Spin polarization properties of thiophene molecule adsorbed to the edge of zigzag graphene nanoribbon

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ABSTRACT

Spin polarization properties of thiophene molecule adsorbed to the edge of zigzag graphene nanoribbon (GNR) are studied based on density functional theory calculations. It is shown that there is charge transfer between the thiophene molecule and the zigzag GNR, which changes the bond lengths of the thiophene molecule. Another consequence of the charge transfer is the spontaneous spin polarization of the thiophene molecule. The mechanism of the spontaneous spin polarization is also discussed based on the analysis of the density of states. It is found that the p orbitals of the carbon atoms and the sulfur atom in thiophene molecule become spin split near the Fermi energy, so preferential fillings of the spin-splitted p orbitals make the thiophene molecule spin polarized. This spontaneous spin polarization of thiophene molecules adsorbed to the zigzag GNR could be a new route to graphene-based organic spintronic devices.

1. Introduction

Graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale, hexagonal lattice in which one atom forms each vertex. Graphene is the basic structural element of other allotropes, including graphite, charcoal, carbon nanotubes and fullerenes [1]. Graphene has many extraordinary properties, such as high strength, great efficiency of conducting heat and electricity, nearly transparent, etc [2–4]. Scientists have identified many peculiar physical properties of graphene, for example, massless Dirac fermions, quantum Hall effect, ballistic transport of charges. Graphene can be cut into nanoribbons with different edge structures and the two basic graphene nanoribbons (GNRS) are armchair and zigzag. The electronic states of GNRs largely depend on the edge structures. The quantum confinement, inter-edge superexchange, and intra-edge direct exchange interactions in zigzag GNR are important for its magnetism and band gap [5]. Zigzag GNRs are semiconducting and present spin polarized edges due to an unusual antiferromagnetic coupling between the magnetic moments at opposite edge carbon atoms, which suggests applications in the field of spintronics, and graphene spintronics

has attracted much attention [6–11]. From another point of view, the spin polarization at the edge of the zigzag GNR make it is possible to build spintronic devices in which zigzag GNR are used as the electrodes or buffer layers [12–14]. In a word, there are abroad application prospects of graphene in spintronics based on its excellent intrinsic electronic and mechanic properties.

An emerging branch of spintronics is organic spintronics, in which organic materials are used to perform spin polarization functionalities and even to further design and manufacture all-organic spintronic devices [15–20]. In 2002, Dediu et al. first observed room temperature spin polarized injection and transport in thin films of alpha-sexipheney, which is one of the derivative materials of thiophene molecule.[21] From then on, many organic materials have been studied in organic spintronics experimentally and theoretically [16–30]. Among these diverse organic materials in spintronics, thiophene molecule and its derivatives are the most popular ones and have been widely studied, especially for interface systems. For example, Bergeson et al. found that alpha-sexipheney exhibits sign-changeable magnetoresistance under certain conditions, and they considered that the magnetoresistance and the inversion of its sign are due to the hyperfine interaction in the magnetic field [31]. Cótica et al. chemically synthesized magnetite and poly(thiophene)-coated magnetite nanoparticles and they investigated the correlations between their magnetic, structural, and microstructural properties [32]. They found that the polymer

layer causes a sharp decrease of the spin disorder and reduces the anisotropy constant significantly in the nanocomposites. Wang et al. performed *ab initio* calculations to investigate the spin polarization properties at the interface between a thiophene molecule and cobalt substrate [33]. Their calculations indicated that reduced symmetry in the thiophene molecule leads to spatial dependence of the spin polarization. Spontaneous spin polarization properties for thiophene derivatives have also been discussed both from the Su-Schrieffer-Heeger model and first-principle calculations, which show that the thiophene derivatives could be spin polarized by introducing extra charges [34–36].

Based on the extraordinary electronic, mechanic, optical properties and especially the magnetic functionalities of graphene as well as the broad application prospects of organic spintronics, much effort has been devoted to combine the properties of organic molecule magnets and graphene, the results not only contribute to understanding the spin polarization properties when organic molecules are adsorbed to graphene, but also open the way to the fabrication of all-organic and/or graphene-based organic spintronic devices. On the other hand, the systems of thiophene molecule adsorbed to graphene surface are well studied theoretically and experimentally [37,38], so it is interesting to investigate the spin polarization properties of thiophene molecule which is adsorbed to the spin-polarized edge of zigzag GNR, and this system could be used as a typical model to further understand the electronic properties of graphene-based organic spintronic devices. The details of the calculations and the discussions are as follows.

