Enhanced magnetoresistance due to charging effects in a molecular nanocomposite spin device

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We have investigated a Coulomb-blockade effect and a higher order cotunneling effect in rubrene-Co nanocomposite spin devices, where the Co nanoparticles were uniformly embedded into the rubrene matrix and a large magnetoresistance (MR) effect appeared. A clear Coulomb gap was observed between ± 1.1 V at low temperature. Within the gap, the enhancement of the MR ratio was observed up to $\sim 50\%$, which has not been explained by previous theoretical studies. The enhancement is induced by higher-order cotunneling. Power-law dependence of an electric current for a bias voltage ($I \sim V^{2N-1}$; N is an order of cotunneling) was observed in the Coulomb gap, which corroborates that at maximum fifth-order cotunneling is attributed to the enhancement of the MR ratio.

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I. INTRODUCTION

The observation of a magnetoresistance (MR) effect in molecular nanocomposites[1–7] and inorganic granular spin devices[8–13] provides a good platform for discussing the interesting physics behind spin-dependent tunneling, single-charge (spin) transport, and induced large MR effect. The MR ratio in some of such systems is abnormally high, exceeding the theoretically predicted value of $\sim 12\%$ [calculated by using a modified Julliere formula[14] and by assuming that the spin polarization of Co is 34% (Ref. 15)]. The physics underlying this phenomenon has yet to be conclusively determined, although cotunneling and the Coulomb-blockade (CB) effect are conjectured to play important roles.[5,7–13,16] The CB effect has been reported to enhance the MR ratio and to cause it to oscillate when a bias voltage is applied as a result of spin accumulation in the ferromagnetic particles.[11,12] The cotunneling-induced enhancement of the MR effect in a Coulomb gap is a physical phenomenon whereby electrons transfer through several tunnel junctions simultaneously. Takahashi and Maekawa[16] calculated the tunnel resistance in a double-barrier magnetic tunnel junction with a ferromagnetic island. They predicted a large enhancement of the MR effect due to a second-order effect of cotunneling, where two electrons transport through two junctions simultaneously (hereafter, referred to as the *T-M* model). In the model, the electric current in a double junction is given by the sum of forward and backward tunneling rates of electrons (spins), which is inversely proportional to the square of the tunnel resistance. At higher temperature, the resistance of the double junction can be written as to be proportional to the sum of each tunnel resistance, which describes an electric behavior of thermally assisted sequential tunneling, whereas the resistance at lower temperature is proportional to the product of each tunnel resistance in the Coulomb-blockade regime (inelastic second-order cotunneling). Hence, an MR ratio under conventional sequential tunneling is described as $(R_A/R_F)-1$, where R_A is a tunnel resistance in antiferromagnetic alignment and R_F is a tunnel resistance in ferromagnetic alignment. However, an MR ratio in the second-order cotunneling is described as $(R_A/R_F)^2-1$. For instance, if one uses ferromagnetic electrodes of which spin polarization is 40%, the MR ratio under the sequential tunneling and the second-order cotunneling is calculated to be 38% and 91%, respectively. We can directly expand this model to a case of higher-order cotunneling, where the MR ratio is written as $(R_A/R_F)^N-1$ (N is order of cotunneling). A single ferromagnetic dot system, with two tunnel junctions has been, so far, experimentally investigated in order to obtain a better understanding of the second-order cotunneling effect.[13] However, the observed effect was at most a second-order cotunneling process and the MR ratio was approximately one-third of that ($\sim 78\%$) in rubrene ($C_{42}H_{28}$)-Co nanocomposites.[5] Thus, the origins of the large MR ratio remain unclear. Gaining better understanding of this phenomenon will enhance our understanding of the physics of spin transport, and it will pave the way for further advances in both molecular spintronics and metallic spintronics using ferromagnetic nanoparticles.

