

Room-temperature spin-dependent tunneling through molecules

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We have fabricated assemblies of molecular junctions comprised of superparamagnetic Fe₃O₄ nanoparticles self-assembled with alkane molecules of different lengths as the spacer. The electrical resistance increases exponentially over nearly two decades as the molecular length varies from 0.7 to 2.5 nm, indicating that electrons tunnel through the molecules that are chemically bonded with Fe₃O₄ nanoparticles. Up to ~21% room-temperature magnetoresistance is observed. Remarkably, the tunneling magnetoresistance ratio stays nearly independent of molecular length, which entails room-temperature spin-conserving transport in organic molecules. © 2011 American Institute of Physics. [doi:10.1063/1.3583585]

Spin-dependent transport has been recently studied in a variety of carbon-based materials ranging from amorphous organic semiconductors [e.g., tris(8-hydroxyquinolino)-aluminum (Alq₃) (Refs. 1–3) and rubrene⁴], polymers,⁵ single molecules,⁶ self-assembled monolayers,⁷ to carbon nanotubes⁸ and graphene.⁹ Weak spin-flip scattering, a fundamental attribute shared by all carbon-based materials, give rise to the unique properties needed for potential spintronic applications.¹⁰ To demonstrate spin-polarized electron transport electrically, spin valve, a simple but powerful device, has often been employed. Theoretical investigations have been carried out in molecular junction spin valve devices.^{11,12} For examples, spin-polarized carriers can either tunnel or diffuse along molecular chains, depending on the properties of the molecules. The electronic states of the molecules can be relatively localized or extended as studied in the cases of octane and tricene.¹² The magnetoresistance (MR) in the latter was predicted to be as high as 600%. To date, no sizable MR using molecules as a spin transport medium has yet been demonstrated at room temperature.

Although single molecular junction spin valve is desired, there are many practical challenges to fabricate such devices. Here we have taken a different approach. Similar to granular giant magnetoresistive systems¹³ in which the electrical resistivity undergoes a large change as an external magnetic field is applied to align the magnetic moments of the nanoparticles, here nanoparticles/molecule assemblies we have fabricated contain ferrimagnetic Fe₃O₄ oxide nanoparticles that are wrapped around by alkane molecules. The alkane molecules that are chemically bonded to Fe₃O₄ nanoparticles prevent the nanoparticles from directly contacting with each other. The electrical resistivity exhibits exponential dependence on molecular length, indicating that electrons tunnel through the alkane molecules, not the particle-particle direct contacts. In these materials, we have observed a very large room-temperature MR effect, ~21% at 9 T, the highest in all reported MR value using organic as spacer. More interestingly, as the molecular length d increases from 0.7 to 2.5 nm,

this MR ratio does not decrease at all, although the resistivity varies by about two orders of magnitude.

The fabrication process of the molecule coated nanoparticles has been described in detail elsewhere.¹⁴ We fix the Fe₃O₄ particle size at ~9 nm and vary the molecular length in different samples. We also prepared one reference sample with a significantly larger particle size ~550 nm by a chemical solvothermal reduction method.¹⁵ After the alkane molecules coated Fe₃O₄ nanoparticles were synthesized, they were collected, extensively washed with ethanol to remove physically absorbed molecules, and then dried in a vacuum. The dried nanoparticles naturally coalesced into millimeter-sized blocks by the van der Waals force, which were sliced into ~7 × 7 × 1 mm³ pieces for transport measurements. For comparison, bare Fe₃O₄ nanoparticles need to be cold-pressed with a high-pressure into pellets of similar dimensions for transport measurements. The top and bottom surfaces were coated with silver paint as electrical contacts.

