Tunnel magnetoresistance in polyaniline

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ABSTRACT

The single-molecule electric current in polyaniline was investigated by first-principles calculation with a focus on tunnel magnetoresistance (TMR). The electric current in an aniline oligomer contacting two ferromagnetic electrodes was calculated by alternating the relative magnetic direction of the electrodes from parallel to antiparallel alignments. The oxidized state with imine instead of amine enhanced tunnelling between the electrodes under the parallel alignment. The electronic delocalization by π-conjugation upon varying the oxidation state of polyaniline increased the transmission at the Fermi level to induce the TMR effect under a low applied bias voltage between the electrodes.

1. Introduction

Biological organisms achieve electron transfer regularly in a biological system, and organic conductors have been examined as models to determine the electronic transfer mechanism. Organic conducting polymers have been developed as a new class of electronic materials to replace circuits used in computers currently based on silicon crystals [1]. The polymers have a π-conjugated system in which high electrical conduction is achieved along the polymer chain by adding electron donor or acceptor dopants [2,3].

Polyaniline is a promising conducting polymer because of its remarkable insulator-to-conductor transition [4]. The transition can be achieved by adding an acid dopant. In addition to doping, the oxidation-reduction states of polyaniline also can affect the electrical conduction performance. Depending on the oxidation-reduction state, polyaniline can adopt three kinds of polymer structures. Pernigraniline is in the fully oxidized state with imine links, while leucoemeraldine is composed of completely reduced repeating aniline units, and both are insulators. The emeraldine base has an alternating polyaniline structure composed of imine and aniline. Moreover, emeraldine salt can be obtained by acid-doping, resulting in the formation of a conductor. The charges in polyaniline are transferred by polarons moving along the polymer chain [5,6]. A polaron is an exciton formed by a radical cation at the nitrogen in polyaniline. Many polarons can combine, forming a bipolaron to induce metal-like electrical conduction. In the bulk of polyaniline, polarons or bipolarons hopping between the polymer chains governs the electrical conduction.

Molecular memories have been proposed as post-silicon devices to achieve a non-volatile memory with the high data storage densities using organic polymers and materials [7]. Conventional LSI technology that can handle sub-10 nm silicon devices cannot be used for the fabrication of molecular memory materials. Molecular memories are based on the magnetoresistance effect in the field of spintronics technology. A method to achieve memories is scanning tunnelling microscopy (STM) to manipulate individual molecules, which is known as the bottom-up approach. STM can also measure the current-bias characteristics of a single-molecule attached to the cantilever and substrate, and a prototype for molecular devices [8,9] and quantum computing [10,11]. In particular, the π-conjugated molecules exhibit high performance spin valve characteristics even at small applied bias voltages.

Currently, thin layers of organic conducting polymers are used in a field of organic spintronics investigations [12]. However, spin injection from the ferromagnetic electrodes to the conducting polymer through physisorption does not occur efficiently at the electrode/polymer interface [13]. If a single molecule is contacted on the electrodes through chemisorption, it can exhibit a spin-dependent electronic density of states (DOS) around the Fermi level because of the strong proximity effect with spatially extended metallic states [14]. It is also important that the molecules contacted on the metal electrodes have a DOS around the Fermi level to induce spin-dependent electronic states. Among conducting polymers, polyaniline can adopt various electronic characteristics from insulator to conductor by changing the oxidized/reduced states through doped states. The combination of chemical structures of aniline and imine are the origin of the property switching. Furthermore, these polymers are extremely environmentally stable and can be easily synthesized, making them attractive for applications in electronics and spintronics [15,16]. The advantages of polyaniline were retained in aniline oligomers [17,18], of which molecular junctions had characteristics of reversible bistable switching [19]. In this study, the single-molecule electrical conduction and TMR characteristics of

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aniline oligomers were investigated to apply to tunnel TMR devices and clarify the spin/electron transport mechanism along the polyaniline chain and through the molecule/metal interface.

2. Calculation method

In this study, the oligomer models as a unit cell of leucoemeraldine, emeraldine, and pernigraniline were considered to investigate the influence of polyaniline structures on their oxidation/reduction states [4]. Furthermore, the models were modified by phenylthiol at both terminals to attach to the nickel electrodes through metal-sulfur bonding through the removal of hydrogen atoms from thiol. As a result, three types of oligomer models were constructed for calculation of single-molecule electronic transport. Hereafter, the model aniline oligomers are written as LU, EM, and PE for the leucoemeraldine, emeraldine, and pernigraniline systems, respectively. The chemical structures were optimized using the GAMESS program under B3LYP/6-31G** [20]. This approximation level was enough to optimize the ordinal organic molecules. The coordinates in space of the molecules are listed in the Supplementary Information.

After removing hydrogen from the thiol, the oligomer models were located at a surface of Au(111) or Ni(111). The sulfur-gold and sulfur-nickel distance was set at 2.40 and 2.20 Å, respectively, based on the results of a first-principles calculation taken from the literature [21,22]. The Au(111) and Ni(111) surfaces were composed of three layers with a lateral (4 × 4) supercell, which formed semi-infinite left and right electrodes. To investigate the tunnel magnetoresistance the molecule attached to nickel electrodes, the relative orientation of magnetization of the two electrodes was set in either a parallel- (PA) or antiparallel alignment (APA) [23] (Fig. 1).

