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Magnetoresistance originated from the Au/S interface in Au/1,6-hexanedithiol/Au single-molecule junctions at room temperature

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We report a magnetic response of Au/1,6-hexanedithiol/Au single-molecule junctions at room temperature using a mechanically controllable break junction method. The electrical resistance of the junction was found to increase up to 5.5% under a magnetic field. This phenomenon could originate from the unpaired charge at the Au/S interface.

The study of charge transport in single-molecule junctions has attracted considerable attention toward the development of novel electronic functions at the nano-scale.[1] In single-molecule junctions, interfaces between electrodes and molecules play significant roles in electronic characteristics. Recently, the magneto-response of single-molecule junctions using ferromagnetic (FM) electrodes has been a highlight because hybridization of molecular orbitals (MOs) and electronic states in FM could form unique spin-dependent electronic structures at the interface, called "spinterfaces"[2,3] that are expected to induce changes in magneto-responses, such as magnetoresistance (MR).[4–6] Interestingly, the magnetic characteristics could also be formed due to the hybridization of MO and electronic states in nonferromagnetic metals.[7] Sharangi *et al.* reported ferromagnetism at the C_{60}/Cu interface due to the charge transfer between C_{60} and Cu.[8] Similarly, charge transfer between S and Au has been reported to cause spin-symmetry breaking,[9] which leads to a spin-polarized state and magnetism at the interface.[10,11]

The magnetism that emerges at the interface can open a new path for the development of magneto-responsive electronic devices without the use of FM materials. The MR of single-molecule junctions with Au/S bonds has been indicated in some studies.[12,13] Various mechanisms have been proposed as follows.

Hayakawa *et al.*[12] found that the resistance increased under a magnetic field, *i.e.*, positive MR. They attributed the positive MR to the confinement of π-orbitals under the magnetic field, because they observed that electronic coupling is reduced under the magnetic field. Mitra *et al.*[13] observed both positive and negative MR. They explained the MR due to the changes in scattering conditions of electrons at the Au/S interface under a magnetic field. The MR can be positive and negative depending on the structure of the Au/S interface, which cannot be precisely controlled. Large positive MR was also reported for a self-assembled monolayer of oligophenylene-thiols.[14] This MR was explained by the coupling of unpaired charge localized in the molecule and the tunnelling electron. Combination of the spin between transport electrons and localized charge would create singlet (S) and triplet (T) states used as the transport channels in the junction. The energy levels of the S and T states are modulated by the magnetic field, resulting in MR.

In this work, we investigated the MR of Au/1,6-hexanedithiol/Au single-molecule junctions (Au/HDT/Au) to clarify the role of the Au/S interface on the MR in single-molecule junctions with Au electrodes. The use of alkyl chains with a thiol anchor on gold could point out the role of Au/S interfaces in the MR effect because the localized electronic state at the Au/S interface dominates the charge transport of the alkyl-thiol and -dithiol molecular junctions.[15,16] Our current investigation revealed that the parabolic positive MR of Au/HDT/Au can be produced without π-orbitals.

We employed the mechanically controllable break-junction (MCBJ) method in this study.[17] The single-molecule junction was reported to be sustained for a long period, *e.g.*, tens of seconds to hours even at room temperature using this technique.[18,19] The mechanism of the MCBJ method is briefly shown in Fig. 1(a). A gold (Au) contact prepared on an elastic substrate is precisely broken by bending the substrate with the pushing rod underneath the substrate. In the presence of a molecule, molecular junctions are formed when the Au contact is broken. The molecular junctions are eventually broken by further opening the electrode gap. The electrode gap can be closed by lowering the pushing rod, and the breaking process can be repeated. The formation of molecular junctions can be