In our experiments, four carboxylic acids of different lengths, butanoic acid [CH₃(CH₂)₂COOH, denoted as C4], octanoic acid [CH₃(CH₂)₆COOH, denoted as C8], dodecanoic acid [CH₃(CH₂)₁₀COOH, denoted as C12], and octadecanoic acid [CH₃(CH₂)₁₆COOH, denoted as C18], are chosen and the samples are labeled according to the molecular length such as C_n, n being the number of carbon bonds in the molecules. The Fe₃O₄ nanoparticles are superparamagnetic at room temperature. The Langevin fitting of the magnetization and x-ray diffraction gives the average size of ~9 nm.¹⁴ The Fe₃O₄ nanoparticles are coated with a monolayer of molecules, as schematically illustrated in Fig. 1(a). It is important to note that electrons only choose the tunneling paths with the minimum particle-to-particle separation, which is the length of the molecules. Fourier transform infrared spectroscopy (FTIR) spectra in Fig. 1(b) confirm that the molecules are chemically absorbed on Fe₃O₄ nanoparticles. Similar to the FTIR spectra for oleic acid coated Fe₃O₄ nanoparticles,¹⁴ the missing characteristic C=O (~1708 cm⁻¹), C—O(~1463 cm⁻¹), and O—H(~1285 cm⁻¹) peaks associated with the carboxylic head group —COOH in Fe₃O₄ nanoparticle/C18 assembly are strong evidence that C18 molecules are not physically absorbed to but chemically bonded to Fe₃O₄ nanoparticles.

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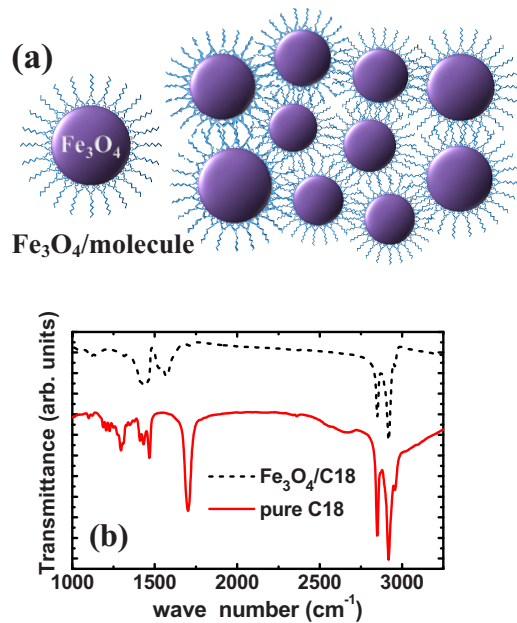


FIG. 1. (Color online) (a) Schematic diagram of the molecule coated Fe_3O_4 nanoparticle assembly. (b) FTIR spectra of C18 molecules coated Fe_3O_4 nanoparticles and pure C18 molecules.

The same evidence is also found in assemblies with three other molecules.

Figure 2(a) contains the electrical resistivity data from three kinds of samples: Fe_3O_4 nanoparticle/molecule assembly slices, a cold-pressed bare Fe_3O_4 nanoparticle sample,

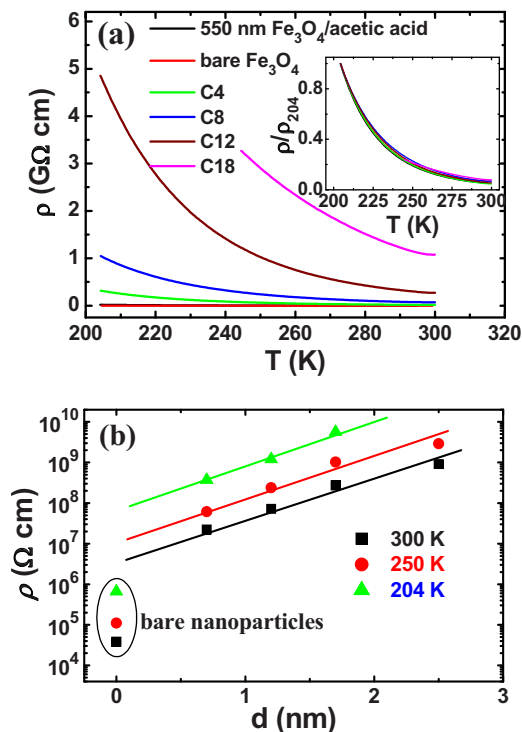


FIG. 2. (Color online) (a) Resistivity ρ as a function of temperature for 550 nm Fe_3O_4 nanoparticles coated with acetic acid, bare 9 nm Fe_3O_4 nanoparticles, and 9 nm Fe_3O_4 nanoparticles coated with C4, C8, C12, and C18 molecules, respectively. The inset is the resistivity data are normalized at 204 K. (b) Semilog plot of ρ vs molecular length d at 204 K, 250 K, and 300 K, respectively. The solid lines are guides to the eyes. The three data points of the resistivity of bare Fe_3O_4 nanoparticles are displayed at $d=0$ for comparison.

