Physics Letters A 382 (2018) 1401–1408

Contents lists available at ScienceDirect

Physics Letters A

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The spin-dependent electronic transport properties of M(dcdmp)$_2$ (M = Cu, Au, Co, Ni) molecular devices based on zigzag graphene nanoribbon electrodes

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ARTICLE INFO

Article history:
Received 21 December 2017
Received in revised form 3 March 2018
Accepted 20 March 2018
Available online 22 March 2018
Communicated by R. Wu

Keywords:
Density functional theory
Zigzag graphene nanoribbon
M(dcdmp)$_2$ molecular device
Spin-dependent transport property
Magnetic resistance

ABSTRACT

The spin-dependent electronic transport properties of M(dcdmp)$_2$ (M = Cu, Au, Co, Ni; dcdmp = 2,3-dicyano-5,6-dimercaptopyrazyne) molecular devices based on zigzag graphene nanoribbon (ZGNR) electrodes were investigated by density functional theory combined nonequilibrium Green's function method (DFT-NEGF). Our results show that the spin-dependent transport properties of the M(dcdmp)$_2$ molecular devices can be controlled by the spin configurations of the ZGNR electrodes, and the central 3d-transition metal atom can introduce a larger magnetism than that of the nonferrous metal one. Moreover, the perfect spin filtering effect, negative differential resistance, rectifying effect and magnetic resistance phenomena can be observed in our proposed M(dcdmp)$_2$ molecular devices.

1. Introduction

With the development of micro-manufacturing, quantum effect plays an important role on devices with small size, thus making designing and manufacturing traditional semi-conductive electronic devices much more difficult under micro/nano-meter. To meet the challenges, scientists have come up with many methods both in theory and experiment. For years, progress in micro fabrication and self-assembly techniques has made it possible to design molecule devices [1]. Since them first put forward, molecular electronic devices attract many researchers' attentions and efforts have been taken to reveal the transport mechanism of them both in experimentally and theoretically [2,3]. Lots of interesting phenomena including field-effect characteristics, negative differential resistance (NDR), rectification effect, spintronics characteristics such as spin-valve, spin crossover, spin filtering, switching effect and so on have been found ever since [4–8]. Researchers also found out that the electronic transport properties of molecular devices not only depend on the structures of the molecules, but also related to the properties of the electrodes [9]. Though the first choice of metallic electrodes connecting molecules through thiol (-SH) or other group is the most common way [10,11]. Electrical transparency, mechanical stability and atomic level control over the bonding geometry are the mainly difficulties making this kind of structure not an ideal choice [12,13]. More suitable electrode materials are required.

Since Geim et al. exfoliated graphene from graphite using a mechanical method [14], graphene has been studied extensively. Both graphene and graphene nanoribbons (GNRs) are discovered and prepared successfully using different methods [15,16]. Research results show that graphene and GNRs are revolutionary for molecular devices due to their special electronic properties, such as weak spin orbital coupling effect [17], high electronic mobility [18], long spin relaxation times and lengths [19], gate tunability [20]. There are two kinds of GNRs, zigzag graphene nanoribbons (ZGNRs) and armchair graphene nanoribbons (AGNRs) [21]. Particularly, many researches are focusing on ZGNRs for their edge magnetism and unique transmission properties [21–23]. Besides the study of pure GNRs or edge modified GNRs, researchers also studied systems by connecting molecules to GNRs [24,25]. The previous researches have demonstrated that NDR effects, spin filtering, and switching

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https://doi.org/10.1016/j.physleta.2018.03.030
0375-9601/

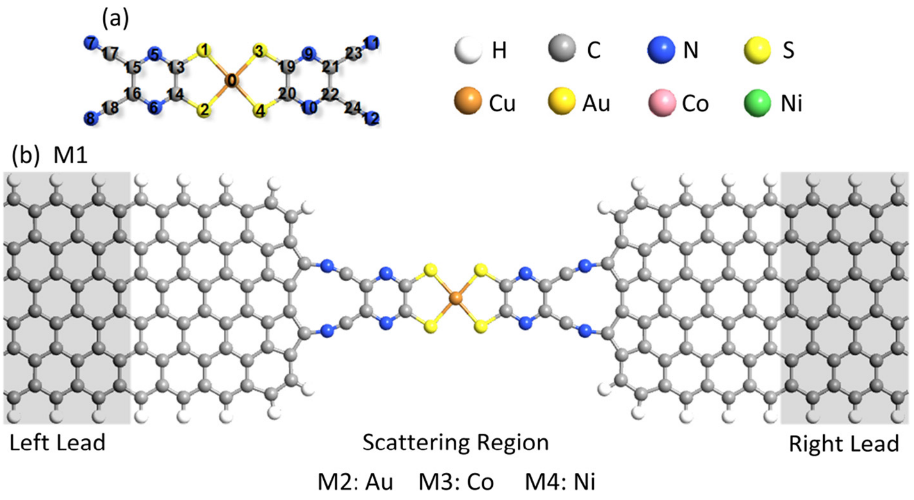

Fig. 1. Study models of the proposed systems. (a) The single molecule of Cu(dcdmp)$_2$, and the ordinal numbers of atoms are marked out on the left part, the symbols of elements show on the right part. (b) The two-leads model of 6-ZGNR-Cu(dcdmp)$_2$-6ZGNR molecular device.

could coexist in a single device [26,27], which suggests that multi-functional and high performance molecular devices will be a trend in future. However, to our knowledge, most of molecules used are anchored with a single atom on each electrode [25,28,29]. Owing to these molecules are not planar nor regular, and the anchored atoms and the structures of the molecules cannot be manipulated easily, which lead to the tunability and modification of the properties on this kind of molecular devices are severely limited.

