Adsorption and Sensing Properties of Formaldehyde on Chemically Modified Graphene Surfaces

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Abstract: Chemically modifying graphene (such as chemical doping) is a commonly used method to improve its formaldehyde sensing properties, but the microscopic mechanisms of heteroatoms in the adsorption and sensing process are still unclear. In this paper, the adsorption and sensing properties of formaldehyde on graphene surfaces modified by X doping (X = B, N, O, P, S, Mg and Al) were systematically investigated by first-principles calculations. The adsorption geometries, adsorption energies, charge transfers, and electronic structures were obtained and analyzed. The adsorption strengths of HCHO molecule on the Mg- and Al-doped graphene surfaces were stronger than those of non-metal (B, N, O, P and S)-doped cases. These results showed that the Mg- or Al-doped graphene was better for HCHO detecting than the non-metal-doped graphene systems. The sensing properties were simulated by the NEGF method for the two-probe nano-sensors constructed from Al- and Mg-doped graphene. The maximum sensing responses of nano-sensors based on Al- and Mg-doped graphene were obtained to be 107% and 60%, respectively. The present study supplies a theoretical basis for designing superior graphene-based HCHO gas sensors.

Keywords: formaldehyde; graphene; first-principles calculation; sensing performance

1. Introduction

As the simplest aldehyde molecule, formaldehyde (HCHO) is extensively utilized by organic chemists for producing resins due to its excellent solvent and adhesion properties [1]. With highly toxic, hazardous, and carcinogenic characteristics, long-term exposure to formaldehyde would severely impair human health [2]. Concerning human health, formaldehyde has been identified as a major contributor to sick building syndrome (SBS) [3–5], such as throat irritations, dizziness, dyspnea, and asthma-related symptoms. Criteria for the limitation and regulation of formaldehyde emissions from housing have been established in many countries [6]. For example, in China, the criterion is 0.10 mg/m³ (GB/T 18883-2002) [7]. With increasing anthropogenic emissions, formaldehyde has slowly transformed from a household hazard to a life-threatening pollutant. As a priority indoor pollutant, there is an increasing interest in fast and simple formaldehyde monitoring methods, and this has stimulated the development of formaldehyde gas-sensing technologies.

Due to its novel and unique structure and physical and chemical properties, graphene has attracted tremendous attention. However, it is confirmed by theoretical and experimental studies that the adsorption of target gas molecules on pristine graphene is very weak and consequently, the change in conductivity by gas molecule adsorption is difficult to measure [8–11]. Following the explosion of interest in graphene used in molecular identifications, the idea of graphene doping emerged [12–16]. Dai et al. [12] performed a systematic theoretical study of the ability of graphene doped with B, N, Al, and S to chemically bind...
various common or polluting gases, and suggested that B and S-doped graphene could be a promising candidate for NO and NO$_2$ monitoring. Zhang et al. [13] found that defective and B-doped graphene showed higher adsorption strength to NH$_3$, NO, and NO$_2$, and demonstrated that the sensitivity of B-doped graphene-based NO$_2$ sensors is also greatly enhanced. Liu et al. [14] revealed that the sensitivity of graphene-based SO$_2$ sensors could be greatly improved by introducing Al doping.

In this paper, the adsorption and sensing performances of X-doped graphene (XG with X = B, N, O, P, S, Mg, and Al) for HCHO gas sensing were investigated by first-principal calculations. The adsorption structures, adsorption energies, charge transfers, and electric structures for HCHO adsorption on XG were obtained and analyzed. The two-probe HCHO nano-sensors were established and the current-voltage (I-V) curves were simulated to evaluate the sensing performance of heteroatom-doped graphene-based sensors for HCHO detection.