We have reported a large MR ratio in rubrene-Co nanocomposite spin devices[5] and have tried to determine the detailed mechanism for the MR enhancement by using the ^{59}Co spin-echo technique in nuclear magnetic resonance.[17] In this study, we narrowed the gap length between the electrodes in the rubrene-Co nanocomposite, thereby increasing the effective electric field between the junction of the Co nanoparticles and producing a CB. By doing this, we discovered an extraordinary enhancement in the MR ratio. This enhancement was ascribed to a higher-order (at most, fifth order) cotunneling effect. In this study, we discuss the origins of this extraordinary enhancement of the MR ratio.

II. EXPERIMENTAL

The rubrene-Co nanocomposite system was fabricated by the following process. First, we patterned the electrode area by using electron-beam lithography and a lift-off technique and deposited 50-nm-thick Cr/Au electrodes on Si/SiO_2 sub-

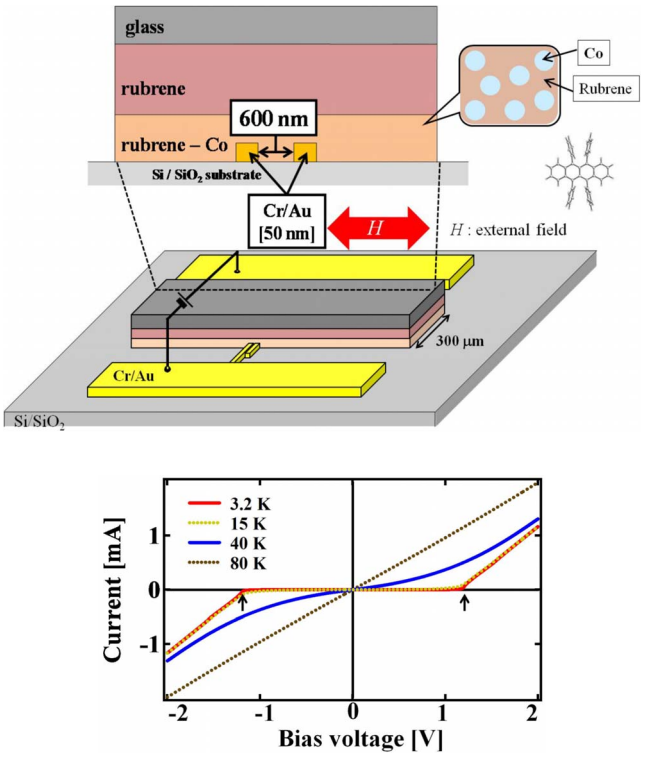

FIG. 1. (Color online) Schematic illustration of a sample and a plot of the temperature dependence of current-bias voltage curve. (a) A schematic structure and a cross-sectional view of a rubrene-Co nanocomposite with a 600 nm gap length. (b) The temperature dependence of current (I)-bias voltage (V) characteristics of the rubrene-Co nanocomposite. A clear CB (indicated by arrows) can be seen at ± 1.1 V.

strates with a gap length of 600 nm between the electrodes. A 130-nm-thick rubrene-Co film with a 300 μm$\times$600 nm channel area was deposited by coevaporation under high vacuum ($\sim 10^{-5}$ Pa). The rubrene-Co films had composition ratios of 3:1 and 4:1 for rubrene:Co in volume. The purity of Co was 99.99%, and rubrene was prepared in powder form (Sigma-Aldrich). Rubrene and glass layers were then deposited as capping layers to prevent the rubrene-Co film from being oxidized. All the measurements were performed using a cryostat with superconductor solenoids (Oxford MAGLAB SYSTEM 2000) and a source meter (Keithley, 236). An external magnetic field (H) was applied parallel to the current direction.

