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Research Article

A First-Principles Study on Hydrogen Sensing Properties of Pristine and Mo-Doped Graphene

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The adsorption of H_2 on the pristine and Mo-doped graphene was investigated by density functional theory (DFT) calculations. The structural and electronic properties of H_2-graphene systems were studied to understand the interaction between H_2 molecule and graphene-based material. Our calculation results showed the pristine graphene was not an ideal sensing material to detect H_2 molecule as it ran far away from the pristine graphene surface. Different with pristine graphene, the Mo-doped graphene presented much higher affinities to the H_2 molecule. It was found that the placed H_2 molecules could stably be chemisorbed on the Mo-doped graphene with high binding energy. The electronic property of Mo-doped graphene was significantly affected by the strong interaction and orbital hybridization between H_2 and Mo-doped graphene sheet. The H_2 molecule would capture more charges from the doped graphene than the pristine system, indicating the higher sensitivity for the graphene doped with Mo.

1. Introduction

Over the past decade, the two-dimensional layered graphene has inspired great interests due to its unique mechanical, optical, transport, and outstanding electronic properties since it was reported in by Professors Novoselov et al. [1]. It has been widely used in lithium-ion battery, solar cell, light emitting diodes, and gas sensors [2–4]. Previous studies showed that the intrinsic graphene could not have high efficiency to interact with the small gas molecules, such as CO, NO, NO, H_2S, CO_2, NH_3, and H_2, due to the inert nature of the π-electron conjugation formed by carbon atoms of graphene [5–8]. Several methods have been constructed to overcome this limitation. Among various methods, doping with transition metal has been confirmed to be proved to be one of the most facial and effective methods to improve the gas sensing property of graphene. Very recently, Cortés-Arriagada et al. has found that Fe-doped graphene (FeG) is a superior material for adsorption and sensing of CO, CO_2, SO_2, and H_2S compared to pristine graphene [9]. Clearly, the previous theoretical studies showed that metal dopant could be used to enhance the gas sensing behavior of graphene.

Hydrogen gas (H_2) has been considered to be an ideal energy resource, always used in the industrial processes and energy-generating devices [10, 11]. However, the light, colorless, odorless, and tasteless properties of H_2 make it easily leak out and difficultly be detected by humans. And, it has the high possibility of explosion due to the low ignition energy and wide flammable range [12, 13]. Therefore, it is of great importance to assemble the devices to detect and control their exposure. Recently, many studies have focused on the hydrogen sensing performance of carbon-based material theoretically and experimentally [14]. Lotfi and his coworkers have studied the enhanced adsorption of hydrogen gas on the transition metal-doped graphene [15]. Chanukorn has also reported that the graphene nanosheets doped with the group 8B transition metal could be used as a more reliable and efficient hydrogen sensor than the bare graphene [16]. Motivated by these research studies, we studied the interactions between hydrogen gas and Mo-doped graphene sheet (MoGs) in this work on the basis of density functional theory calculations. The calculation results showed that the adsorption of hydrogen molecules on the graphene sheet could also be enhanced through doping with Mo elements, leading to the higher sensitivity towards H_2.

2. Computational Details

All the density functional theory (DFT) calculations were performed with CASTEP in Materials Studio (Version 8.0) of Accelrys Inc. The graphene sheet is modeled using a certain number of graphene supercells, consisting of 72 atoms, with a vacuum spacing of 15 Å. The exchange correlation contribution to the total electronic energy was treated with the Perdue–Burke–Ernzerhof (PBE) functional. The cutoff energy of 550 eV is used in all relaxation processes. The k-point set in all the slabs is $4 \times 4 \times 1$. The convergence criteria of optimization for the energy and force were 0.02 meV/atom and 0.05 eV/Å, respectively. The MoGs are constructed by replacing one C atom with one Mo atom (concentration of Mo 1.4% atomic ration). The optimized structures of pure graphene and MoGs are shown in Figure 1. C_1, C_2, and C_3 were used to label the three C atoms around the center C (Mo) atom, respectively. The calculation showed that the length of bond elongated from 1.419 Å for the three C–C bonds to 1.921 Å, 1.930 Å, and 1.926 Å for Mo–C_1, Mo–C_2, and Mo–C_3, respectively. The transformation of chargers within the adsorbed H_2 molecule and sensing material was studied through the calculation of electron density difference. The density of states of the constructed geometries was also investigated to research the interaction between the H_2 molecule and sensing material.

