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Enhanced gas-sensing performance of graphene by doping transition metal atoms: A first-principles study

Dongxiang Zhao, Xiaoli Fan *, Zhifen Luo, Yurong An, Yan Hu

State Key Laboratory of Solidification Processing, Centre of Advanced Lubrication and Seal Materials, School of Material Science and Engineering, Northwestern Polytechnical University, 127 YouYi Western Road, Xi'an, Shaanxi 710072, China

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ABSTRACT

By performing the first-principles calculations, we investigated the sensitivity and selectivity of transitional metal (TM, TM=Sc, Ti, V, Cr and Mn) atoms doped graphene toward NO molecule. We firstly calculated the atomic structures, electronic structures and magnetic properties of TM-doped graphene, then studied the adsorptions of NO, N_2 and O_2 molecules on the TM-doped graphene. By comparing the change of electrical conductivity and magnetic moments after the adsorption of these molecules, we found that the Sc-, Ti- and Mn-doped graphene are the potential candidates in the applications of gas sensor for detection NO molecule.

1. Introduction

Graphene is an atomic-thin 2 D carbon sheet in which the C atoms arrange in the honeycomb lattice [1,2]. Graphene has many special properties [3,4], such as a high specific surface area, excellent electrical conductivity, high mechanical strength and so on. Based on these advanced properties, graphene has been considered as one of the most important 2D materials with great potentials in vast applications involving nanoelectronic devices [5], solar cell technology [6], liquid crystal electronics [7], and gas sensor [8]. Especially in the application of gas sensor, graphene has the advantages of fast response and good stability [9]. Graphene sensor can be used for detecting simple gas molecules, such as NO_2, H_2O, O_2 and NH_3 etc [10–15].

Despite its potential in gas sensing, graphene's ability to detect NO gas is limited. According to previous studies [16], the interaction between NO molecule and graphene is very weak and there is barely charge transfer between them, which means that graphene is not a good candidate that can be used in sensing NO molecule. However, NO is toxic and easy to be oxidized in the air, which not only seriously endangers the health of human beings and environment, but also produces greenhouse gases such as NO_2 and CO_2. So, it is very significant and necessary to develop a gas sensor that can detect NO molecule in the air. One solution to this is increasing the interactions between NO and graphene by changing the properties of graphene through doping.

Previous studies show that transitional metal (TM) atoms doping effectively changes the properties of graphene [17–33]. For example, the TM-doped graphene show enhanced chemical reactivity for the adsorptions of small molecules [24–26]. Ma et al. [27] found that doping Pd significantly enhances the strength of interaction between CO, NH_3, O_2, NO_2 molecules and graphene. Particularly, the Cr-doped graphene is suitable for detecting HCN molecule [28]. Additionally, Zhang et al. [29] and Liu et al. [30] show that the sensitivity of graphene-based chemical gas sensor for detecting SO_2, CO, NO_2 and NH_3 molecules could be drastically improved by introducing the appropriate dopants or defect.

In this paper, we study the effect of TM atoms of Sc, Ti, V, Cr and Mn doping on the sensibility of graphene toward NO molecule. These TM atoms are cheaper and lighter compared with others such as Pt, Pd and so on, so they are convenient to apply to practice. By applying the first-principles method, we firstly calculated the TM-doped graphene, and then studied the adsorption of NO molecule on the TM-doped graphene. We also calculated the adsorption of O_2 and N_2 molecules on the TM-doped graphene. Our calculations show that doping of all the five TM atoms increase the chemical reactivity of graphene, resulting in chemical interaction between the adsorbed molecules and doped graphene. By comparing the changes of electronic and magnetic properties of the TM-doped graphene after the adsorption of NO, N_2 and O_2 molecules, we find that the electrical conductivity of Ti-, Cr- and

* Corresponding author.
E-mail address: xlfan@nwpu.edu.cn (X. Fan).

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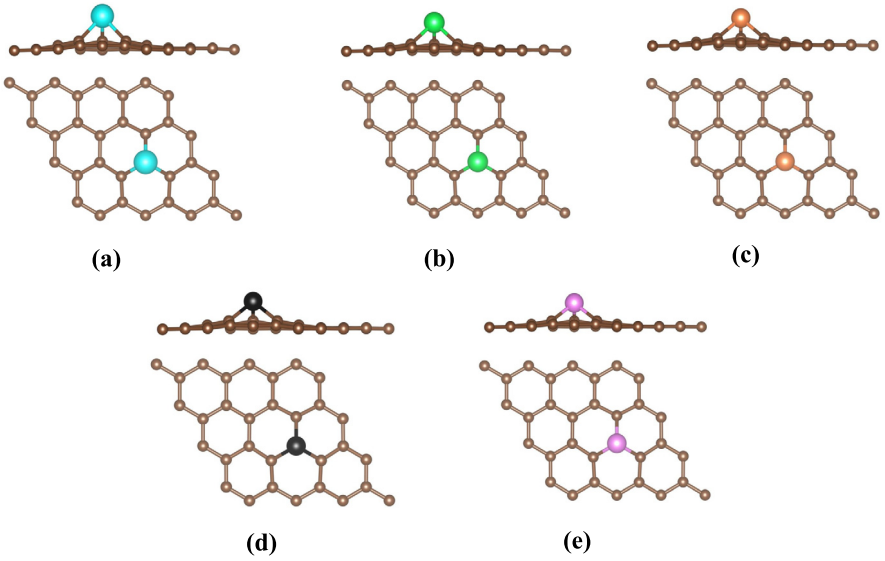