III. RESULTS AND DISCUSSION

Figure 1(a) depicts the schematic structure of the rubrene-Co nanocomposite, which has a composition ratio of 3:1 for rubrene:Co in volume and a cross-sectional view of the device. The nanocomposite consists of Co nanoparticles dispersed in the rubrene matrix. We have previously reported[5] that the diameter of Co nanoparticles ranged from 0.8 to 2.3 nm, which was estimated by an M-H curve obtained by the superconducting quantum interference device (SQUID) and a theoretical fitting using two Langevin functions to the magnetization curve at 290 K, and have also reported that the averaged distance between two Co nanoparticles was also estimated to be $0.5 \sim 2.0$ nm and no percolation path was formed. The spin-transport properties of such nanocomposites are understood in terms of spin-dependent tunneling. Specifically, molecular matrices function as tunneling barriers.[1–7] Figure 1(b) shows the temperature dependence of current (I)-bias voltage (V) characteristics of the rubrene-Co nanocomposite. Clear kinks in the I-V curve are visible at ± 1.1 V at a temperature of 3.2 K. Judging from the temperature dependence of the I-V curves, these kinks were not caused by a breakdown of the rubrene matrix but rather by the CB effect. Spin transport to an adjacent Co nanoparticle is suppressed when the charging energy (E_c) of a Co nanoparticle exceeded the thermal energy (k_BT) or the bias energy (eV). Spin transport occurred when either the bias voltage or the temperature is increased ($E_c < eV$ or k_BT). The CB effect diminished at higher-bias voltages ($|V| > 1.1$ V), and spin transport was governed by sequential tunneling between the Co nanoparticles. The CB effect becomes weaker at 15 K relative to that at 3.2 K due to the higher thermal energy. When the thermal energy was much larger than the charging energy ($k_BT \gg E_c$), the CB effect was not observed and spin transport occurred by sequential tunneling at 80 K. The temperature dependence of the I-V characteristics was reproducible over the entire temperature range in all devices we fabricated.

Figures 2(a)–2(c) show the correspondence between the bias-voltage dependence of the MR ratio and the current at 80, 15, and 3.2 K, respectively. At 80 K, the I-V curve is linear due to sequential tunneling and no CB effect is observed. At this temperature, the MR ratio is low ($< \sim 1\%$) and it decreases monotonously as the bias voltage is increased. This indicates that no enhancement of the MR ratio occurs at 80 K. The observed I-V curve at 15 K exhibits a clear CB effect and the (MR ratio)-V curve shows a drastic enhancement in the MR at around ± 1.1 V, whereas the MR ratio remains constant between -1.1 and $+1.1$ V. The obtained (MR ratio)-V curve agrees well with that predicted by the T-M model, which in theory can be applied to a ferromagnetic double junction.[16] In terms of the T-M model, our finding can most likely be attributed to a second-order cotunneling that lies in the range ± 1.1 V. When the temperature is lowered to 3.2 K, the rubrene-Co nanocomposite exhibits a two-step increase in the MR ratio at ± 1.1 V and between -1.1 and $+1.1$ V. The additional enhancement in the MR ratio between -1.1 and $+1.1$ V with decreasing bias voltage is not predicted by the T-M model, and we conjecture that it is due to higher-order cotunneling. Figure 2(d) shows a log-log plot of the I-V characteristics in the rubrene-Co nanocomposite at different temperatures; it allows us to elucidate the spin-transport mechanism in the Coulomb gap. The current in the Coulomb gap exhibits a power-law dependence on the bias voltage ($I \sim V^{2N-1}$, where N is the number of junctions, i.e., $N=2$ in a second-order tunneling), which implies that the carrier (=spin) transport properties can be attributed to cotunneling, as in the case of the carrier transport in Au nanoparticles.[18] From the theoretical fitting ($I \sim V^{2N-1}$), the cotunneling order (N) can be estimated at each temperature. N is estimated to be about 2.1 at 15 K from the power-law dependence, which provides conclusive evidence that

