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Sulfur dioxide molecule sensors based on zigzag graphene nanoribbons with and without Cr dopant

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ABSTRACT

Structure, electronic, and transport properties of sulfur dioxide (SO_2) molecule adsorbed on pure and Cr doped zigzag graphene nanoribbons (ZGNRs) are investigated by means of first principle density functional theory and nonequilibrium Green's function computations. It is found that Cr doped ZGNR is more sensitive to SO_2 molecule than pure ZGNR. The pure ZGNRs with and without SO_2 molecule show similar I–V curves, but the current of Cr doped ZGNR will significant increase after SO_2 molecule adsorption.

1. Introduction

Graphene and graphene based nanostructure are focus of intensive research activities due to their impressive material properties [1,2] and promising application potential [3,4] in novel electronic devices. However, two-dimensional (2D) graphene is semimetal, which seriously limits its applications in electronics. It should have adjustable band gaps for further applications in nanodevices from the perspective of semiconductor technology. Carving 2D graphene sheet [5] is an effective method to open a band gap and thus we can get zigzag and/or armchair graphene nanoribbons (ZGNRs/AGNRs). The electronic properties of GNRs are chemically derived and tunable by the ribbon width and length [6]. Hydrogen terminated ZGNRs are metallic or semiconducting, which is depending on the edge spin orientation [7]. The spins of ZGNR are ferromagnetic coupling within each edge and antiferromagnetic coupling between the two edges [8]. Real materials of GNRs are likely to contain structural defects and impurities of noncarbon elements. It has been proposed that the effect of such impurities may play an important role on the properties of GNRs [9].

Sulfur dioxide (SO_2) is a colorless gas and one of the main pollutants with toxicity from industrial complexes and vehicles. It can interact with air and then results in the formation of "acidic rains". A great amount of efforts have been devoted to find an effective technique for SO_2 detection. Experimental and theoretical studies have shown that graphene can be used as a sensing material to detect various gas molecules [10–15]. In a recent study, we have found that SO_2 molecule is adsorbed weakly on intrinsic graphene and the sensitivity of graphene-based chemical gas sensors for SO_2 can be drastically improved by Cr doped [15]. In this work, we focus on the feasibility of ZGNRs being used as gas sensors, on the basis of the first principles method, by calculating and analyzing the spin-dependent electronic behavior of undoped ZGNR and Cr doped ZGNR before and after absorbing SO_2 molecule. Both effects of different positions of Cr in ZGNRs and spin-polarized edges states are considered from the view of the adsorption energies, charge transfers, density of states (DOS), transmission spectra, I–V characteristics, and the molecular projected self-consistent Hamiltonian (MPSH). This work will have some deep insights into the electron transport properties of them, and may give some inspirations to design high-performance nanoscale graphene sensors.

2. Computation methods and models

The spin-resolved density functional theory (DFT) calculations were performed using the generalized gradient approximation (GGA) with Perdew–Wang 1991 (PW91) function [16] for the exchange and correlation effects of the electrons, as implemented in Vienna ab initio simulation package (VASP) [17,18]. As is known, the equilibrium distance between adsorbate and the graphene

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sheet will be somewhat overestimated and consequently the binding energy will be underestimated in GGA, but valuable results still can be obtained within this frame. In spite of not explicitly accounting for the van der Waals interaction, this numerical technique has been widely used to study the doping and adsorption of graphene [14,19]. Electron–ion interactions were described by the projector augmented wave (PAW) method and the energy cut-off was taken to be 400 eV. The k-point was set to $1 \times 1 \times 10$ (z direction along the ZGNR growth direction) for the Brillouin–Zone (BZ) integration in structure optimization and the force convergence criterion was set to 0.03 eV/Å. We used vacuum pad of >10 Å in the x and y directions, which is sufficient to minimize the interaction between them. The adsorption energy, E_{ad}, is defined as

$$E_{ad} = E_{sheet} + E_{SO_2} - E_{total}, \tag{1}$$

where E_{sheet}, E_{SO_2}, and E_{total} are the energies of the isolated graphene sheet, the isolated SO_2 molecule, and the relaxed graphene sheet with an adsorbed SO_2 molecule, correspondingly.

Several two-probe models were constructed to perform for further geometric optimization and electron transport properties study using the DFT coupled with the nonequilibrium Green's function (NEGF) formalism implemented in the Atomistix ToolKit (ATK) [20]. The SGGA schemes were used with PW91 correlation functional for the sake of being consistent with the previous VASP computation. Double-zeta polarized (DZP) basis set was chosen and the k-point sampling was 1, 1, and 100 in the x, y, z direction, respectively. The cut-off energy was set to 150 Ry and the force tolerance of structural relaxations of each two-probe system was accepted to be less than 0.05 eV/Å. The current can be calculated from the Landauer–Büttiker formula [21]:

$$I = \frac{2e}{h} \int_{-V/2}^{V/2} T(E, V)\, dE. \tag{2}$$

The region of the bias window is $[-V/2, V/2]$ and $T(E, V)$ is bias-dependent transmission coefficient [22,23].