The spin-transport calculations were performed using the Atomistix Toolkit software (QuantumWise A/S) [24]. In the software, non-equilibrium Green's function (NEGF)-DFT calculations were performed using SIESTA code [25]. Only valence atomic orbitals were considered in the self-consistent calculation under norm-conserving scalar relativistic Troullier-Martins pseudopotentials [26]. The basis functions of valence electrons were determined to be double-ζ basis sets with polarization functions for all atoms. In addition, a spin-polarized generalized gradient approximation using the Perdew-Burke-Ernzerhof method was selected for determining the exchange-correlation potential [27]. The current of the spin-up (↑) and spin-down (↓) states was

calculated using the Landauer-Büttiker formula [28], as follows:

$$I_\sigma(V_b) = \frac{e}{h} \int_{\mu_L}^{\mu_R} T_\sigma(E, V_b)[n_F(E-\mu_L)-n_F(E-\mu_R)] dE \tag{1}$$

where μ_L and μ_R are the chemical potentials of the left and right electrodes, respectively. In addition, the electron occupation in the electrode reservoirs, $n_F(E)$, and the transmittance, $(T_\sigma(E, V_b)$ ($\sigma = \uparrow$ and $\downarrow$)), at an energy level, E, under a bias voltage, V_b, were used for Eq. (1). The $T_\sigma(E, V_b)$ value at an energy level of E under a bias of V_b was obtained from Green's function derived from the Hamiltonian of the DFT calculation, and the contact broadening function was derived from the self-energy of the left and right electrodes [29]. The total current (I) was calculated as $I = I_\uparrow + I_\downarrow$ with bias voltages varying in intervals from 0.01 to 1.0 V. In this study, the μ of the Fermi level at $V_b = 0$ was determined to be zero.

In addition to the current, the DOS was also obtained using Green's function. Moreover, the molecular projected self-consistent Hamiltonian (MPSH) states were calculated using Green's function. In general, the most important MPSH states to analyse the electronic transport mechanism are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [30].

The TMR ratios under a certain bias voltage of an oligomer model attached to the nickel electrodes were calculated by Julliere's equation [31]:

$$\text{TMR} = \frac{I_{PA} - I_{APA}}{I_{APA}} \tag{2}$$

where I_{PA} and I_{APA} are the values of total current under the magnetic configurations of PA and APA, respectively.

3. Results and discussion

First, the electrical conduction of the oligomer model contacted on the two gold electrodes was calculated to analyse the tunnelling mechanism. Fig. 2 showed the current-bias curves of the oligomer models. No difference in the current between the spin-up and spin-down states was observed, only the total current was described in the plots. There was almost no current difference between the LU and EM models. The current of PE was a little higher than those of LU and EM. The current of all oligomers was amplified from a bias of approximately 0.4 V. This may have been due to resonance tunnelling by some resonance states at certain MPSH levels.
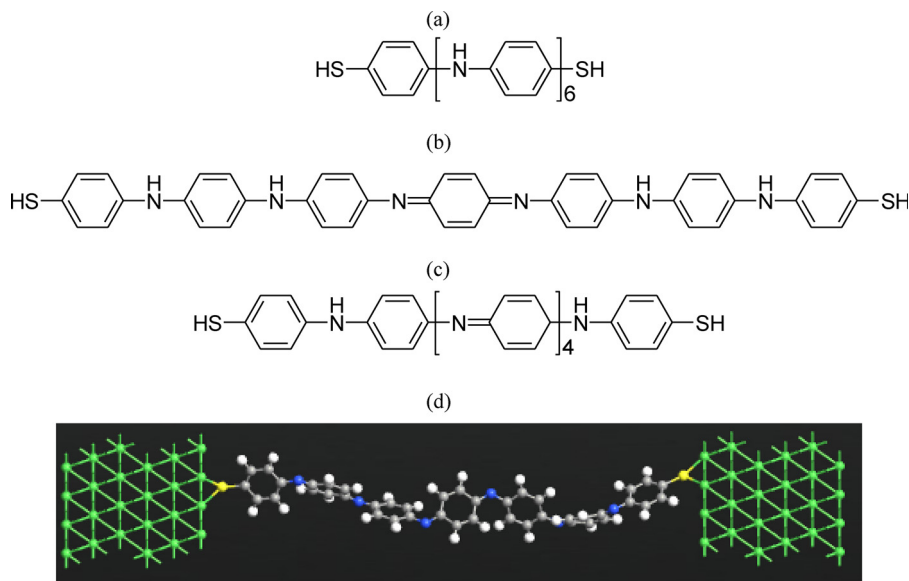
(a)

(b)

(c)

(d)

Fig. 1. Molecular structures of an aniline oligomer terminated by benzenethiol; (a) luecoemeraldine (LU), (b) emeraldine (EM), and (c) pernigraniline (PE). (d) Device structure of an aniline oligomer model sandwiched between two metal electrodes.