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Density functional theory calculations of adsorption of hydrogen fluoride on titanium embedded graphene

E.H. Song, Y.F. Zhu *, Q. Jiang

Key Laboratory of Automobile Materials, Ministry of Education, and Department of Materials Science and Engineering, Jilin University, Changchun 130022, China

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ABSTRACT

In order to search for a gas sensor to detect hydrogen fluoride (HF), the adsorption of HF on transition metal-embedded graphene (TM/graphene) is investigated by density functional theory calculations. Compared with the relatively weak adsorption on other TM/graphene systems, HF molecule tends to be adsorbed on Ti/graphene with appreciable adsorption energy. Based on these calculations, two gas sensing mechanisms are proposed and revealed that both surface reconstruction and charge transfer result in a change of electronic conductance of Ti/graphene. Thus, this developed Ti/graphene would be an excellent candidate for sensing HF with lower cost and higher activity.

1. Introduction

Solid-state gas sensors are renowned for their high sensitivity, which in combination with low production costs and miniature sizes have made them universally and widely used in many applications [1,2]. Recently, carbon nanotubes and semiconductor nanowires as gas sensors have fast response time and high sensitivity at room temperature to detect toxic gases in industrial, environmental and military monitoring [3–6].

Subsequently, the synthesis of graphene and the experimental observation of Dirac charge carrier properties in graphene-based devices have been considered to be a solution for ultra high sensitivity [7–9]. Graphene has been regarded as one of the most promising candidates for the next generation of electronic materials [10,11]. Recently, graphene as a matrix of heterogeneous catalysts has been extensively studied due to the huge surface-to-volume ratio (large catalytic reaction area) [12], such as transition-metals embedded graphene [13–15], metal clusters embedded graphene [16,17], and even modified graphene under electric fields [18–20]. The transition-metals embedded graphene structures have been fabricated experimentally with good thermal stabilities [21] where there are stronger bondings between metals and neighboring carbon atoms [22]. This is because, as a single atomic layer of graphite maximizes the surface area, graphene shows metallic conductance even in the limit of zero carrier density, limiting crystal defects with minor noises [23,24]. The working principle of graphene devices as gas sensors is based on the changes of their electrical conductivity induced by surface adsorbates, which act as either donors or acceptors due to their chemical natures and preferential adsorption sites.

Recent computational studies have shown that the detectable range and sensitivity of graphene can be widened and enhanced substantially through either doping technology or surface engineering. Recently, Krasheninnikov et al. have researched the stability of TM atoms adsorbed on pristine and defected graphene by comparing their relative energies and evaluating migration barriers. It is found that the atomic structure of the latter is more stable than the former [14]. Additionally, graphene decorated with metals has high sensitivity to CO, NO, NH_3, CH_4, H_2CO, HF and NO_2 [23–30]. However, seldom studies have been made on the sensing properties of HF adsorbed on transition metal-embedded graphene (TM/graphene) system. The corresponding sensing properties also need to be verified in detail.

In this manuscript, we report that the sensitivity of graphene system to HF gas could be enhanced up to a higher level based on density functional theory (DFT) calculations, which exceeds by orders of magnitudes the state-of-the-art sensors, such as the case with Ti embedding. This may provide insight to the development of next generation gas sensors for virtual applications.

2. Computational method

All calculations were performed using the spin-unrestricted density functional theory (DFT) as implemented in the $DMol^3$ code [31,32]. The exchange–correlation functions were computed within a uniform generalized gradient approximation (GGA) with the revised Perdew–Burke–Ernzerhof [33]. The advantage of GGA over the local density approximation (LDA) in this work is that the GGA will not lead to a strong bonding of the molecules as in LDA. So, if the molecules bind in GGA, they will definitely bind in a real system (and in LDA) too. The distance between the adsorbate and the graphene surface, however, will be somewhat overestimated and consequently the binding energy will be underestimated [25]. The all-electron relativistic

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* Corresponding author. Fax: +86 431 85095371.
E-mail address: yfzhu@jlu.edu.cn (Y.F. Zhu).