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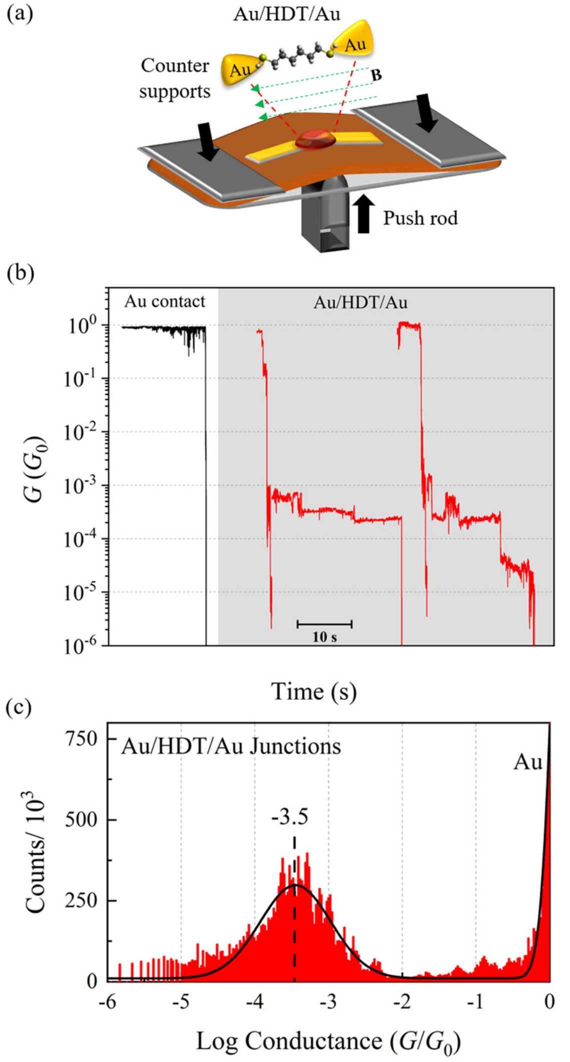

Fig. 1 (a) Scheme of the MCBJ technique and the structure of Au/HDT/Au. (b) Representative G transient curves obtained for the contact of bare and HDT-modified Au. (c) Histogram of G transient curves for HDT-modified Au showing the most probable conductance peak.

detected through the transient curve of electrical conductance (G) during the breaking process. As the Au contact is elongated, G gradually decreases. When the contact becomes an atomic scale, G changes in a stepwise manner in the integer multiples of G_0 where $G_0 = 2e^2/h \sim 7.75 \times 10^{-5}$ S. It is known that a single-atomic contact of Au presents $G = 1\ G_0$. The conductance plateau at $G < 1\ G_0$ is assigned to the single-molecule junction. During the break-junction process, we could observe multiple plateaus representing single-molecule junctions with different morphologies.[20]

In our experiment, the house-built MCBJ machine[5] was used and the single-molecule junctions can be sustained for more than 10 s, which allowed us to measure MR. The targeted molecules were adsorbed on the electrodes by putting a droplet of a 1 mM solution of them in ethanol. After the molecular solution was dried at room temperature in an Ar atmosphere, the substrate was immediately mounted onto the MCBJ setup. The MR measurements were carried out when the G value was stable for 1 s after the motion of the pushing rod. After one sweep of MR is completed, the pushing rod was raised and held for 1 s to check the stability again. This measurement sequence was repeated until the junction was broken. The magnetic field was applied at room temperature in parallel to the current flow direction. The change in the electrical resistance (R) was evaluated using the MR ratio defined as the following MR(%) = $(R_B - R_0)/R_0 \times 100$ where the R_0 (R_B) variable is the resistance without (with) the external magnetic field.

Fig. 1(b) shows G transient curves for Au electrodes without molecules (*i.e.*, bare Au contact) and modified with HDT molecules at bias voltage, V_b = 30 mV. The formation of Au atomic contact can be observed at 1 G_0. In the presence of the HDT molecules, plateaus appear below 1 G_0, indicating the formation of single-molecule junctions. For HDT molecules, the plateaus are observed in the range of 10^{-4} G_0. Fig. 1(c) shows the G histograms constructed from 126 G transient curves for Au electrodes modified with HDT molecules. We found the G peak at log (G/G_0) = −3.5, *i.e.*, 3.6×10^{-4} G_0 for the Au/HDT/Au by fitting the Gaussian function. This is close to the values assigned for the atop-atop configuration.[21,22] We should note that the single-molecule junction other than the most probable single-molecule junction configuration could be formed during the BJ experiment.[23]

Fig. 2(a) shows a typical G transient curve with two examples of MR responses (inset) obtained at the position indicated by the arrow for Au/HDT/Au. In this transient, we could perform 55 MR measurements, among which 7 measurements revealed the response in the magnetic field. This indicates that the MR response appears only in the specific structures of single-molecule junctions. We estimated the MR ratio by fitting the MR curves with the parabolic function as shown in the black line overlapping with the MR responses. Fig. 2(b) shows the MR ratios of all MR curves taken in the G range between 1 G_0 and 10^{-5} G_0 as a function of G. All the MR curves show a positive effect. For all observed MR curves, we averaged every MR ratio of Au/HDT/Au in Fig. 2(b) to be around 5.5%.

