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Controlling spin off state by gas molecules adsorption on metal-phthalocyanine molecular junctions and its possibility of gas sensor

Wenkai Zhao [a,*], Dongqing Zou [b], Zhaopeng Sun [a], Yongjiang Yu [a], Chuanlu Yang [a,*]

[a] School of Physics and Optoelectronics Engineering, Ludong University, Yantai 264025, People's Republic of China
[b] School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China

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ABSTRACT

Employing Green's function (GF) technique in combination with spin-polarized density functional theory (DFT), we study the electronic structure and magnetic properties of metal phthalocyanine (MPc) (M = Mn, Fe, Co, Ni, Cu, Zn) with or without four different gas molecules (NO, CO, O_2 and NO_2) adsorbing on the M atom of MPc molecule. The corresponding stable adsorption structural configurations and transport properties of MPc molecular junctions are also investigated. Our results indicate that the magnetic moment of MPc for M = Mn, Fe and Co can be modified by the specific gas molecule adsorption, which is mainly ascribed to competitive relation of HOMO-LUMO Gap and Hund's rules. However, for M = Ni, Cu and Zn, it is difficult to detect gas molecule because the interaction of M atom and these gases is most of weak van der Waals interaction. Remarkably, the spin of MPc molecule can be switched to a magnetic off-state by specific gas absorption, giving rise to a potential application on controllable spintronic devices. In addition, CO, NO, O_2 and NO_2 gas molecules can be detected selectively by measuring spin filter efficiency of these MPc molecular junctions. On the basis of our results, MPc (M = Mn, Fe, Co) molecular junctions can be considered as a promising nanosensor device to detect individual gas molecules.

1. Introduction

Gas molecule detection is critical to industrial emission monitoring, environmental monitoring and medical applications, and many other applications [1,2]. With the development of device miniaturization, it is possible to monitor single molecules using today's nanotechnologies [3]. Therefore, nanometer scale and even molecular scale materials can assemble into suitable devices to develop sensors due to their small size, high selectivity and sensitivity, rapid response and low energy consumption [4]. Among these molecular scale materials, organic molecules have unique chemical sensitivity characteristic, which their molecular electronic states can be modified by ligand adsorption [5]. Therefore, utilizing this property, organic molecules have great potential to design for molecular scale sensors and detect gas molecular type.

Metal phthalocyanines (MPcs) which have a planar aromatic structure are the most important organic molecules and exhibit surprising varieties of functions [6–8]. The metal in MPc is dsp^2 hybridization form which might present potential application in molecular sensing. Previous studies of MPc had emphasized on the electronic transport properties of MPc molecules sandwiched between one- or two-dimensional electrodes. For example, in experimental respect, a copper phthalocyanine (CuPc) molecule in contact with two Au atomic chains has been artificially fabricated by Nazin et al. in using scanning tunneling microscopy [9]. In theoretical respect, Tada et al. reported the electrical transmission of CuPc connected between Au chain electrodes and found that the conductance of the junction is 0.0003 G_0 which is due to weak interactions between Au chains and CuPc molecule [10]. In addition, based on DFT with local density approximation, Fadlallah et al. have investigated electronic conductance and local electronic correlations effect on the M atom of a series MPc molecular junction [11]. Also, the transport properties of MPc molecules sandwiched between graphene nanoribbons electrodes or single-walled carbon nanotubes (SWNT) electrodes had also been investigated previously. Their results indicated that MPc molecule can present as a nearly perfect spin filter and obvious negative differential resistance phenomenon [12,13].

In our previous paper, we have reported on the MnPc gas sensors and found that CO, NO, O_2, and NO_2 gas molecules can be detected selectively by measuring the change in total current [14]. In this paper, we consider the M atom composed from Mn to Zn

* Corresponding authors.
E-mail addresses: kaypu@ldu.edu.cn (W. Zhao), ycl@ldu.edu.cn (C. Yang).

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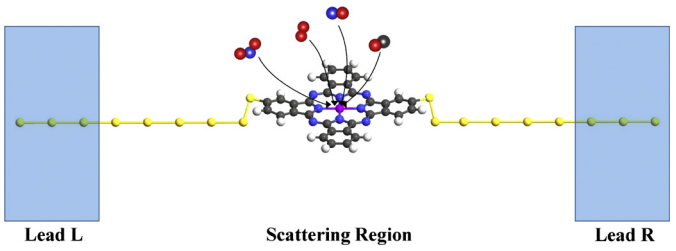

Fig. 1. Schematic diagram of the molecular junction system AuS-MPc-AuS (M = Mn, Fe, Co, Ni, Cu, Zn).

(M = Mn, Fe, Co, Ni, Cu, Zn) and bonded it to gold electrodes through thiolate groups. The changes in zero bias conductance and spin polarization due to the CO, NO, O_2 and NO_2 gases adsorption on the central M atom of the Pc are investigated. According to the changes, we propose a new kind of way to detect these gas molecules.