and a reference sample of 550 nm Fe_3O_4 nanoparticles coated with acetic acid molecules. As the temperature is lowered, all samples show a steep rise in resistivity, which is better seen in the inset of Fig. 2(a). It is evident that the resistivity of all samples follows nearly the same temperature dependence. Since this common temperature dependence is independent of molecular length or the nature of the particle-to-particle contacts, it must originate from Fe_3O_4 , the common constituent material in all samples. Several earlier studies on bare Fe_3O_4 nanoparticle composites found that the resistivity could be described by the thermally assisted inter-particle hopping over a variable charging energy barrier, i.e., $\rho \sim \exp[(T_0/T)^{1/2}]$, where T_0 is a constant and T is the temperature.¹⁶ Although $\exp[(T_0/T)^{1/2}]$ seemingly fits our data of C4 sample and other samples which yields approximately the same $T_0 \sim 5.7 \times 10^4$ K [inset of Fig. 2(a)], we believe that this model is not applicable here. In this model, T_0 is related to the charging energy of nanoparticles;¹⁶ therefore, large particle samples would have a much smaller charging energy and a much lower T_0 . We note that the resistivity of Fe_3O_4 crystals or thin films has a negative temperature coefficient. This was explained by the decreasing density-of-states (DOS) at the Fermi level (E_F) as the temperature is lowered, which was observed in photoemission spectroscopy.¹⁷ Moreover, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{NiFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$ magnetic tunnel junction devices also show a rapid low-temperature rise in tunneling resistivity or a strongly decreasing tunneling probability,¹⁸ which indicates a decreasing DOS in Fe_3O_4 at low temperatures. Here the DOS of Fe_3O_4 may also be responsible for the common temperature dependence observed in our samples.

To scale the resistivity for samples with different molecular lengths in Fig. 2(a), we divide the resistivity by ρ_{204} , the resistivity measured or extrapolated at 204 K. We found that the scaling factors vary exponentially with d at 204, 250, and 300 K, as shown in Fig. 2(b). Therefore, the molecular length dependence can be described by $\rho \sim e^{\beta d}$, which are represented by the straight lines in the semi-log plot of ρ versus d in the figure. The slope of the straight line, β , is found to be 0.2 \AA^{-1} . Compared with the previously reported data on Au nanoparticles coated with alkanethiolate or Au-alkanethiolate-Au molecular junctions ($\beta \sim 0.7\text{--}1.0 \text{ \AA}^{-1}$),¹⁹ the relatively lower value of β here may be attributed to a much stronger strength in $\text{Fe}_3\text{O}_4\text{--COO}^-$ bonds than that in Au-S bonds, for β is sensitive to the metal-molecule contact.²⁰ A similar magnitude of β has also been reported recently in Pd(II) alkanethiolate molecules²¹ and Alq_3 .³ The vertical-axis intercept in the plot represents the contact resistance in nanoparticles/molecule assemblies. The contact resistance is more than one order greater than that of the cold-pressed bare Fe_3O_4 nanoparticle sample, which is also dominated by the inter-particle contact resistance. The contact resistance difference in these two kinds of samples reflects different nature of the particle-to-particle interfaces, which is a subject of ongoing investigations. The slope of the straight lines for different temperatures is nearly the same, indicating that the β value is not sensitive to temperature.

