Carbon 98 (2016) 607–612

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

High-efficiency spin-filtering and magnetoresistance effects in supramolecular spin valves

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ARTICLE INFO

Article history:
Received 5 September 2015
Received in revised form
8 November 2015
Accepted 16 November 2015
Available online 22 November 2015

Keywords:
Spin-filtering effect
Magnetoresistive effect
Supramolecular spin valve

ABSTRACT

By using nonequilibrium Green's functions in combination with the density functional theory, we investigate the transport properties of the supramolecular spin valves made of ferrocene and pristine (p-type or n-type) graphene nanoribbons. The results show that ferrocene adsorption on pristine graphene nanoribbons gives rise to perfect magnetoresistive effect. While for ferrocene adsorption on p-type graphene nanoribbons, the perfect magnetoresistive effect disappears but a high-efficiency spin-filtering effect can be observed. More interestingly, the ferrocene adsorption on n-type graphene nanoribbons bring about the disappearance of spin polarization effect, and thus spin-filtering and magnetoresistive effect cannot be observed. Our researches also confirm that the doping type of graphene nanoribbons is a key factor for obtaining a high-performance supramolecular spintronic device.

1. Introduction

Recently, spintronic devices have attracted wide attention due to their potential applications in logical operations and data storage [1]. The spintronic devices have been considered to one of the effective solutions for realizing the new revolution of information industry. At present, the frontier and hot issue in the field of spin electronics are the study of single-molecule spintronic devices. Various single-molecule spintronic devices, such as single-molecule spin valves [2–6], single-molecule spin filters [7–11], single-molecule spin field-effect transistors [12,13], single-molecule spin diode [14], etc., have been studied theoretically and experimentally. Among them, the single-molecule spin valves receive more attention.

At present, the single-molecule spin valves in experimental and theoretical studies are mainly based on sandwich structure model, namely, ferromagnetic bulk metal/molecule/ferromagnetic bulk metal [5,7,10,12,14–19]. However, there are many drawbacks in this model, such as complex interface structure, magnetic bulk electrodes occupying more circuit space, the interaction between magnetic metal electrode and molecule, the magnetic interaction between magnetic metal electrode due to the limitation of molecular length, etc. In order to solve these problems, a new type of molecular device, the supramolecular spin valve, is proposed. The first supramolecular spin valve is successfully prepared by Urdampilleta et al. [20] By supramolecular interactions, a single-walled carbon nanotube is laterally coupled to $TbPc_2$ single-molecule magnets, and thus a supramolecular spin valve is constructed. The result shows that the magnetoresistance (MR) ratio can reach about 300% [20]. Subsequently, Hong and Kim investigated spin transport mechanisms of this supramolecular spin valve by applying a simple model, and proposed that the MR effect in this device is driven by spin-dependent Fano resonance [21]. Though the experiment about the supramolecular spin valve has made progress, the theoretical research on the corresponding devices is rare. In the present work, ferrocene and armchair graphene nanoribbon (AGNR) are used to construct supramolecular spin valves, and thus the corresponding spin transport mechanisms are investigated. The computational results show that this device can possess high-efficiency spin-filtering and MR effects, which is determined by the doping type of AGNR. Our study provides a new thinking to obtain high-performance supramolecular spintronic devices.

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http://dx.doi.org/10.1016/j.carbon.2015.11.046
0008-6223/