3. Results and Discussion

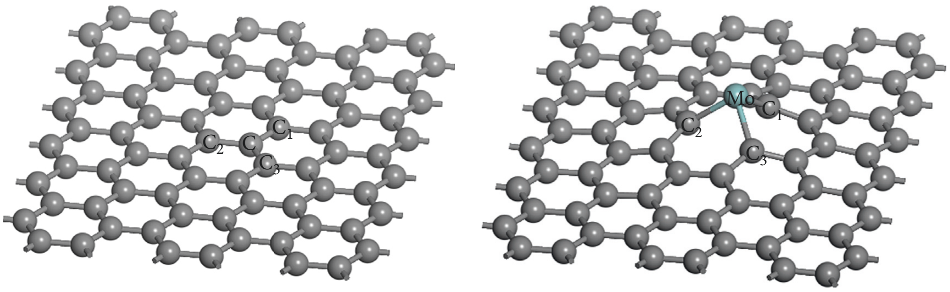
Firstly, we have calculated the binding energy between the Mo atom with graphene sheet (E_{bing}) as follows: $E_{\text{bing}} = E_{\text{G}} + E_{\text{Mo}} - E_{\text{Mo-G}}$, where E_{G}, E_{Mo}, and $E_{\text{Mo-G}}$ are defined as total energies of the graphene with one C vacancy, the single Mo atom, and the Mo-doped graphene, respectively [8]. The calculation results showed the binding energy of Mo in the Mo-doped graphene was ~4.99 eV, indicating the possibility of Mo-doping. To investigate the interaction between the target gas molecule and our built-up material, one H_2 molecule was introduced into the system. There are four possible geometries constructed for the intrinsic and Mo-doped graphene systems: H_2 perpendicular to and parallel along X axis to the sensing surface (modes V1 and V2 for graphene and modes M1 and M2 for Mo-doped graphene). The optimized results are shown in Figure 2. The adsorption energy (E_{ads}) of the established adsorption modes are calculated with the following equation:

$$E_{\text{ads}} = E_{\text{adsorbate-substrate}} - E_{\text{substrate}} - E_{H_2}, \qquad (1)$$

where $E_{\text{adsorbate-substrate}}$ is the total energy of the adsorbate-substrate system in the equilibrium state and $E_{\text{substrate}}$ and E_{H_2} are the the total energies of the sensing material and adsorbed H_2 present, respectively [17]. The final adsorption energy for V1 and V2 are −0.056 and −0.048 eV, respectively, much lower than those for M1 (−0.55 eV) and M2 (−0.57 eV). The negative value of adsorption energy corresponds to a stable adsorption structure. Similar calculation results were also found in the studies of H_2CO in the Al-doped graphene and the H_2S in the Al-doped graphene sheet [18].