All Fe_3O_4 nanoparticles/molecule assemblies exhibit large negative MR, defined as $\Delta\rho/\rho(0)=[\rho(H)-\rho(0)]/\rho(0)$, where $\rho(0)$ and $\rho(H)$ are the resistivity in zero- and applied fields, H , respectively, as shown in Fig. 3. Although the absolute change in resistivity, $\Delta\rho=\rho(H)-\rho(0)$, varies dramati-

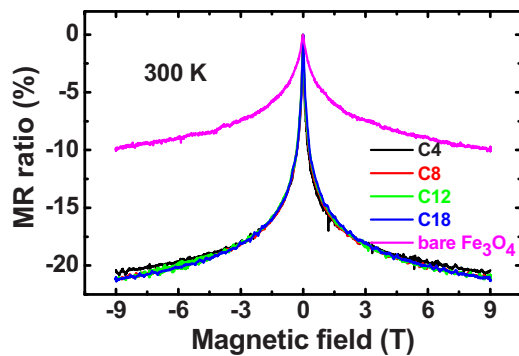


FIG. 3. (Color online) MR measured at 300 K for bare 9 nm Fe_3O_4 nanoparticles and 9 nm Fe_3O_4 nanoparticles coated with C4, C8, C12, and C18 molecules, respectively.

cally from sample to sample, quite strikingly, if normalized by the zero field resistivity of each sample, the MR ratio $\Delta\rho/\rho(0)$ is approximately the same for all four nanoparticles/molecule samples. This means that the spin-dependent tunneling does not depend on the length of the molecules. Figure 3 shows the MR data measured at 300 K, which reaches the maximum value of 21% at a 9 T magnetic field, the highest MR value ever reported in molecular spin valves. As the temperature is decreased from 300 to 150 K, the MR ratio magnitude steadily increases from $\sim 21\%$ to $\sim 33\%$, as shown in Fig. 4. Meanwhile, the MR ratio remains invariant as the molecular length varies at low temperatures.

Accompanying these MR curves, there is one for cold-pressed bare Fe_3O_4 nanoparticle sample. Similar smaller MR effect ($<10\%$) in cold-pressed Fe_3O_4 powder (ranging from nanometers to microns in diameter) composites was previously reported by several researchers.^{22,23} This MR effect, termed as “powder MR” or PMR, bears some resemblances with the smaller MR effect in the bare Fe_3O_4 nanoparticles sample here; however, it is clearly of completely different origin. The MR effect in our samples is a tunneling MR effect that occurs when electrons tunnel through molecular barriers as evidenced in the exponential molecular length dependence. Moreover, if the much larger resistivity in Fe_3O_4 nanoparticles/molecule assemblies were due to the percolation paths of tunneling through direct nanoparticle contacts rather than tunneling through molecular barriers, we would have observed the same small MR ratio as that in bare Fe_3O_4 nanoparticle sample or other PMR samples. It should also be emphasized that it is the same tunneling that gives rise to

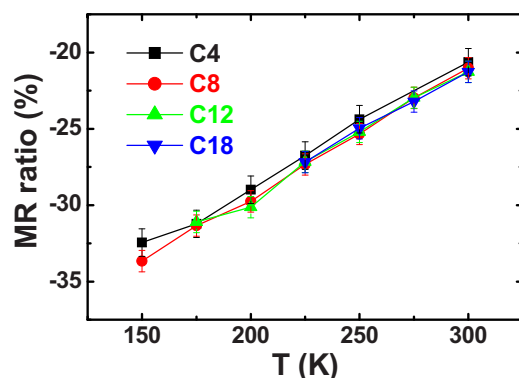


FIG. 4. (Color online) MR ratio for Fe_3O_4 nanoparticles coated with C4, C8, C12, and C18 molecules at different temperature.

both the exponential d -dependence of the resistance and molecular length independence of the MR. Then the only logical conclusion we can draw is that the spin-flip length is much greater than 2.5 nm, the length of C18, which implies that organic molecular channel is a very efficient spin transfer conduit.

In summary, up to 21% room-temperature MR has been demonstrated in self-assembled Fe_3O_4 /alkane molecule assemblies. We find that the MR is independent of alkane molecular length, which is caused by the weak spin-orbit and weak hyperfine interactions for σ -electrons. Alkane molecules can serve as a building block for efficiently transmitting spin quantum information.

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