2. Method and model

The supramolecular spin valves we study are shown in Fig. 1. Here we examine three different types of supramolecular spin valves. For Fig. 1(a), the two ferrocene molecules are adsorbed onto the edge carbon atoms of pristine 7-AGNR (here 7 is the number of carbon dimmer lines across the ribbon width). In fact, we also examine the case that the two ferrocene molecules are adsorbed onto the center carbon atoms. The result shows that the former is more stable than the latter by comparing their total energy. For Fig. 1(b), the p-type 7-AGNR is considered. Thus, one center carbon atom in the central scattering region is substituted by a boron atom, which is based on the fact that the boron atom doped at the center is more stable than that at the edge [22,23]. Here two ferrocene molecules are adsorbed onto the boron atoms of p-type 7-AGNR. Since 7-AGNR is semiconductor [24], the transport properties of the devices at low bias will be concealed. Thus, for the models in Fig. 1(a) and (b), boron-doped 7-AGNRs are used as the left and right electrodes. In order to investigate the effect of n-type AGNR on the transport properties of the supramolecular spin valve, nitrogen-dpoed 7-AGNR is also considered. Here the nitrogen atom is chosen to replace the edge carbon atom of 7-AGNR because the substitutional doping of nitrogen atom at the edge is more stable than that at the center [22,23]. As is shown in Fig. 1(c), the two ferrocene molecules are adsorbed onto the nitrogen atoms of n-type 7-AGNR. For convenience, the three models in Fig. 1(a)–(c) are named as M1, M2, and M3, respectively. For ferrocene adsorption on graphene, there are two possible configuration [22]: (i) the cyclopentadienyl rings are oriented vertically to the graphene; (ii) the cyclopentadienyl rings are oriented parallel to the graphene. However, previous reports show the first adsorption configuration is more stable. Thus, we only investigate first adsorption configuration in the present work. For M1–M3, the Fe atoms in ferrocene molecules are separated in a large distance, and thus their spin coupling can be ignored [25–27]. This means that they can be set in parallel or antiparallel magnetic configurations. During the experiment, this process can be manipulated as follows [28]: we can put two ferromagnetic stripes next to left and right ferrocene molecules, respectively. The relative magnetization orientation of the corresponding ferromagnetic stripes is changed by applying the external magnetic field. Thus, the parallel and antiparallel magnetic configurations of the device can be realized by tuning relative magnetization orientation of two ferromagnetic stripes. Moreover, it is known that magnetic anisotropy can ensure the magnets to keep their magnetization direction. Recently, Hirjibehedin et al. observed lager magnetic anisotropy for a single atomic spin embedded into a molecular-bonding network [29]. Thus, we believe that with the advancement of experiment technology, Fe atoms in ferrocene can realize large magnetic anisotropy to maintain their magnetization direction in the experiment. In order to facilitate the discussion, M1 [M2, M3] in parallel and antiparallel magnetic configurations is called as $M1_{\uparrow\uparrow}$ and $M1_{\uparrow\downarrow}$ [$M2_{\uparrow\uparrow}$ and $M2_{\uparrow\downarrow}$, and $M3_{\uparrow\uparrow}$ and $M3_{\uparrow\downarrow}$], respectively. The transport properties are investigated by using the ATOMISTIX TOOLKIT (ATK) package, which applies the nonequilibrium Green's function method combined with density functional theory [30,31]. In the electron transport calculation, a double-zeta plus polarization basis set was used for boron, nitrogen, and iron atoms, and a single-zeta plus polarization basis set is used for carbon and hydrogen atoms to achieve a balance between the calculation efficiency and the accuracy. Previous reports show that in the transport calculation, the single-zeta plus polarization basis set for carbon and hydrogen

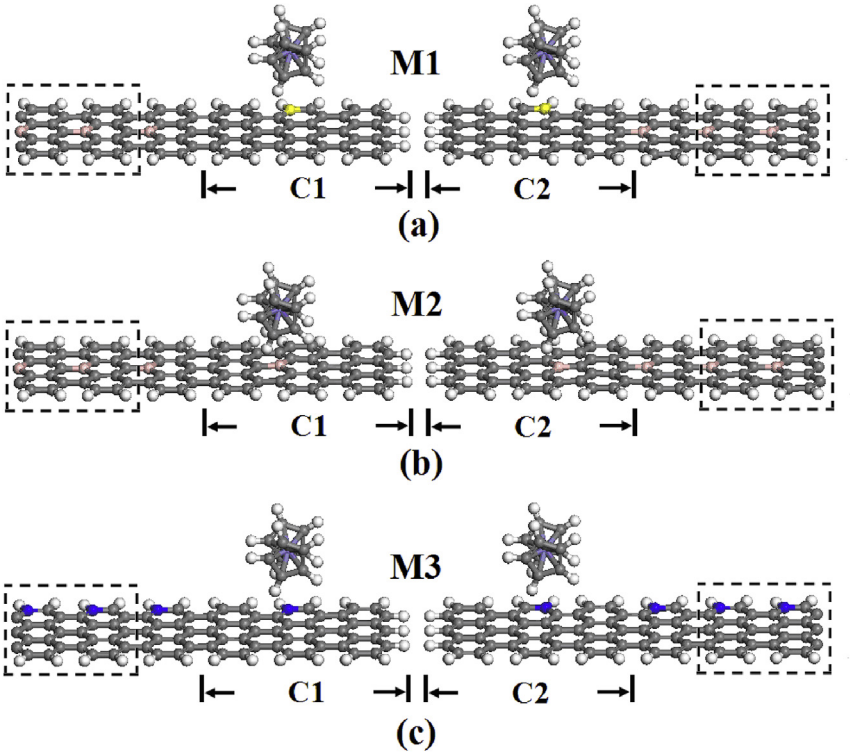

Fig. 1. Schematics of three different types of supramolecular spin valves. (a) Ferrocene adsorption on pristine armchair graphene nanoribbons. (b) Ferrocene adsorption on p-type armchair graphene nanoribbons. (c) Ferrocene adsorption on n-type armchair graphene nanoribbons. Yellow, pink, and blue balls represent the edge carbon atoms, the boron atoms, and the nitrogen atoms, respectively. The Fe atoms are located on top of the edge carbon atoms, boron atoms, and nitrogen atoms for three different types of supramolecular spin valves, respectively. The function of armchair graphene nanoribbons in the dotted line is acted as left and right electrodes. (A color version of this figure can be viewed online)