Fig. 1. Side and top views for the atomic structures of transitional metal (TM, TM=Sc, Ti, V, Cr and Mn) atoms doped graphene. (a) Sc-doped, (b) Ti-doped, (c) V-doped, (d) Cr-doped, (e) Mn-doped. The brown, cyan, green, orange, black, pink balls represent C, Sc, Ti, V, Cr and Mn atoms, respectively. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

Table 1
Calculation results on transitional metal (TM, TM=Sc, Ti, V, Cr and Mn) atoms doped graphene. h (Å) represents the elevation of the doped atoms above the graphene plane, d_{TM-C} (Å) represents the distances between the doped atom and its nearest neighboring C atom. E_b (eV) is the binding energy. E_g represents the energy gap. M (μB), M_{TM} (μB), M_{NN-C} (μB) and M_{SNN-C} (μB) are the total magnetic moment, atomic magnetic moments of the doped TM atom, nearest neighboring and secondary nearest neighboring C atoms.

TM	h (Å)	d_{TM-C} (Å)	E_b (eV)	E_g (eV)	M (μB)	M_{TM} (μB)	M_{NN-C} (μB)	M_{SNN-C} (μB)
Sc	1.85	2.06	−6.89	metallic	0	0	0	0
Ti	1.58	1.93	−9.74	0.43	0	0	0	0
V	1.47	1.87	−9.86	0.17[a]	0.95	1.03	−0.05	−0.05
Cr	1.40	1.82	−10.11	0.40	1.95	2.17	−0.11	−0.11
Mn	1.36	1.79	−10.15	metallic	2.38	2.47	−0.08	−0.07

[a] Represent band gap for one of the two spin channels of the half-metal.

Mn-doped graphene and magnetic moments of Sc-, Ti-, Cr- and Mn-doped graphene change obviously after the adsorption of NO molecule, indicating the sensitivity toward NO molecule. Additionally, the electrical conductivity of the Mn-doped graphene, and the magnetic moments of the Sc- and Ti-doped graphene change more obviously after the adsorption of NO molecule relative to the counterpart of N_2 and O_2 molecules, indicating the sensitivity as well as the selectivity of graphene toward NO molecule in air.

2. Computational methods

All the calculations in the present study were performed by using the first-principles method based on the density functional theory (DFT) within the Vienna *ab-initio* simulation package (VASP) [34–36]. The electron–ionic interaction was calculated by the projector augmented wave (PAW) potentials [37] and the plane wave basis. The electronic exchange-correlation interaction was calculated by the Perdew–Burke–Ernzerhof [38] formulation of the generalized gradient approximation (GGA) method. Integration of the first Brillouin zone is performed by the Gamma-centered (9 × 9 × 1) k-mesh based on the Monkhorst–Pack method. The cut off energy of the plane wave basis set is set as 400 eV. A vacuum region of 20 Å was added to minimize the interaction between the adjacent image.

Our calculated lattice constant for graphene is 2.47 Å, which agreed well with the experimental result [39]. Graphene is simulated by the 4 × 4 × 1 supercell of repeated slab model. The total energies and atomic configurations of NO, N_2 and O_2 molecules were calculated, and the bond lengths of N–O, N–N and O–O are 1.17 Å, 1.12 Å and 1.24 Å, respectively. O_2 and NO are paramagnetic molecules with the respective magnetic moments of 2 μB and 1 μB. These results are consistent with the previous reported data [40,41].

3. Results and discussions

3.1. Transitional metal (TM, TM=Sc, Ti, V, Cr and Mn) atoms doped graphene

We firstly studied the transitional metal (TM, TM=Sc, Ti, V, Cr and Mn) atoms doped graphene with one C atom substituted for one TM atom in a 4 × 4 superlattice of graphene, and the corresponding doping concentration is 3.13%. Fig. 1 shows the side and top views of the atomic structures for TM-doped graphene. We can see that the doped TM atoms are all above the graphene's plane instead of embedding in the plane because their atomic radius are significantly larger than that of C atom. Not only this, the doping of TM atoms affect the graphene's structure by pulling up the nearby C atoms above the C atoms plane. These configures are consistent with a previous study [42]. Our calculation results on the TM-doped graphene are listed in Table 1. The binding energies of TM atoms substitutional doping graphene were calculated by the following formula:

$$E_b = E_{TM-G} - E_G - E_{TM} \quad (1)$$

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