2. Computational details

The geometrical configurations of MPc (M = Mn, Fe, Co, Ni, Cu, Zn) molecule with and without four different molecular gases (CO, NO, O_2 and NO_2) adsorption on surface are optimized based on DFT as implemented in the Atomistix ToolKit package, which adopts atomic orbitals basis set and Troullier–Martin norm-conserving pseudopotentials [15]. Here, C, N and M (M = Mn, Fe, Co, Ni, Cu, Zn) atoms are described by $2s2p$ and $3d4s$ valence electrons and the core electrons are represented by the corresponding pseudo-potential, respectively. Moreover, in order to achieve a balance between calculation efficiency and accuracy, we choose double-ζ polarized (DZP) basis set for the electron wave function and the real-space grid cutoff energy is 200 Ry. In addition, we add long-range van der Waals (vdW) interactions term which is described by Grimme (DFT+D2) into standard DFT calculations to give a better description of gas adsorption geometrical configuration [16]. Here, the exchange correlation functional is adopted by Perdew, Burke, and Ernzerhof (PBE-SGGA) spin generalized gradient approximation [17]. The geometrical configurations are completely optimized until the atomic forces are less than 0.01 eV/Å^{-1}.

The spin transport calculations are carried out based on DFT in combination with the GF technique, as both implemented in the Atomistix ToolKit packages [18,19]. The corresponding calculation parameters of basis sets and grid cutoff energy in the transport calculations are identical as we have described above. As shown in Fig. 1, the molecular junction is divided into three parts: two electrodes (left (L) and right (R)) and a central scattering region. The blue shaded rectangles represent the electrodes (L/R) and the other region is the central scattering region which contain parts of gold atoms. For the electronic transport calculation, the Brillouin zone sampling is chosen $1 \times 1 \times 100$ k-point grids. Prior to the transport properties calculation, all the molecular junctions are completely optimized until the atomic forces are less than 0.02 eV/Å^{-1}. The spin-resolved transmission coefficient $T_\sigma(E)$ through the junctions is obtained by the formula:

$$T_\sigma(E) = \mathrm{Tr}\left[\Gamma_L G_S^{R\dagger} \Gamma_R G_S^R\right]_\sigma, \quad (1)$$

where σ represents a spin index, $\sigma = \uparrow$ (up-spin) and $\sigma = \downarrow$ (down-spin), and G_S^R is the retarded Green's function of the central scattering region. Here, $\Gamma_{L/R}(E)$ is the broadening function which accounts for the level broadening and can be obtained from:

$$\Gamma_{L/R}(E) = i\left[\Sigma_{L/R}^R(E) - \Sigma_{L/R}^R(E)\right] \quad (2)$$

where $\Sigma_{L/R}^R(E)$, the left/right (L/R) electrode self-energies, which represents the effect from the L and R electrodes upon the scattering region. The Green's function of the scattering region can be formulated as as follows:

$$G_S^R(E) = \left[ES_s - H - \Sigma_{L/R}^R - \Sigma_{L/R}^R\right]^{-1}, \quad (3)$$

where S_s is the overlap matrices and H is the Hamiltonian of the central scattering region. Further details regarding the methods for calculating electronic transport properties can be found in the literature [18–21].

3. Results and discussions

Adsorption configurations. First, we study the most stable adsorption site of gas molecules (CO, NO, O_2, NO_2) on the central metal atom of MPc (M = Mn, Fe, Co, Ni, Cu, Zn) surface. In consideration of the symmetry of gas molecule, we initially classify these gas molecules into three categories as shown in Fig. 2. For diatomic gases of different atom (CO and NO), there are two types of adsorption orientations, i.e., their molecular axis is aligned perpendicular and oriented parallel with respect to the MPc surface. Moreover, the C (N) or O atom as well as their center of gas molecules which are close to M atom are also examined. As a whole, there are five possible starting adsorption sites (see Fig. 2a). For diatomic gases of the same atom (O_2), there are only three possible starting adsorption sites (see Fig. 2b). For triatomic gas (NO_2), we consider the O and N atom are close to M atom, respectively, and two types of adsorption orientations are also tested, i.e., the N atom pointing to or away from the surface, respectively. In summary, there are six possible starting adsorption sites (see Fig. 2c). In order to find the most favorable location for gas molecules to be adsorbed, all the initial structures are relaxed according to above considerations, and the calculated total energy can be found in the Supporting Information. Then, we compare the total energy of all the relaxed adsorption configuration and select the gas adsorption

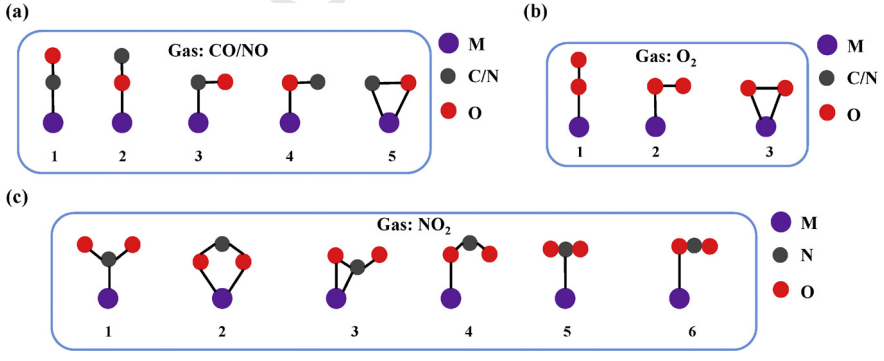

Fig. 2. Possibly initial adsorption sites of gas molecules (CO, NO, O_2 and NO_2) on the central metal atom of MPc molecule (M = Mn, Fe, Co, Ni, Cu, Zn).

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