2. Computation and Method Details

Density functional theory (DFT) calculations are implemented in the Vienna ab initio simulation package [17–19], using the generalized gradient approximation (GGA) exchange-correlation functional method [20]. Projector-augmented wave (PAW) pseudopotentials with the valence electron configurations of 2s2p for B, C, N, and O, 1s for H, 3s3p for Mg, Al, P, and S, respectively, were employed with a plane-wave energy cutoff of 500 eV. A semiempirical DFT-D2 method [21] was applied to correct the van der Waals interaction between the gas molecule and the substrate. An energy convergence of $10^{-5}$ eV was achieved and the atomic forces were converged down to 0.01 eV/Å for atomic relaxations. The adsorption energy was calculated by

$$\Delta E_{ads} = E_{tot} - E_{sub} - E_{mol} + \Delta E_{ZPE}$$

where $E_{tot}$, $E_{sub}$, and $E_{mol}$ are the total energies of the doped graphene substrate with gas molecule adsorption, the doped graphene, and the isolated gas molecule, respectively. $\Delta E_{ZPE}$ is the zero-point energy difference after and before adsorption of the gas molecule. A negative $\Delta E_{ads}$ represents that the adsorption makes the system more stable. Furthermore, the Bader charge analyses were carried out to determine the charge transfers between the gas and the substrate [22,23].

The sensing properties caused by adsorption molecules were investigated within a DFT-combined non-equilibrium Green’s function (NEGF) method performed by NanoDcal code [24,25]. The electron-electron interaction was treated with PBE-96 functional [20]. A double-$\zeta$ plus polarization (DZP) basis set was adopted to describe the valence electron in this work. The cutoff energy of 100 Hartree was chosen for the plane-wave basis. The electric current $I$ through the nano-sensor was defined using the Landauer-Büttiker formula [26]:

$$I = G_0 \int_{\mu_L}^{\mu_R} T(E, V_b) \left[ f(E - \mu_L) - f(E - \mu_R) \right] dE$$

in which $G_0$ is the unit of the quantum conductance, $T(E, V_b)$ is the transmission coefficient of electrons incident at energy $E$ under a bias voltage $V_b$ and $f(E - \mu_{L/R})$ is the distribution function of the electrons in the left or right electrode. $\mu_{L/R}$ is the chemical potential of the left or right electrode. In the calculation of the electron transport properties, the bias voltage is the electrochemical potential difference between the two electrodes as $V_b = (\mu_L - \mu_R)/e$.

3. Results and Discussion

A (4 × 4 × 1) graphene supercell with 32 carbon atoms was modelled in our study, and the optimized lattice constant was $a = b = 9.87$ Å, which is in agreement with previous study results [27]. One carbon atom in the graphene supercell was replaced by a heteroatom X (X = B, N, O, P, S, Mg, and Al) and the X-doped graphene was fully relaxed. A typical XG structure is shown in Figure 1a. Because the radii of B, N, and O atoms are close to that of the
C atom, their XG structure remained as the planar form, similar to perfect graphene. Due to their large atomic radii of the dopants (P, S, Mg, and Al), these dopants protruded from the graphene plane, and carbocycle around the heteroatom were significantly deformed. The local deformations of the graphene surface induced by Mg and Al were generally greater than those of non-metal dopants (B, N, O, P and S). The above results are consistent with previous studies [12,28,29]. The local atomic structure and electronic structure changes induced by heteroatom doping are able to increase the chemical reactivity.

![Figure 1.](image)

**Figure 1.** (a) Typical atomic geometry of heteroatom-doped graphene sheet. The blue ball indicates the heteroatom and the brown balls are carbon atoms, (b) average bond lengths (\(d_{X-C} = (d_1 + d_2 + d_3)/3\)) between the heteroatom and adjacent carbon atoms, and (c) heights of the dopant protrusion from the graphene with or without HCHO adsorption.