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procedure [34], which includes all core electrons explicitly and introduces some relativistic effects into the core, was used for the core treatments. In addition, double numerical plus polarization was chosen as the basis set.

A hexagonal graphene supercell (4×4 graphene unit cell) containing 32 atoms was introduced to model a system where one C atom was substituted by a transition-metal atom, approaching the isolated impurity limit. The modulus unit cell vector in the *z* direction was set to 20 Å, which led to negligible interactions between the system and their mirror images. For geometric optimization, the Brillouin zone integration was performed with $5 \times 5 \times 1$ k-point sampling, which brings out the convergence tolerance of energy of 1.0×10^{-5} Eh, and that of maximum force of 0.002 Eh. For the density of states (DOS) calculation, the k-point was set to $20 \times 20 \times 1$ to achieve high accuracy. Charge transfers were calculated with the Hirshfeld charge analysis method [35]. The electron density difference $\Delta\rho$ is calculated, which illustrates how the charge density changes during this adsorption process. $\Delta\rho$ is defined as $\Delta\rho = \rho_{\text{total}} - (\rho_{\text{sheet}} + \rho_{\text{HF}})$ in which ρ_{total}, ρ_{sheet} and ρ_{HF} denote electron density of Ti/graphene adsorbed system, Ti/graphene and HF molecule for the adsorbed system, respectively. The adsorption energy E_{ad} between the adsorbate and TM/graphene was defined as,

$$E_{\text{ad}} = E_{\text{t}} - \left(E_{\text{TM/graphene}} + E_{\text{adsorbate}}\right) \quad (1)$$

where the subscripts t, TM/graphene, and adsorbate denoted the total energies, and the energies of the corresponding substances.

3. Results and discussion

Fig. 1 shows the adsorption energy of HF on TM/graphene system, there are ten categories of adsorption systems. To evaluate the interaction between a HF molecule and a TM/graphene, E_{ad} described in Eq. (1) and the binding distance, *l*, with all possible configurations are calculated. As listed in Fig. 1, the adsorption energy of HF on Ti/graphene $E_{\text{ad}} = -0.49$ eV, which is larger than that of other TM/graphene systems. It is found that the Ti/graphene system is the most stable atomic arrangement with the largest adsorption energy.

Before we consider the adsorption behaviors of HF on Ti/graphene system, the stability of Ti/graphene system due to possible Ti clustering problems on graphene sheet is studied. Fig. 2 shows the geometric and electronic properties of Ti/graphene. The Ti atom is located on top of the single vacancy H site, forming three bonds with the nearest carbon atoms, as shown in Fig. 2a. The bond length between Ti and neighboring C ($l_{\text{Ti–C}}$) is 1.945 Å, and the distance between Ti and the graphene sheet is 1.726 Å. Meanwhile, there is about 0.558*e* charge transfer (*Q*) from Ti to graphene sheet according to the Hirshfeld charge population analysis. The charge transfer can also be verified by the difference of electronic densities of Ti/graphene, as shown in Fig. 2b, where the red and blue regions represent the areas of electron accumulation and loss, respectively. Obviously, different electron affinities of Ti and C change the electron distribution of Ti/graphene system. However, the whole graphene structure remains covalent in nature due to the electrons are mainly located within the bonds rather than heavily centered on the C atoms, as shown the top view in Fig. 1b.

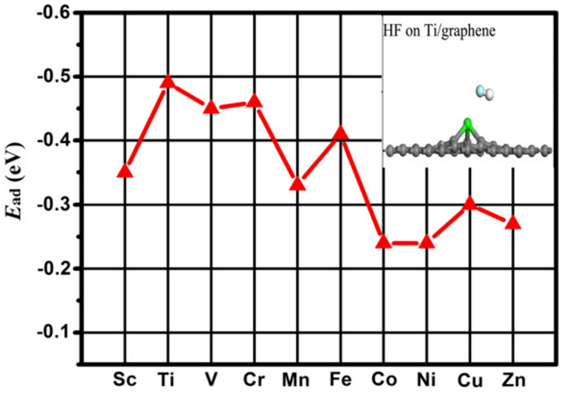

Fig. 1. Adsorption energies, E_{ad} of the HF molecule adsorbed on TM/graphene. The inset shows the most stable configuration of HF on Ti/graphene. The lines are used to guide the eye.