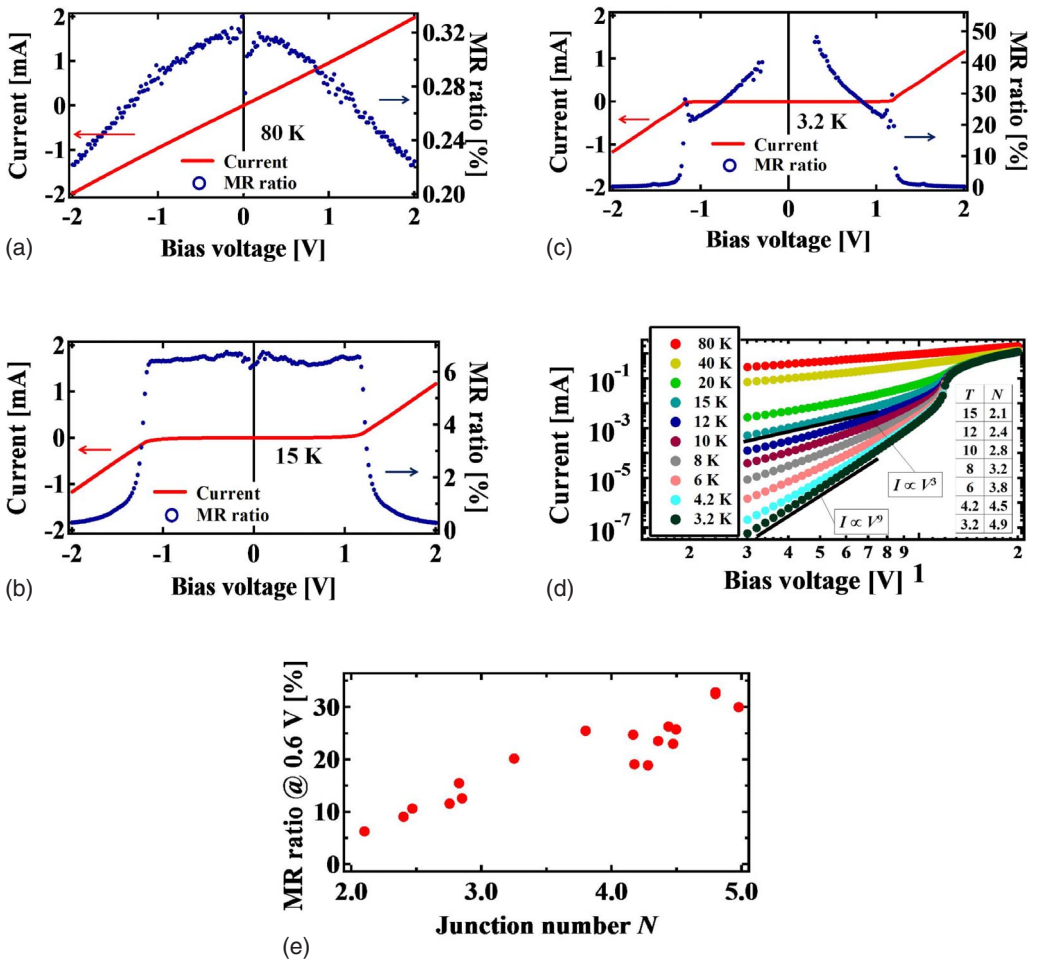

FIG. 2. (Color online) Spin-transport properties of the rubrene-Co nanocomposites. The bias voltage dependence of the MR ratio (blue circles) and the electric current without an external magnetic field (red lines) at (a) 80, (b) 15, and (c) 3.2 K. The MR ratio is defined as $\frac{I(B=3T)-I(B=0T)}{I(B=0T)}$, and it is calculated from the *I-V* curves at 0 and 3 T. (d) Log-log plots of the *I-V* characteristics of rubrene-Co nanocomposite at different temperatures. The *I-V* characteristic in the Coulomb gap is $I \propto V^9$ at 3.2 K and $I \propto V^3$ at 15 K, and the power of the bias voltage decreases monotonously as the temperature increased. The black lines ($I \propto V^9$ and $I \propto V^3$) are guides for the eyes. The inset is the number of junctions (N) which contributes to cotunneling at different temperatures. It decreases as temperature increases. (e) The dependence of the MR ratio on the number of junctions at $V=0.6$ V in the low-temperature region. The monotonous increase in the MR ratio with the number of junctions implies that cotunneling governs the MR enhancement.