The model systems we study in this work are illustrated in Fig. 1, which are 5-ZGNR in width and 11 dimer lines of carbon atoms in length with edges passivated by monoatomic hydrogen. In our models, a supercell with 11 dimer lines is proper for considering the adsorption and impurity effects [9]. We consider the case that a doped Cr atom substitutes a C atom in this system with a single SO_2 molecule adsorbed to it. Five different doping sites for Cr are investigated [labeled by 1–5 from the edge to the center, in Fig. 1(a)]. Depending on the location of Cr, the ZGNR with Cr at site 1 is referred to as Cr1-ZGNR, and so on. As shown in Fig. 1(c), each of the proposed ZGNR-based device includes three parts: scattering region and two (left and right) semi-infinite electrodes [24]. Both the scattering region and electrodes have the same width.

3. Results and discussion

Firstly, we have calculated the spin-dependent total energies E for five different doping sites (1–5) of Cr in ZGNR (Fig. 1(a)). It is found that Cr prefers to stay at the edge of ZGNR, site 1. The calculated E of Cr1-ZGNR is much lower than those of Cr2-ZGNR (by 0.587 eV), Cr3-ZGNR (by 0.986 eV), Cr4-ZGNR (by 1.079 eV), and Cr5-ZGNR (by 1.372 eV). It can be understandable as H is less electronegative than C and the Cr–H bond is stronger than the Cr–C bond. This is similar to the results of N [25,26] and B [25,27]. We will only discuss Cr1-ZGNR in the following.

In addition to different sites of Cr doping, the stability of these models also depends on different magnetic phases. In order to find the most stable ground state of the magnetic ribbons, we computed the total energies for different magnetic phases of pure

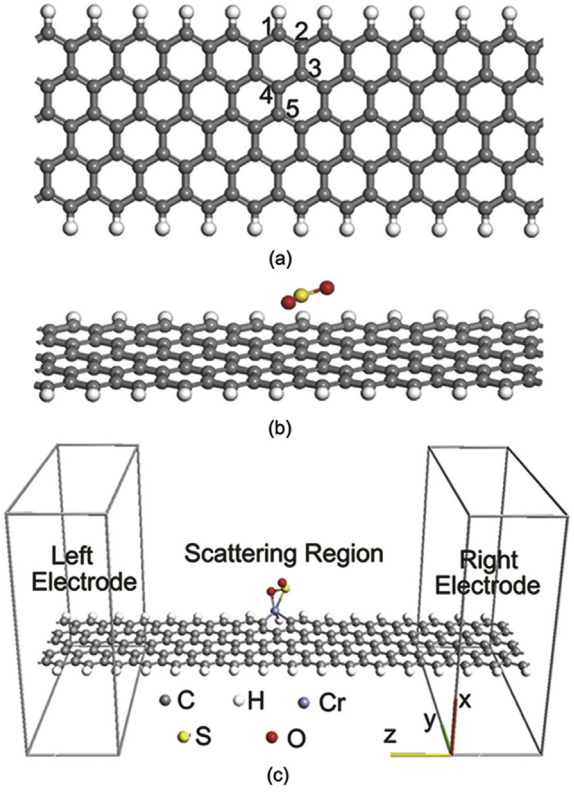

Fig. 1. (Color online.) (a) Atomic structure of 5-ZGNR consisting of 11 replicas of the ideal ZGNR dimer lines. The numbers (1–5) indicate the explored Cr doping sites. (b) The stable adsorption configuration of SO_2 on pure 5-ZGNR. (c) Schematic diagram of the two-probe system with one Cr atom substitutionally doped in site 1 and adsorbed SO_2 molecule.

Table 1
The energy difference ΔE (eV) of four ZGNRs.

	ZGNR	SO_2+ZGNR	Cr1-ZGNR	SO_2+Cr1-ZGNR
FM	−0.571	−0.569	−3.730	−2.531
AFM	−0.711	−0.794	−3.002	−1.271

ZGNR, SO_2+ZGNR, Cr1-ZGNR, and SO_2+Cr1-ZGNR, including nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) ones. The stabilities depending on the spin configurations can be estimated by the energy difference ΔE between the magnetic (FM or AFM) and NM state ($\Delta E = E_{FM/AFM} - E_{NM}$) in Table 1. As can be seen from Table 1, the total energy of the AFM phase of pure ZGNR is 0.140 eV lower than that of FM phase. Therefore, energetically, the AFM is the most favorable phase for pure ZGNR, which is consistent with earlier investigations [9,26]. For SO_2+ZGNR, the ground state is also AFM coupling. After SO_2 adsorbing on ZGNR, the calculated E_{ad} is 0.079 eV and the nearest distance between C and S atom of SO_2 molecule is 3.434 Å. The net charge transfer Q (Bader charge [28]) is $0.082e$ from ZGNR to SO_2. However, Cr1-ZGNR and SO_2+Cr1-ZGNR are both FM coupling in the ground state. In comparison with the results of pure ZGNR and Cr1-ZGNR, we can infer that Cr doping alter the magnetic coupling of ground state in ZGNR due to the impurity effect. For SO_2 on Cr1-ZGNR (SO_2+Cr1-ZGNR), $E_{ad} = 1.591$ eV, $d = 1.869$ Å (the Cr–O bond length), and $Q = 0.783e$ (from Cr1-ZGNR to SO_2). All of these illuminate that SO_2 molecule undergoes strong chemisorption on Cr1-ZGNR and weak adsorption on pure ZGNR, which are similar to the results of SO_2 molecule on Cr doped and pure graphene sheet [15].

The spin-polarized device density of states (DOS) of these structures and the projected density of states (PDOS) of SO_2+Cr1-ZGNR