To gain deeper insight into the electron structure of Ti/graphene, the partial density of states projected on Ti-3*d* and neighboring C-2*p* orbitals is plotted, as shown in Fig. 2c. Due to the formation of C−Ti bonds and charge transfer from Ti to C, Ti-3*d* and C-2*p* orbitals are partially filled. As a result, the high density of states is localized around E_{F} while the localized Ti-3*d* orbital is important to adsorb HF, which will be discussed later.

Considering the possible clustering problem of Ti atom embedded graphene, we also computed the energy barrier for Ti diffusions in graphene from the vacancy site H to its neighboring one. Fig. 2d and f shows the initial and final structures, respectively, where the Ti-vacancy pair moves or migrates to neighboring site. One C bond breaks and a pentagon forms during the migration (Fig. 2e). The diffusion energy barrier E_{r} is approximately 4.02 eV, which implies that metal clustering problem is absent and Ti/graphene system is the energetically stable structure. Therefore, we can deduce that the carbon vacancies or dangling bonds of carbon atoms can improve the stability of Ti atom on graphene, and tune the electronic structure of Ti atom.

Herein, we consider the adsorption of HF on graphene and Ti/graphene, respectively. Fig. 3a shows the most stable configuration of HF on graphene system with $E_{\text{ad}}(\text{HF}) = -0.10$ eV. Meanwhile, there is about 0.001*e* charge transfer from HF to Ti/graphene, which occupies HF-2π* orbital and subsequently leads to the elongation of $l_{\text{H–F}}$ from 0.932 to 0.933 Å (Fig. 3b and c). In this case, the electrons mainly accumulate on F ion, H ion loses a lot of electrons. However, the whole graphene structure remains covalent, shown in the top view in Fig. 3b. There is nearly no hybridization between HF-2*p* and graphene-2*p* orbitals near E_{F} from the computed partial density of states (PDOS) (Fig. 3c). Thus, we deduce that the interaction between the HF molecule and the intrinsic graphene is of weak van der Walls interaction type, and the adsorption is by weak physisorption. Therefore, intrinsic graphene cannot be a good sensor material to detect HF gas.

For HF adsorption on Ti/graphene, the most energetically favorable configuration is characterized by HF, being tilt to the graphene sheet where $E_{\text{ad}}(\text{HF}) = -0.49$ eV, which is more favorable than other configurations. There is about 0.152*e* charge transfer from HF to Ti/graphene, which occupies HF-2π* orbital and brings out $l_{\text{H–F}}$ elongation from 0.932 to 0.943 Å, as shown in Fig. 3e and f. In this case, the electrons mainly accumulate on F ion where the strong hybridization between Ti-3*d* and HF-2*p* orbitals is observed near E_{F} from the computed PDOS (Fig. 3f). HF obviously acted as a charge donor, while the Ti/graphene is the main charge acceptor. Meanwhile, the enhancement of HF sensitivity in Ti/graphene is also verified by a large electrical conductivity change after adsorption. The values of charge transfer 0.152*e* in Ti/graphene system, which are almost one order of magnitude larger than 0.024*e* in Al/graphene system [30]. The values of charge transfer could bring about significant conductivity change, which is beneficial for sensing applications. Based on the above analysis, it is predicted that the Ti/graphene system exhibits much more sensitive to the HF adsorption among the mentioned systems.

To better understand the effects of HF adsorption on electrical conductivity, the band structure of both systems with and without the adsorption is calculated. Fig. 4a shows that intrinsic graphene has a zero band gap. When the HF molecule adsorbed on intrinsic graphene (Fig. 4b), the band gap (E_{g}) has no distinct change in the band structure and E_{g} remains zero. In fact, it is simply a combination

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