second-order cotunneling occurs within the Coulomb gap and is consistent with the *T-M* model. The number of junctions increases as the temperature is reduced, suggesting that cotunneling becomes more effective at low temperature and that the cotunneling order increases. At 3.2 K, N is estimated to be 4.9, implying that fifth-order cotunneling occurs. As temperature decreases, Co nanoparticles with larger diameter can contribute to spin conduction because of the decrease in thermal energy in the system, yielding an increase in the order of cotunneling. As discussed above, the resistance of the system under occurrence of the higher-order cotunneling is proportional to N^{th} square of the tunnel resistance, which means the total electric current is strongly suppressed. It does not seem realistic that the cotunneling occurred in a whole area of the device because the average number of junctions in 600 nm gap was estimated to be 200–300 from the mean diameter and the mean distance of the Co nanoparticles. The Coulomb energy per one nanoparticle was estimated to be 4–6 meV from the *I-V* characteristics if we assume that all junctions contributed to the cotunneling. However, cotunneling is governed by electronic structures of nanoparticles with large Coulomb energies (=smaller diameter). The diameter of the smallest Co nanoparticle in this study is 0.8 nm (Ref. 5) and its charging energy is estimated to be ~60 meV based on a model by Sheng and co-workers,[19] which is about 1 order of magnitude larger than that calculated in the model in which all junctions contributed to the cotunneling. Hence, it is thought that observed higher-order cotunneling is induced by bottleneck structures where the small nanoparticles are located in between large nanoparticles.

Figure 2(e) shows dependence of the MR ratio on the junction number (N) at $V=0.6$ V (i.e., within the Coulomb gap) in all devices having the same composition ratio in the temperature range 3.2–15 K. As N decreases, the MR ratio also decreases to ~6%. This is sufficient evidence that the MR ratio depends strongly on the number of junctions (N) in cotunneling. Therefore, the additional enhancement in the MR ratio that occurs within ±1.1 V is ascribed to the

higher-order cotunneling in the Coulomb gap; this effect is not considered in conventional theoretical models.

We now discuss the origin of the enhancement at ± 1.1 V. It is well known that the interaction between spin transport and the CB effect enhances the MR ratio.[20] No MR enhancement is observed at around ± 1.1 V at 80 K [see Fig. 2(a)] since no CB effect is seen in the *I-V* curve. When the temperature is reduced to 15 K [see Fig. 2(b)], a clear threshold at ± 1.1 V due to the CB effect is observed in the *I-V* curve, and the MR is enhanced by up to ~6%. Furthermore, as we cooled the samples to 3.2 K, the MR enhancement became stronger by up to ~30% at around ± 1.1 V [see Fig. 2(c)]. A similar phenomenon was observed in Co-Al-O granular films in which the tunnel MR ratio also increased in the vicinity of thresholds in the *I-V* characteristics.[11] In this present study, MR enhancement was observed with sharp peaks at around ± 1.1 V and oscillation of the MR ratio above the Coulomb energy (± 1.54 V) was observed. The above-mentioned features in the temperature dependence of the MR enhancement are in good agreement with the MR oscillations caused by charging effects predicted by Barns and Fert[21] and those experimentally observed in Co-Al-O granular samples.[12] It is noted that the MR ratio goes to almost zero at higher-bias voltage ($|V| > 1.1$ V) where we have observed ~0.5%-resistance (R) change in an *R-H* curve. Under the higher-bias voltage application, only sequential tunneling occurs in the system and the higher-order cotunneling mechanism does not work. As it is widely known, the bias-voltage dependence of MR ratio is ascribed to magnon excitation which induces decreased spin polarization of conducting spins. It has been reported that the bias-voltage dependence of the MR ratio in molecular spin devices is not good enough and the MR ratio becomes a half of the maximum at ~100 mV in rubrene-based spin devices.[22] Hence, it can be understood that the decrease in the MR ratio at the higher-bias voltage is attributed to the decrease in spin polarization induced by the magnon excitation.