For a doping case, we placed the HCHO molecule around the heteroatom in various orientations and distances to produce several initial adsorption geometries and relaxed them to find the most stable atomic configuration with the lowest adsorption energy. For each case, greater-than-seven initial atomic geometries were fully relaxed. The most stable structures are collected in Figure 2, where the top and side views are the adsorption geometries viewed directly above and from the side of the graphene plane, respectively. The nearest distances between the heteroatom and oxygen atom in the adsorbed HCHO molecule, ZPE corrections, Bader charge results, adsorption energies, and C–O bond lengths of the adsorbed HCHO molecule are listed in Table 1 and also presented in Figure 3. The ZPE correction of gas molecule was calculated to improve the accuracy of the adsorption energies. For all heteroatom doping systems, the ZPE correction of the HCHO molecule was in a range from 0.020 to 0.042 eV. For B, N, O, S, and P doping systems, the adsorption energy of HCHO molecule was in the range from \(-0.173\) to \(-0.252\) eV, the nearest distances between the heteroatom and HCHO molecule were from 2.946 Å to 3.311 Å, and the charge gains of the adsorbed HCHO molecule were in the range of 0.022–0.074 e. The weak adsorption strength together with a large adsorption distance and small charge transfer implies that the HCHO molecule is physically adsorbed on the XG (X = B, N, O, S, and P) surface. Interestingly, the slightly protruded O dopant is pushed below the graphene plane after HCHO adsorption. For the Mg- or Al-doped system, it has a strong adsorption strength (\(\Delta E_{ads} < -1.39\) eV) of the HCHO molecule with a short adsorption distance (\(d < 2\) Å) and large charge transfer (\(\Delta q > 0.36\) e). These results indicated the strong chemical X–O (X = Mg or Al) bonds formed between the XG substrate and HCHO molecule. However, the strong HCHO adsorption on the Mg- or Al-doped graphene implies a long recovery time [30,31]. The sensors based on the sensing material can detect a lower concentration of formaldehyde with higher sensitivity. In addition, the X–C bond lengths and the heteroatom heights shown in Figure 1b,c further support the strong adsorption of HCHO molecule on the XG (X = Mg or Al) substrate. For example, the N–C bond length...
and N dopant height did not change much after HCHO adsorption, while the Mg–C bond and Mg atom height became larger upon HCHO adsorption.

**Figure 2.** Top and side views of the lowest energy adsorption configurations for HCHO molecules on (a–g) B-, N-, O-, P-, S-, Mg-, and Al-doped graphene substrates. The red and white ball represents O and H atoms, respectively. Heterochromatic atoms embedded in graphene represent the heteroatom dopants.

**Table 1.** For the HCHO molecule adsorbed on XG (X = B, N, O, P, S, Mg, and Al) surfaces, the nearest distances between heteroatom X and the HCHO molecule, charge gains of the adsorbed HCHO molecule, zero-point energy corrections of the HCHO molecule, and adsorption energies and C–O bond length of the adsorbed molecule are presented.

| Heteroatom | B (d/Å) | N (Δq/e) | O (ΔE_{ZPE}/eV) | P (ΔE_{ads}/eV) | S (d_{C–O}/Å) | Mg (ΔE_{ZPE}/eV) | Al (ΔE_{ads}/eV) |
|------------|---------|----------|-----------------|----------------|---------------|------------------|-----------------|
| B          | 2.946   | 3.011    | 3.125           | 3.029          | 3.311         | 1.944            | 1.838           |
| N          | 0.044   | 0.022    | 0.052           | 0.074          | 0.029         | 0.366            | 0.401           |
| O          | 0.025   | 0.032    | 0.031           | 0.030          | 0.020         | 0.035            | 0.042           |
| P          | –0.233  | –0.245   | –0.252          | –0.184         | –0.173        | –1.396           | –1.413          |
| S          | 1.217   | 1.216    | 1.220           | 1.221          | 1.217         | 1.276            | 1.287           |
which is in agreement with previous studies [30,32,33]. For B, N, O, S, or P doped systems, graphene substrate may also be correlated to the HCHO density of states at the Fermi level. The strong interaction between the HCHO molecule and the Mg- or Al-doped Fermi level were substantially changed and the adsorbed HCHO created a DOS peak at the Fermi level, so the NG and PG systems had little sensing response to HCHO molecule. The shown in Figure 4a,b, the adsorbed HCHO did not contribute to the DOS at the Fermi levels at absolute zero temperature), rendering them a metallic property. However, as shown in Figure 4a, the adsorbed HCHO did not contribute to the DOS at the Fermi level ("Fermi level" is the term used to describe the top of the collection of electron energy levels at absolute zero temperature), rendering them a metallic property. How-

Figure 3. (a) The nearest adsorption distance between the heteroatom and HCHO molecule, (b) the adsorption energy of HCHO molecules on the XG substrate, (c) Bader charge gains \( \Delta q \) of HCHO molecule from the XG substrate, and (d) C–O bond length of HCHO molecule. The black dashed line in panel (c) indicates zero charge transfer, and the blue one in panel (d) denotes the C–O bond length of the free HCHO molecule.

