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# Effects of ferromagnet–molecule chemical bonding on spin injection in an $Fe_3O_4$–molecule granular system

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# Effects of ferromagnet–molecule chemical bonding on spin injection in an Fe₃O₄–molecule granular system

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## Abstract

Spin injection at the interface of $Fe_3O_4$/stearic acid molecule is investigated in a comparative study of $Fe_3O_4$ nanoparticles chemically bonded with molecules (ChemNPs) and $Fe_3O_4$ nanoparticles with physically absorbed molecules (PhyNPs). The resistance of PhyNPs is two orders of magnitude larger than that of ChemNPs, indicating that the resistance of PhyNPs is dominated by the energy barrier at the $Fe_3O_4$–molecule interface. A magnetoresistance of $-12\%$ under a field of 5.8 kOe at room temperature is observed in ChemNPs, in sharp contrast to the zero magnetoresistance in PhyNPs, reflecting that the chemical bonding is crucial for spin injection. We attribute this result to the induced magnetic moment in molecules by proximity effect, which is likely the origin of the spin-dependent tunnelling through molecules. In addition, the estimated relatively large spin polarization of ChemNPs suggests electronic hybridization at the interface and improved oxygen stoichiometry of the $Fe_3O_4$ surface.

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Molecular spintronics is an emerging highly interdisciplinary area that combines the features of spintronics and molecular electronics, due to the possibility of achieving molecular scale spintronics devices and expected long spin coherent length in molecules [1, 2]. The demonstrations of photo-generated spin efficient transport through molecule-linked semiconductor quantum dots [3], spin-polarized carrier transport through a self-assembled-monolayer (SAM) molecular barrier [4, 5] and organic semiconductor layer [6, 7] have reflected their potential use in spintronic applications. Among the different factors which influence the performance of molecular spintronic devices, the interfaces between ferromagnetic electrodes and molecules are shown to play an important role. Recently, there have been several reports on the observations of induced magnetic moment in molecules chemisorbed on ferromagnets (FMs) due to proximity effects [8–10]. This induced magnetic moment can be switched by a magnetic field and has an important impact on spin injection at interfaces [11, 12]. Moreover, it was shown that the sign of magnetoresistance

(MR) can be tuned by engineering the interface barrier height in vertical organic spin-valve devices [13]. However, the role of FM–molecule interface bonding on spin injection is rarely studied.

To characterize spin transport through molecules, various experimental approaches have been devised to fabricate FM/molecule/FM junctions, such as SAMs [4], the Langmuir–Blodgett technique [14] and scanning tunnelling microscopes [15]. These approaches, however, require complex fabrication process and suffer from a low yield of working devices. Here, we use the assemblies of molecule-ligand-wrapped $Fe_3O_4$ nanoparticles to form the networks of molecular junctions. This simple and reliable approach has been demonstrated to be a promising platform to investigate spin transport on molecular scale [16, 17]. For instance, spin-conserved tunnelling through alkane molecular chains at room temperature was demonstrated using this approach [18].

The ability to engineer the FM/molecule interface is critical for studying the spin injection mechanism. In this work, we have carried out systematic studies of the impact on spin injection across the chemical bonding between $Fe_3O_4$

nanoparticles and stearic acid [$CH_3(CH_2)_{16}COOH$, denoted as C18] molecules, in comparison with $Fe_3O_4$ nanoparticles with physically absorbed C18 molecules, named PhyNPs. The $Fe_3O_4$ nanoparticles are separated well by the molecules to prevent the nanoparticles from directly contacting each other in both types of samples. The electrical resistance of PhyNPs is found to be more than two orders of magnitude larger than that of $Fe_3O_4$ nanoparticles chemically bonded with monolayer C18 molecules, named ChemNPs, reflecting the fact that the resistance is dominated by the physical contacts of nanoparticles and molecules. The MR of ChemNPs is about −12% at room temperature. In contrast, no MR is observed in PhyNPs, indicating the importance of chemical bonding for spin injection into molecules. The estimated spin polarization of ChemNPs is larger than $Fe_3O_4$ nanoparticles wrapped with inorganic materials, suggesting that electronic hybridization at the interface and improved oxygen stoichiometry of the $Fe_3O_4$ surface may enhance the spin polarization of ChemNPs.

## 2. Experiment details

ChemNPs are synthesized by the co-precipitate method. The detailed fabrication process has been described in earlier publications [17, 18]. The particle size of $Fe_3O_4$ is fixed at ∼9 nm by controlling the reaction time. For ChemNPs, a weak coordinate bond is formed between C18 molecules and $Fe_3O_4$. To obtain PhyNPs, ChemNPs are dispersed into a blend of deionized water and ethyl alcohol. The solution is heated to 90 °C, which is between the boiling point of ethyl alcohol and water. The chemical bond is broken at such a high temperature while the ethyl alcohol boils. After the ethyl alcohol is completely vaporized in about 20 min, a large amount of 20 °C deionized water is added into the solution for rapid cooling. Due to the van der Waals force and insolubility of C18 molecules in water, the molecules are physically adsorbed on the nanoparticles. We also prepared one controlled ChemNPs sample, named re-bonded ChemNPs, which was synthesized from PhyNPs by a similar procedure to synthetic ChemNPs. Finally, the collected nanoparticles are dried in vacuum to prevent possible oxidation and then cold-pressed into about 1 mm thick pieces. Because of the same amount of C18 molecules adsorbed on nanoparticles in ChemNPs and PhyNPs, the structural order and inter-particle distance are similar in both compressed samples. The top and bottom surfaces of the pieces are coated with silver paints as electrical contacts and then sliced into ∼5 mm × 5 mm pieces for transport measurements. The magneto-transport is carried out on a close-cycle refrigerator with the magnetic field parallel to electrical contacts.