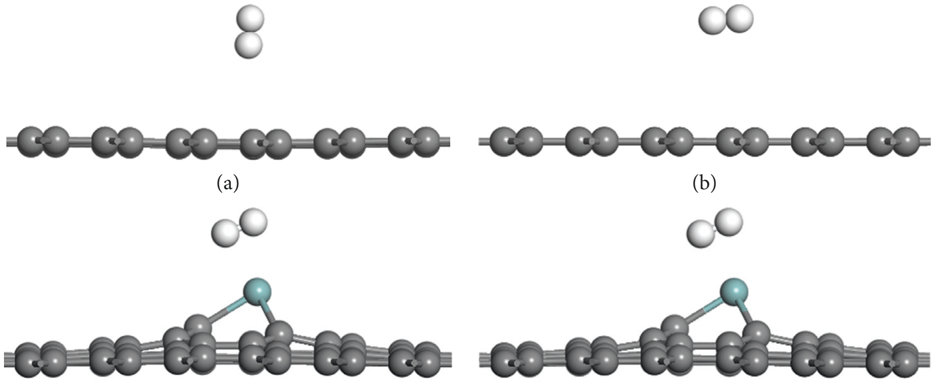
As can be seen in Figures 2(a) and 2(b), the H_2 molecules move farther away in modes A1 and A2 than those in modes M1 and M2 from the sensing material surface. The optimized results showed that the adsorption of H_2 does not have a significant effect in the structural distortion of intrinsic graphene. The bond lengths of C–C in both V1 and V2 slightly elongated to be 1.420 Å. Moreover, the length of the bond in the H_2 molecule remains 0.753 Å as the free-standing H_2 molecules, indicating that H_2 would not interact directly with intrinsic graphene surface. Our results agree well with the precious study [19]. Compared with intrinsic graphene system, the Mo–C bonds obtained from the initial structure with H_2 perpendicular to the doped surface were lengthened to be 1.927 Å, 1.977 Å, and 1.931 Å for Mo–C1, Mo–C2, and Mo–C3 in the mode M1 (shown in Figure 2(c)), respectively. The initial structures of a H_2 molecule adsorbed on the Mo-doped graphene are shown in Figure S1. It should be noted that we found the finally optimized geometries for the constructed modes of H_2 adsorbed on Mo-doped graphene being not affected by the orientation of the placed H_2 molecules. For the H_2 molecules parallel along X axis to the sensing surface, the corresponding values for Mo–C1, Mo–C2, and Mo–C3 bonds are 1.930 Å, 1.975 Å, and 1.931 Å, respectively. In the modes M1 and M2, the bond lengths of H_2 expand from original 0.735 Å to 0.857 Å and 0.858 Å, respectively. Based on the above research, it can be seen that the H_2 molecules have a stronger interaction with the MoGs. The larger elongation of Mo–C bond and higher adsorption energy of the Mo-doped system imply that the H_2 molecule has a chemical bond with the MoG sheet. Different with the doped system, the H_2 molecule only shows the physical adsorption on intrinsic graphene with weak van der Waals interaction between them [20].

Then, we study the accumulation of charges between the adsorbed H_2 and graphene systems with the method of calculating the deformation electron density. In the intrinsic graphene modes of V1 and V2, the majority of electron accumulations sites are distributed in the bond, as shown in Figure S2. The results mean that the bond in the intrinsic graphene and H_2 are of covalent nature. There is no obvious charge accumulation between H_2 and graphene observed. However, in the modes M1 and M2, the H_2 captures electrons from the doped graphene system, further confirming the binding between adsorbed H_2 and Mo-doped graphene. As can be seen in Figure 3, the H_2 molecules in modes M1 and M2 gain 0.28 e and 0.29 e, respectively. Accordingly, the Mo-dopant loses electronic charge of 0.27 e and 0.26 e in modes M1 and M2. The other charges mainly comes from the C neighbors. The calculated results reveal that the chemisorbed H_2 molecule in the modes M1 and M2 will capture electrons from the doped graphene, agreeing well with the results in previously studies [2, 21].



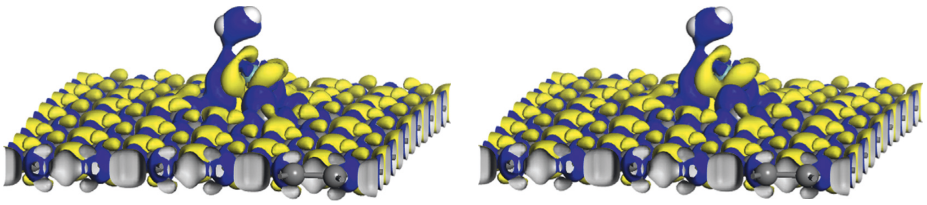
(a) (b)

Figure 1: Optimized geometries of intrinsic and Mo-doped graphene: gray and light blue spheres are denoted as C and Mo, respectively.



(a) (b) (c) (d)