As shown in Figure 3a,b, there is a clear connection between the adsorption energy and the adsorption distance, charge transfer, and C–O bond length. For a heteroatom doping system, if its adsorption energy is small, it usually has a large adsorption distance, smaller charge transfer, and shorter C–O bond in general. For instance, for the S doping case the adsorption strength was the weakest, while the adsorption distance was the longest and the charge transfer and the C–O bond of adsorbed HCHO were the smallest. The Al doping case had the strongest adsorption, while the adsorption distance was short and the charge transfer and the C–O bond of HCHO were large. The charge transfer and the C–O bond length of the HCHO molecule in different heteroatom doping cases are plotted in Figure 3c,d. Compared with the free HCHO molecule \((d_{C–O} = 1.214 \text{ Å})\), the C–O bond length expanded to a different extent. The charge transfer results suggested that the HCHO molecule behaves as an acceptor obtaining electrons from the doped graphene substrate, which is in agreement with previous studies [30,32,33]. For B, N, O, S, or P doped systems, the adsorption strength was weak, which is consistent with the result that HCHO electron gain is less than 0.08 e and the C–O bond is stretched only 0.01 Å. The Al-doped graphene case had the maximum C–O bond expansion of over 0.07 Å with respect to that of the isolated HCHO molecule. The corresponding charge transfer was as much as 0.40 e. A large expansion of the C–O bond and charge gain implies that the HCHO molecule is very reactive and can form a strong chemical bonding with Al-doped graphene.

The densities of states for N-, P-, Mg- and Al-doped graphene with HCHO adsorption are shown in Figure 4. The TDOS of NG and PG systems had non-zero states at the Fermi level ("Fermi level" is the term used to describe the top of the collection of electron energy levels at absolute zero temperature), rendering them a metallic property. However, as shown in Figure 4a,b, the adsorbed HCHO did not contribute to the DOS at the Fermi level, so the NG and PG systems had little sensing response to HCHO molecule. The AlG and MgG systems are also metallic. Upon HCHO adsorption, the DOS around the Fermi level were substantially changed and the adsorbed HCHO created a DOS peak at the Fermi level. The strong interaction between the HCHO molecule and the Mg- or Al-doped graphene substrate may also be correlated to the HCHO density of states at the Fermi level. Besides, their DOSs become discontinuous (MgG-HCHO system around \(-0.5 \text{ eV},\))
AIG-HCHO system from 0.7 to 0.9 eV) after HCHO adsorption, which might decrease the conductivity of the MgG and AIG systems.

![Figure 4](image-url)  
**Figure 4.** Total and projected densities of states for the (a) N-doped graphene (NG), (b) P-doped graphene (PG), (c) Mg-doped graphene (MgG), and (d) Al-doped graphene (AlG) systems with HCHO adsorption. The black and red dashed lines indicate total DOS of X-doped graphene with and without HCHO adsorption. The blue region represents the projected DOS of the adsorption HCHO molecule. The Fermi level is shifted to zero and represented by vertical dashed lines.

To evaluate the sensing performance of AIG and MgG for HCHO gas detecting, we analyzed the quantum transport properties with and without HCHO molecule adsorption employing the NEGF-DFT method with the NanoDcal code. Because of the anisotropy of graphene, two kinds of transport models were built for the AIG or MgG substrate with HCHO adsorption (Figure 2f,g), i.e., the current flows along the armchair and zigzag directions of the graphene lattice. For the two transport directions of the AIG nano-sensor for HCHO detection are shown in Figure 5, which consist of three parts, i.e., the central AIG substrate with HCHO adsorption scattering region and the two semi-infinite electrodes.

