules, such as NO_2, H_2O, and NH_3, could induce the charge-carrier ability of graphene; however, detailed mechanisms need further studies. Kang et al. [14] studied the interaction of Ca-doped graphene with dioxin and demonstrated that

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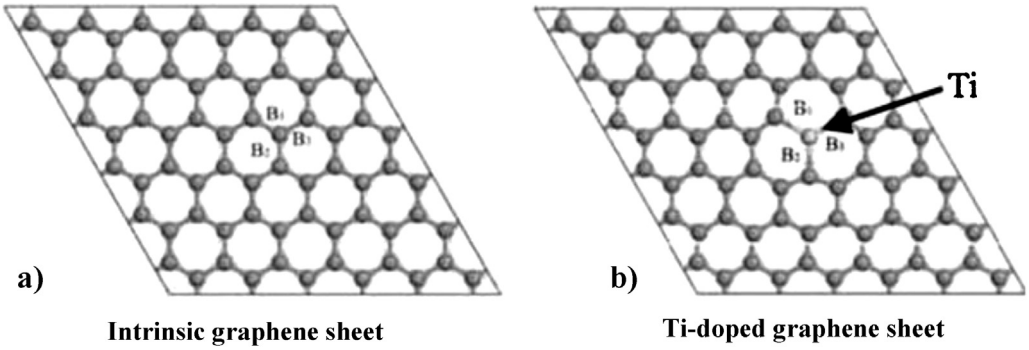

Fig. 1. Ball and stick model of (a) pure, (b) Ti-doped, and (c) N-doped graphene sheets. Color code: C, gray; O, red; Ti, light-gray; N, blue; H, white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the doped Ca could aid in dioxin removal. Chu et al., [17] proposed a hydrogen storage medium (i.e., Ti-doped graphene) by computational calculations. The sensitivity of Al-doped graphene in detecting gases was compared with that of pure graphene. The results showed that the doped Al could significantly improve the interactions [18].

In this study, density functional theory (DFT) calculations were carried out to investigate the interactions between harmful gases (H_2CO, CO, NO, and SO_2) and graphene sheets (pure, N-doped, or Ti-doped) at the electronic level. The results of this study may provide meaningful insights into the use of graphene as a gas sensor in environmental monitoring.

2. Computational details

The DFT program DMol^3 in Materials Studio (Accelrys, San Diego, CA) was used to investigate the interactions between HCHO molecules and Ti-doped or pure graphene. Physical wave functions were expanded in terms of numerical basis sets in DMol^3 codes to produce highly accurate results while keeping the computational cost low. The double numerical basis set with polarization was used, which is comparable with the 6-31G** basis set [19,20]. The core electrons were treated with DFT semi-core pseudopotentials [21]. The exchange-correlation energy was calculated using the Perdew–Burke–Ernzerhof generalized gradient approximation. Special points sampling integration over the Brillouin zone was employed using Monkhorst–Pack schemes with a $2 \times 2 \times 1$ k-point mesh [22]. A Fermi smearing of 0.006 Ha (1 Ha = 27.211 eV) and a global orbital cutoff of 5.2 Å were employed. The convergence criteria for the geometric optimization and energy calculation were set as follows: self-consistent field tolerance, 1.0×10^{-6} Ha/atom; energy tolerance, 1.0×10^{-5} Ha/atom; maximum force tolerance, 0.002 Ha/Å; and maximum displacement tolerance, 0.005 Å. The TS and Grimme methods are used to deal with the noncovalent force in the simulation system. During the optimization process, the HCHO molecule and the graphene sheet were allowed to relax [23–25].

2.1. Model building

2.1.1. Pure graphene sheet

A model of pure graphene sheet was built by cleaving the crystal cell of graphite. A vacuum with a slab approximately 15 Å was added onto the graphene sheet so that the adsorbent molecule would only interact with one side of the graphene sheet. The optimized structural model of 5×5 pure graphene sheet is shown in Fig. 1a.

2.1.2. Ti-doped graphene sheet

Based on the model of pure graphene, a Ti-doped graphene model was built by replacing a carbon atom with a titanium atom. The length of the three bonds connecting the titanium atom and the three carbon atoms was optimized. The optimized structural model of the Ti-doped graphene sheet is shown in Fig. 1b.

2.1.3. N-doped graphene sheet

Similar to the Ti-doped graphene model, an N-doped graphene model was built by replacing a carbon atom with an N atom. A geometry optimization procedure was then carried out. The optimized structural model of the N-doped graphene sheet is shown in Fig. 1c.

2.1.4. Gas-Ti- or N-doped graphene system

To determine the most favorable adsorption structure of the HCHO molecule on the Ti-doped graphene sheet, three initial structures of the HCHO molecule were considered (Fig. 2).

The adsorption energy (E_{ads}), which indicates the intensity of interaction between the HCHO molecule and the pure or Ti-doped graphene sheet, was derived according to the following equation:

$$E_{ads} = E_{graphene+H_2CO} - (E_{graphene} + E_{H_2CO}) \quad (1)$$

where $E_{graphene+H_2CO}$, $E_{graphene}$, and E_{H_2CO} represent the total energy of the system, the energy of the H_2CO molecule, and the energy of the pure or Ti-doped graphene sheet, respectively. A negative E_{ads} value indicates stable adsorption. The more negative the E_{ads} value, the more stable the adsorbed structures.

3. Results and discussion

3.1. HCHO adsorption

The E_{ads} between the HCHO molecule and the pure graphene sheet was approximately −0.8 eV. The stability of E_{ads} was maintained when the initial HCHO configuration changed. As shown in Table 1, the difference among the three cases was very small (approximately 0.01 eV). In addition, the HCHO molecule maintained its initial configurations after being adsorbed on the pure graphene sheet (Fig. 3). These results indicate that the initial configuration of the HCHO molecule has little effect on its interaction with

Table 1
Mulliken atomic charges changes caused by doped Ti and N atom.

	Ti_{17}/C_{17}	C_{16}	C_{18}	C_{42}
Pure graphene	0	0	0	0
Ti-doped graphene	0.418	−0.265	−0.265	−0.269
N-doped graphene	−0.465	0.180	0.181	0.180

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