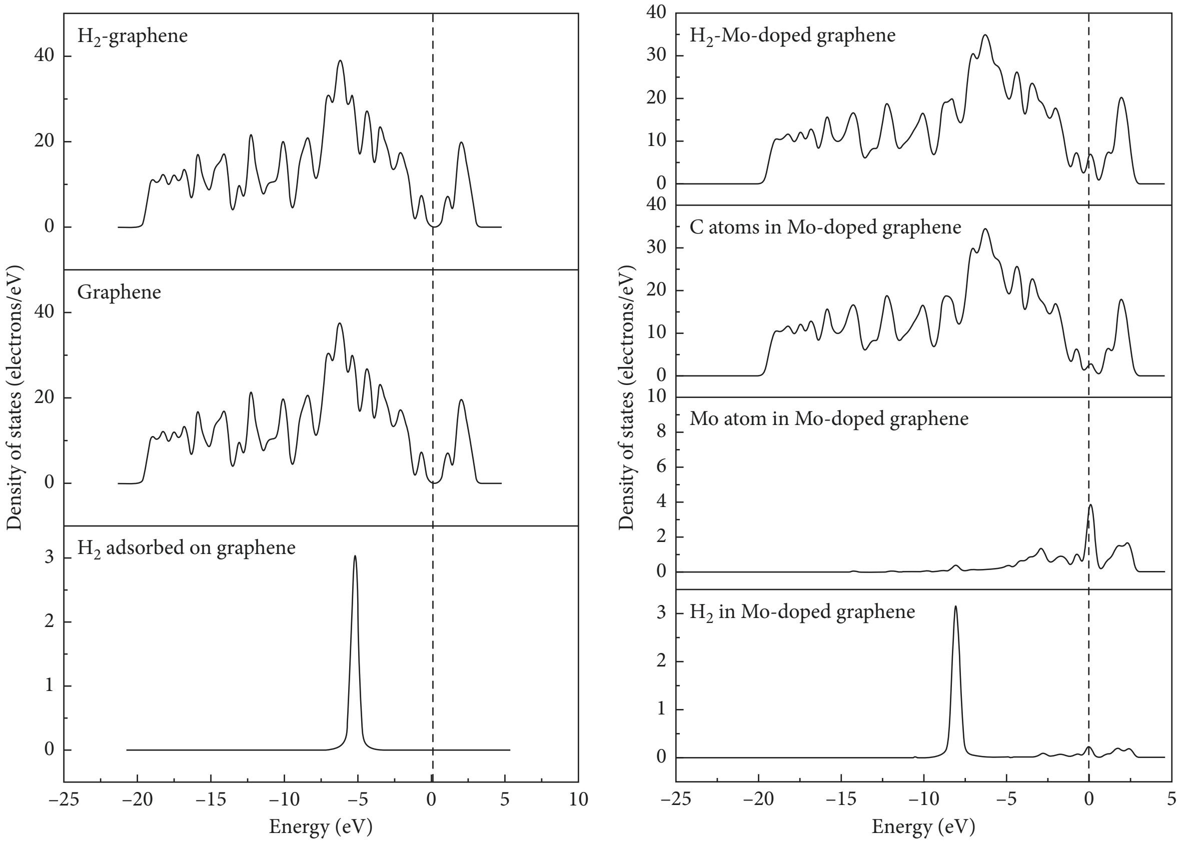
Figure 2: Calculations of structure of H_2 molecules (white color) on the graphene-based material surfaces (a) with H_2 perpendicular to graphene surface (V1); (b) with H_2 parallel along X axis to graphene surface (V2); (c) with H_2 perpendicular to Mo-doped graphene surface (M1); (d) with H_2 parallel along X axis to Mo-doped graphene surface (M2).



(a) (b)

Figure 3: The plots of the deformation electron density for M1 and M2 modes (blue color: electron trap; yellow color: electron release).

The electronic densities of states (DOS) for the pristine and Mo-doped graphene systems were also studied to better understand the interaction between the H_2 molecule and sensing material (modes V1 and M1), as shown in Figure 4. The calculation results of modes V2 and M2 are shown in Figures S3 and S4, respectively. The molecular orbitals of the adsorbents are recognizable in the supercell DOS, meaning that there is no obvious hybridization between the H_2 molecule and intrinsic graphene sheet. The calculation results further prove the placed H_2 has little effect on the graphene state, indicating that the intrinsic graphene presents poor sensing performance to H_2 [20, 22]. In the doped systems of M1 and M2, the doped graphene state is obviously affected by the adsorption of the H_2 molecule. As can be seen, the electronic structure of the material changes a lot after the H_2 adsorbed on the material's surface. The calculation of PDOS (partial density of states) for adsorbed H_2, Mo, and C atoms in the doped system is also shown in Figures 4(b) and S4. The adsorbed H_2 molecule obviously hybridizes with the doped Mo atom and carbon atoms of the graphene sheet [22–24]. And, the PDOS of H_2 also reveals the H_2 in M1 and M2 is no longer a free one compared with that in Figure S3, demonstrating the direct interaction between the H_2 molecule and Mo-doped graphene. The research implies that the hydrogen sensing performance could be enhanced through doping with Mo, and the Mo-doped



(a)

(b)

FIGURE 4: The electronic density of state for (a) H_2-graphene system (Mode V1) and (b) H_2–Mo-doped graphene system (Mode M1) with preferred configuration.

graphene has the prospect of being an effective material to sensing the H_2 molecule.