![Figure 5](image-url)  
**Figure 5.** Top and side views of two-probe AIG nano-sensor for HCHO molecule detection along (a) armchair and (b) zigzag directions. The purple shadow regions represent the semi-infinite intrinsic left and right graphene electrodes, which are contacted with the central AIG substrate adsorbed by HCOH in the molecule scattering.

The current-voltage curves and sensing response (defined by $S = \frac{(R_R - R_I)}{R_I} \times 100\%$, where $R_R$ and $R_I$ is the resistances (currents) of the sensor before and after adsorption of HCHO under bias voltage, respectively) are presented in Figure 6. The currents are reduced upon HCHO adsorption. This phenomenon may be attributed to losing charge carriers of the AIG or MgG substrate after HCHO adsorption. We also observed the same phenomenon for the transition metal-doped graphene systems [30].
The sensing responses along the armchair and zigzag directions show the anisotropy of graphene’s transport properties. The maximum sensing responses of AlG and MgG nano-sensors to HCHO molecule adsorption were 107% and 60%, respectively. For the Al- and Mg-doped systems, the average response was larger than 30%, especially for the armchair-orientated AlG nano-sensor, in which the average response reached 67%. The high sensitivity indicated that AlG and MgG can be applied as the sensing material for HCHO gas detecting.

![Current-voltage curves and sensing responses](image)

**Figure 6.** Current-voltage curves and sensing responses of (a) Al-doped graphene (AlG) and (b) Mg-doped graphene (MgG) nano-sensors without and with HCHO adsorbed. The current flows in the armchair and zigzag direction of the graphene lattice.

The transmission spectra of AlG and MgG nano-sensors before and after CHOH molecule adsorption under the bias from 0 to 0.8 V are plotted in Figures 7 and 8 to explore the mechanisms for HCHO detecting. The transmission coefficients of AlG and MgG nano-sensors with or without HCHO adsorption along two transport directions were almost zero at the bias window. As the bias increased, the area of transmission spectra in the bias windows became larger. These characteristics are similar to those of graphene nanoribbon and doped graphene [30,34]. According to Equation (2), the current flowing through the device is equal to the integral of the transmission coefficient in the bias windows. Figures 7 and 8 show that the transmission spectrum area of AlG and MgG nano-sensors in the bias window after HCHO adsorption was obviously smaller than before. Therefore, we can conclude that HCHO adsorption might reduce the current. It was also found that under zero bias, the transmission coefficient of MgG and AlG without or with HCHO adsorption were asymmetric with respect to the Fermi level. We can expect that the bias augment could not lead a linear increase of the area of transmission spectra, which could render a non-linear change in current.
Figure 7. The transmission spectra of the AlG nano-sensor for HCHO detection along armchair and zigzag directions under the bias voltage of (a–c) 0, 0.4, and 0.8 V. The black dashed lines represent the bias windows.

Figure 8. The transmission spectra of MgG nano-sensor for HCHO detection along armchair and zigzag direction under the bias voltage of (a–c) 0, 0.4, and 0.8 V. The black dashed lines represent the bias windows.

4. Conclusions

In summary, we investigated the adsorption and sensing properties of formaldehyde on graphene doped by various heteroatoms (B, N, O, P, S, Mg, and Al). The most stable atomic configurations of heteroatom-doped graphene adsorbed with HCHO, adsorption energies, Bader charge transfers, and electronic structures were picked up. We found that the adsorption strengths of the HCHO molecule on the Mg- and Al-doped graphene
surfaces were stronger than those of non-metal (B, N, O, P and S)-doped cases. The results indicated that the Mg- or Al-doped graphene is better for HCHO detecting. The two-probe HCHO nano-sensors were built for the Mg- and Al-doped graphene along the armchair and zigzag directions and the I-V curves were simulated to evaluate the sensing performance by the NEGF-DFT method. The maximum sensing responses of Al- and Mg-doped graphene nano-sensors were 107% and 60%, respectively, while the average responses for both cases were larger than 30%. Based on our theoretical results, we predict that the Al- and Mg-doped graphene can be potentially used as sensing materials for highly sensitive HCHO detection.

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