Fig. 3 shows R against the external magnetic field (a) parallel and (b) perpendicular to the current flow direction for the Au/HDT/Au. The resistance increased in both curves under the magnetic field (positive MR). We should note that the different baseline of resistance value between MR curves is due to the different contact geometry of the single-molecule junction.[22,23] The ratios observed for parallel and perpendicular orientations were almost 8%, respectively. This suggested no significant anisotropy in the MR behavior of Au/HDT/Au.

The spin scattering model proposed by Mitra *et al.*[13] would not be appropriate because only positive MR is observed for a variety of structures in the study. Our results could be explained by modifying the mechanism related to the formation of S and T transport channels proposed by Xie *et al.*[14] They suggested that an unpaired charge is localized in the aromatic molecule at the S side and the coupling between the localized charge and transported charge produces S and T transport channels. As the alkane-chain is used in our study, we can assume that the

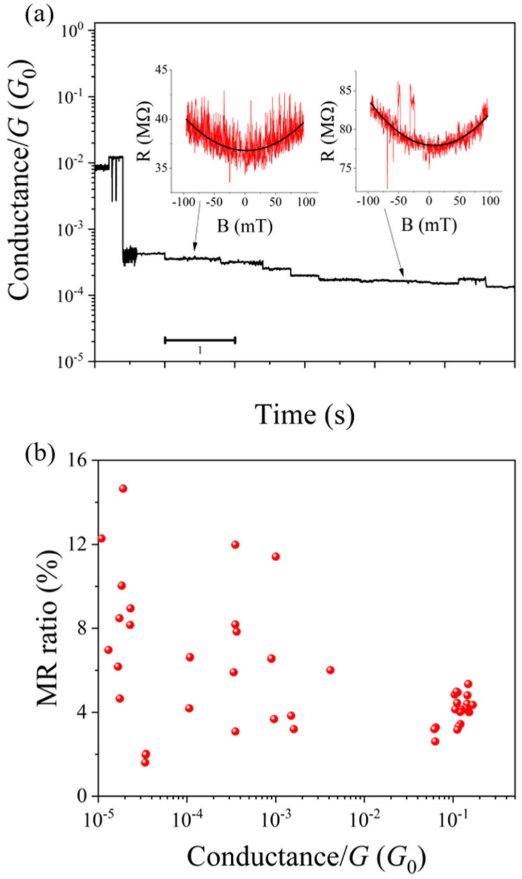

Fig. 2 (a) A G transient curve of Au/HDT/Au and the MR curves with the parabolic fit (inset). (b) The plot of MR ratio as a function of G for Au/HDT/Au.

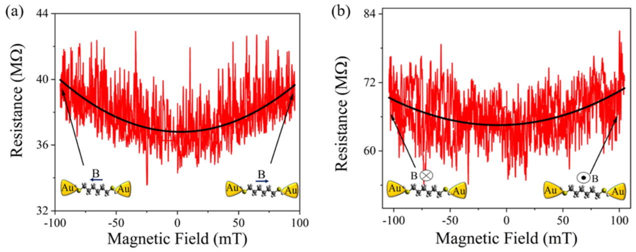

Fig. 3 The observed MR effect of the Au/HDT/Au junction in (a) parallel and (b) perpendicular magnetic field orientation with respect to the current direction.

unpaired charge is localized not in the molecule, but in the 5*d*-orbital[25,26] of an Au atom or in a radical S atom.[24] As a result of the coupling between localized charge at the Au/S interface and transported electrons, S and T transport channels can be formed. The changes in the energy levels of the S and T transport channels under the magnetic field could produce the MR. The MR ratio observed in our study is much smaller than that reported by Xie *et al.*, which is up to 30%. The smaller MR in our study would be due to the weak contribution of the Au/S energy state on the charge transport.

In summary, we studied a magneto transport through the single-molecule junctions of the Au/HDT/Au at room temperature by using MCBJ measurement. The junctions exhibited positive MR with average ratios of 5.5%. The MR behaviour does not show anisotropy, and it was well-fitted by the parabolic function. The MR could be associated with the unpaired charge injection at the Au/S interface.

RA: conceptualization, conducting a research and investigation process, specifically performing the experiments, or data/evidence collection, writing original draft, writing – review & editing; RY: conceptualization, formal analysis, writing – review & editing; HT: conceptualization, writing – review & editing, supervision.

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Conflicts of interest

There are no conflicts to declare.

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