Since GNR is a quasi-1-dimension geometry, the connected molecule has a plane structure may have advantages on the process of modeling a molecular device. Besides, a tunable molecule is also required. Since 1999, the acceptor M(dcdmp)$_2$ with other donor molecule crystals have been successfully synthesized [30,31]. The replaceable metal atom means this ligand molecular device has a broader control possibility. This kind of molecule can also have different donor coordination [32]. The founds of different stoichiometry in dithiophene–tetrathiafulvalene (DT-TTF) salts increase the tunability of M(dcdmp)$_2$ [33]. And study of molecular crystal with M(dcdmp)$_2$ show that this kind of crystal usually have a good mobility [30,33]. Up to now, there are many researchers have investigated the transport properties of molecular crystal or subpart of the DT-TTF-Cu(dcdmp)$_2$ by theoretical or experimental method. Marta Mas-Torrent et al. studied temperature dependence of the electrical properties, and the mobility of DT-TTF for single-crystal organic field effect transistors [34,35]. We also have studied the fluorination effects on the electronic transport properties of donor part of DT-TTF [10]. However, transport properties of the acceptor Cu(dcdmp)$_2$ part, particularly the metal replaced M(dcdmp)$_2$ are still under reveal. In this work, by using density functional theory combined nonequilibrium Green's function method (DFT-NEGF), we studied the electronic transport properties of M(dcdmp)$_2$ molecular junctions with six carbon chain width zigzag graphene nanoribbon (6ZGNR) as electrodes. There are two families of central metal atoms are studied: 1) nonferrous metals (NM) Cu and Au; and 2) 3d-transition metals (TM) Co and Ni. We firstly analyze the properties of single M(dcdmp)$_2$ molecules, then we illustrate the zero bias transport properties of our four devices. Followed, we depict the nonzero bias transport characters in detail. Finally, we will give our conclusions of our work.

2. Models and methods

The rectangle planar molecule structure of M(dcdmp)$_2$ (M = Cu, Au, Co, Ni) are given out in Fig. 1(a), and our two-probe molecular junction devices constructed by M(dcdmp)$_2$ and 6ZGNR electrodes are shown in Fig. 1(b). Here, only M = Cu is showed in the molecule and device, and the device is named as M1 for short. For other devices, which the central metal atom is replaced by Au, Co or Ni, are named as M2, M3 or M4, respectively. To account the interfacial interaction, the transition part between electrodes and molecule is set to be one periodic of 6ZGNR unit cell. To perfectly model a single molecular device, a vacuum of 12 Å was introduced perpendicular to the transport direction. The connect method between electrodes and central molecule is based on the geometry of both molecule and electrode materials and we also referred to the work of previous studies [25,27,29]. Research results have pointed out that ZGNR can be adjusted as ferromagnetic (FM) or antiferromagnetic (AFM) [36,37]. Though AFM is the ground state for ZGNR, FM state presents more active and shows metallic properties [38]. For all our proposed devices, the FM and AFM states, as well as two kinds of spin orientation between left and right electrodes, namely the parallel configuration (PC) and antiparallel configuration (APC), are considered in our calculations. For PC, $(L_M, R_M) = (1, 1)$, and for APC, $(L_M, R_M) = (1, -1)$, where L_M or R_M means the magnetic moment direction of left or right electrodes, and a positive value means the magnetic moment points up while a negative value means the magnetic moment points down. We then calculated and compared total energy of each configuration to determine the ground state of our devices, and the results are shown in Table 1. From Table 1, we can find that the FM-AP state is the ground state for M1 and M2, while the FM-P state is the ground state for M3 and that is the AFM-AP state for M4. Therefore, the FM spin state is used both in left and right ZGNRs electrodes in our calculations.

Table 1
Energy differences of the devices with different configurations (unit: meV). $E_{\mathrm{FM(P)}}$ stands for total energy of ferromagnetic ZGNR electrode under parallel spin configuration. Other symbols are by analogy.

	$E_{\mathrm{FM(P)}}-E_{\mathrm{FM(AP)}}$	$E_{\mathrm{FM(P)}}-E_{\mathrm{AFM(P)}}$	$E_{\mathrm{FM(P)}}-E_{\mathrm{AFM(AP)}}$
M1	3.48	−1719.58	−1737.78
M2	1.87	−1747.37	−1693.13
M3	−934.04	−1939.32	−1927.97
M4	96.69	369.59	463.36

All our calculations were carried out by Virtual Nanolab–Atomistix ToolKit (VNL-ATK) calculation package [39–41], which combine density functional theory (DFT) with non-equilibrium Green's function formalism (NEGF) method. The exchange correlation function of generalized gradient approximation (GGA) proposed by Perdew et al. [42] (PBE) was used for our calculations.