2. Computational methods

The Vienna Ab Initio Simulation Package (VASP) is used in our first-principles density functional theory calculations [39,40]. The projector augmented-wave (PAW) method is used to describe the ion-electron interaction. The Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) is adopted in the package to treat the electron exchange correlation, which yields the correct ground-state structure of the combined systems [41]. PBE GGA is also used to descript spin-polarization properties in variety adsorption systems, for example, linear monoatomic chains adsorbed on beryllium oxide nanotube, hydrogen-assisted dissociation of CO on Fe (100), thiophene molecule adsorbed at ferromagnetic electrodes, et al. [42–44]. In our calculations, a sufficiently high-energy cutoff (500 eV) has been adopted in each calculation to reach a convergence of the total energy. Structure relaxations are performed to get a stable state with the convergence threshold of the forces on each atom is 0.02 eV/Å. We first do structure relaxation for isolated thiophene molecule and zigzag GNR to get the stable structure, respectively. Based on these stable structures, we put the thiophene molecule at different possible positions at the edge of the zigzag GNR by keeping them in the same plane, and then the whole system is put in a unit cell with about a 15 Å vacuum space to avoid interactions between the images reproduced by periodic boundary conditions.

3. Results and discussions

The molecular structure of the thiophene and the Zigzag GNR are shown in Fig. 1. We tried many possible initial absorption positions, for example, S atom is placed on top of C5 or C6, H1 or H2 is placed on top of C5 or C6, etc. We do structure relaxation for each possible case and get their total energies. It is found from the calculations that the case of S atom placed on top of C6 has the minimum energy, so we think that this absorption is the most possible one, as shown in Fig. 1. This absorption position is accepted in the following calculations. It should be pointed out that
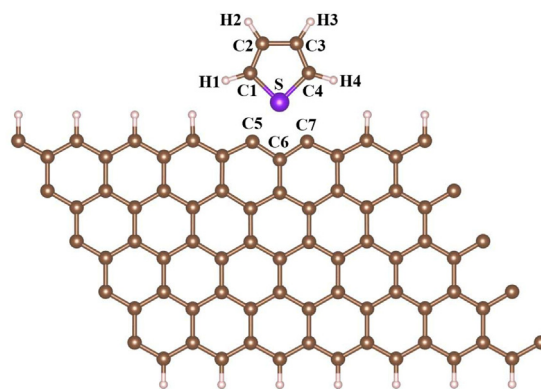

Fig. 1. Geometry of a thiophene molecule edge-adsorbed to zigzag GNR. C, S, and H atoms are shown as brown, yellow, and pink spheres, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

both cases for H-saturated and unsaturated systems are considered in our calculations. For H-saturated and unsaturated systems, atoms C5 and C7 are passivated by the S atom in the thiophene molecule when S atom is placed on top of C6. The C5 atom is passivated by hydrogen atom when the S atom is placed above C7 atom, and reversely, the C7 atom is passivated by hydrogen atom when the S atom is placed above C5 atom. From the calculations, it is found that all the physical results are similar except for a bigger spin polarization of the thiophene molecule for unsaturated systems based on the highly reactive unfilled valence carbons. However, GNRs are usually considered with H atoms passivating the edges, as this enhances the ribbon stability without damaging its magnetic features, so in this paper only H-saturated systems are shown in the follows. In this paper, we only considered the positions of thiophene molecule in the plane in graphene nanoribbon. Other cases, for example, the thiophene molecule is perpendicular to the graphene nanoribbon plane as well as the effects of the plane angle to the spin polarization properties will be studied further.

The bond length changes of the thiophene molecule before and after adsorption are shown in Table 1. For the isolated thiophene molecule, it is obvious that the C1—C2 and C3—C4 bond lengths are shorter than that of C2—C3, however, the bond lengths related to the S atom are the same. Based on this structural asymmetric arrangement, it is reasonable to predict that the thiophene structure will be changed after edge-adsorbed to the zigzag GNR. In comparison with the isolated thiophene, it is obvious that the bond lengths of C1—C2 and C3—C4 become shorter and other bond lengths become longer when thiophene molecule is edge-adsorbed to zigzag GNR. Based on these asymmetric bond lengths changes, one can expect the particular charge density distributions and spin density distributions.

Fig. 2(a) and (b) show the charge density distributions and the spin density distributions of the system, respectively. The charge density is defined as $\Delta\rho = \rho_{tot} - \rho_g - \rho_{th}$, where ρ_{tot} is the charge density of the whole system, ρ_g is the charge density of the zigzag GNR and ρ_{th} is the charge density of the thiophene molecule. The red region in Fig. 2(a) corresponds to $\Delta\rho > 0$, while the green

Table 1
Bond length changes (in Å) between isolated thiophene molecule and the edge-adsorbed one to zigzag GNR.

bonds	C1—C2	C2—C3	C3—C4	C1—S	C4—S
Isolated	1.37428	1.42299	1.37460	1.71667	1.71667
Adsorbed	1.35912	1.43829	1.35908	1.75416	1.75431
Difference	−0.01516	0.0153	−0.01552	0.03749	0.03764