4. Conclusion

The first-principles calculations of the interaction between H_2 and graphene-based material show that the H_2 sensing behavior of graphene can be highly enhanced by doping with Mo. The H_2 molecule runs away from the pristine graphene and is more likely to be physically adsorbed on intrinsic graphene due to weak van der Waals interaction between them. In contrast, there is clear evidence showing that H_2 molecules can be stably chemisorbed on the Mo-doped graphene with shorter distance from the sensing surface. Both the changes in the electronic structure and the orbital hybridization between H_2 and MoGs confirm the promising H_2 sensing property of the graphene doped with Mo. Therefore, our work gives a new insight into the design of hydrogen sensor based on the Mo-doped graphene.

Data Availability

The figure data used to support the findings of this study are included within the Supplementary Materials file.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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Supplementary Materials

Supplementary materials contain four main figures. Figure S1: the initial structures of a H_2 molecule adsorbed on the Mo-doped graphene with different orientations. Figure S2: the plots of the deformation electron density for built-up V1 and V2 modes. Figure S3: the electronic density of state (DOS) for the H_2-graphene system (mode V2). Figure S4: the electronic density of state (DOS) for the H_2-Mo-doped graphene system (Mode M2) with preferred configuration. (*Supplementary Materials*)

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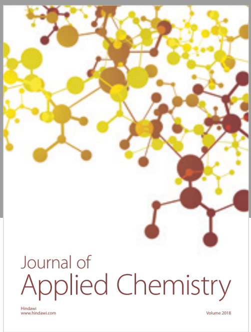
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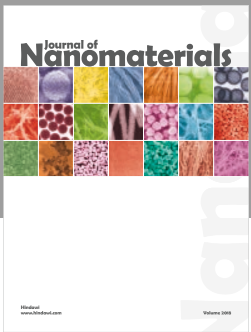
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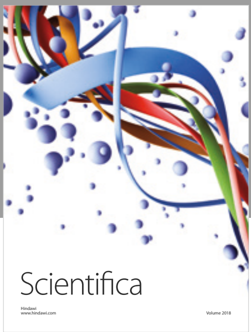
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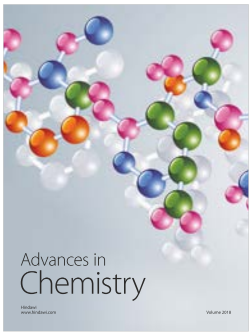
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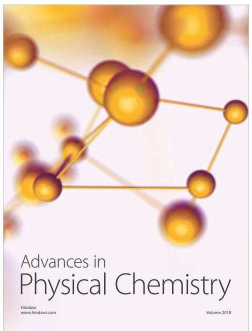
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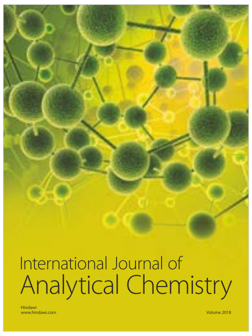
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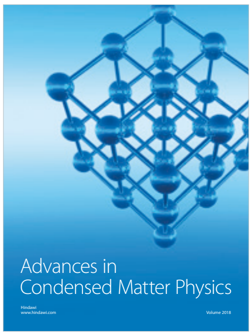
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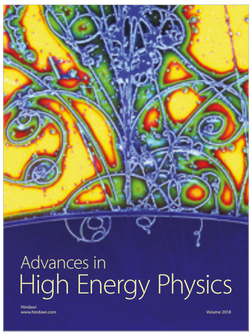
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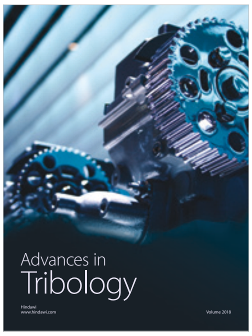
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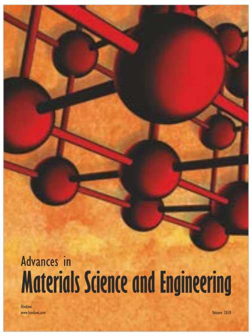
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