The electrical and magnetic properties of a rubrene-Co nanocomposite with a composition ratio of rubrene to Co of 4:1 in volume were also investigated in order to clarify the effect of grain size and the charging energy of the Co. In this case, changing the composition ratio modifies the diameter of the Co nanoparticles and the interparticle distance.[7] The diameters of the Co nanoparticles become smaller and the charging energy of the Co nanoparticles increases with a decrease in the composition ratio. Thus, the *I-V* characteristics and the (MR ratio)-*V* characteristics are expected to be modified. Figure 3 shows these *I-V* characteristics and the (MR ratio)-*V* characteristics within ± 2.0 V at 3.2 K. It shows that the *I-V* curve is strongly suppressed due to the CB effect. No threshold voltages are observed in the inset, which shows a log-log plot of the *I-V* curve within ± 2.0 V. The bias voltage has a power-law dependence in this range, and a characteristic (MR ratio)-*V* curve with two-step enhancement [similar to that shown in Fig. 2(c)] was not observed. This is implied by the fact that the total charging energy of the Co nanoparticles increases when the Co nanoparticles become smaller, resulting to the threshold voltage increasing to more than 2 V. [The breakdown of the Coulomb gap was observed at 3 V (not shown here)]. Therefore, it is thought that only cotunneling-assisted enhancement of MR is observed within ± 2 V. This result also confirms the fact that the spin-transport properties are governed by the charging effect of the Co nanoparticles and that cotunneling caused by the CB effect is the dominant source of the strong MR effect in rubrene-Co nanocomposites in the Coulomb gap.

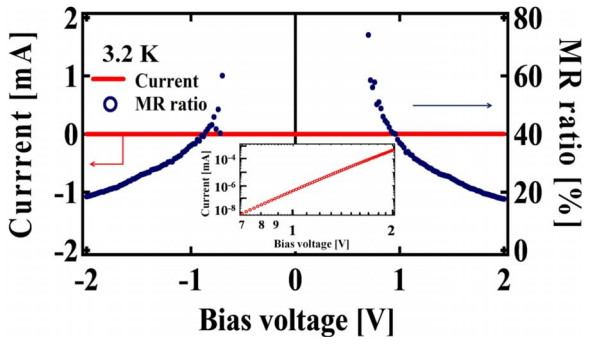

FIG. 3. (Color online) Spin transport property of rubrene-Co (4:1) nanocomposite. The bias voltage dependence of the MR ratio (blue circles) and the electric current in the absence of an external magnetic field (a red line) at 3.2 K in a rubrene-Co nanocomposite with a composition ratio of 4:1 for rubrene:Co. The vertical axis scale is the same as those in Figs. 2(a)–2(c). The current from −2 to 2 V appears to be almost zero, implying that CB is dominant in this bias voltage region. The inset is a log-log plot of the (electric current)-(bias voltage) characteristic and it shows that the current depends on the power of the bias voltage. Cotunneling is dominant for the MR enhancement between −2 and 2 V. Enhancement due to CB is not observed in this bias region.

IV. SUMMARY

In summary, we have found an extraordinary two-step enhancement in the MR ratio in rubrene-Co nanocomposite spin devices. The enhancement observed in molecular nanocomposite systems at the Coulomb staircase is ascribed to CB, whereas the enhancement within the Coulomb gap is attributed to higher-order cotunneling effects. Higher-order effects ($N=5$) to the enhancement have not been reported in either experimental or theoretical studies. The cotunneling order increased up to ~5 at 3.2 K. In addition, in the enhancement of spin polarization,[17] a cotunneling effect was found to be the dominant source of the extraordinarily large MR ratio in molecular nanocomposite spin devices.

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