## 3. Results and discussion

The $Fe_3O_4$ nanoparticles are separated by either chemically bonded or physically absorbed C18 molecules to form a network of $Fe_3O_4$/C18/$Fe_3O_4$ molecular junctions, as schematically illustrated in figures 1(*a*) and (*b*), respectively. The length of C18 molecules is about 2.5 nm, which serve as a tunnelling barrier. In order to verify that two types of
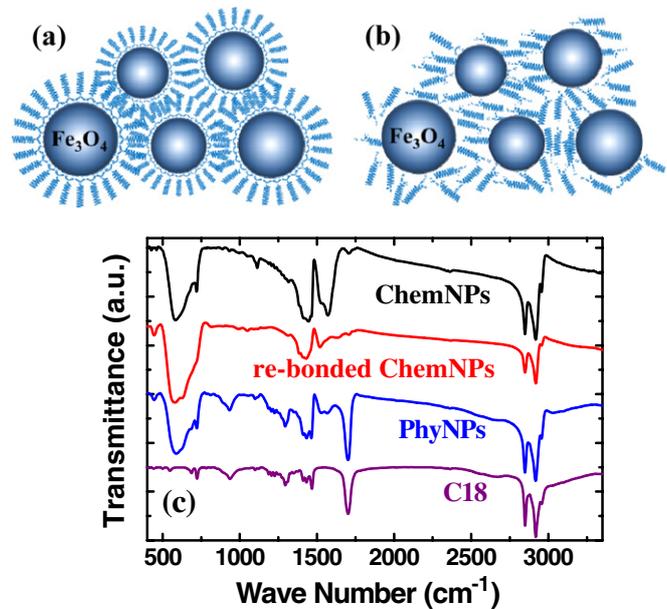


**Figure 1.** (*a*), (*b*) Schematic diagrams of C18 molecules chemically bonded with and physically absorbed by $Fe_3O_4$ nanoparticles, respectively. (*c*) FTIR spectra of ChemNPs (black), re-bonded ChemNPs (red), PhyNPs (blue) and pure C18 molecules (purple).

molecule-wrapped $Fe_3O_4$ nanoparticles were obtained, both types of nanoparticles and pure C18 molecules were pelletized with KBr to carry out Fourier transform infrared spectroscopy (FTIR) measurements. Figure 1(*c*) shows the FTIR spectra of pure C18 molecules, ChemNPs, PhyNPs and re-bonded ChemNPs, respectively. All samples exhibit two intense absorption lines at about 2848 and 2918 cm$^{-1}$. As these two absorption lines are the characteristic features of the symmetric and asymmetric H–C–H stretching, respectively, this observation represents the existence of single-bond carbon chains. The three absorption lines at 1702 cm$^{-1}$, 1467 cm$^{-1}$ and 1294 cm$^{-1}$ associated with the vibrations of C=O, C–O and O–H bonds of carboxylic head group (–COOH), respectively, are shown in both PhyNPs and pure C18 molecule samples, strongly suggesting that C18 molecules are indeed physically absorbed by $Fe_3O_4$ nanoparticles in PhyNPs samples. In contrast, the three characteristic absorption lines of carboxylic head group disappear and two new absorption lines at 1430 cm$^{-1}$ and 1580 cm$^{-1}$ of the symmetric and asymmetric carboxylate (COO$^-$) stretching, respectively, are present in the ChemNPs and re-bonded ChemNPs samples, which shows that two oxygen atoms of carboxylate are symmetrically bonded to the surface Fe ions. These results undoubtedly reveal that C18 molecules are chemically bonded to $Fe_3O_4$ nanoparticles [18, 19]. A broad band between 500 and 700 cm$^{-1}$ is shown in samples consisting of $Fe_3O_4$ nanoparticles, which is ascribed to the vibration of the surface oxygen of $Fe_3O_4$.

　　All the nanoparticle samples exhibit strong nonlinear current–voltage (*I*–*V*) behaviour at room temperature, as shown in a semi-log plot in figure 2. For ChemNPs, it is shown that the resistance is dominated by the tunnelling process in C18 molecules [18]. The slight decrease in current in re-bonded ChemNPs may suggest that the stoichiometry of $Fe_3O_4$ is partially altered during the second synthesis
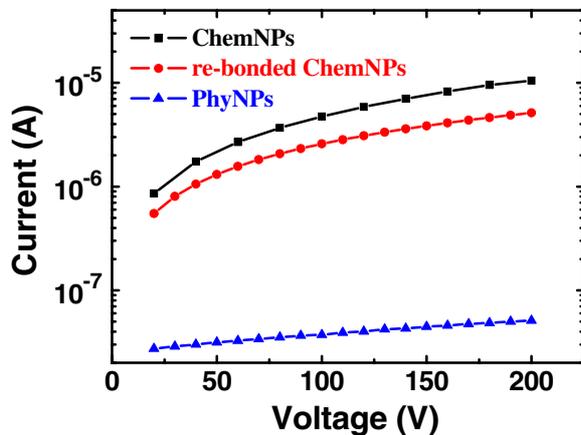
**Figure 2.** *I–V* curves of ChemNPs (black), re-bonded ChemNPs (blue) and PhyNPs (red), respectively, at room temperature.



**Figure 3.** MR measured at 300 K for ChemNPs (black), re-bonded ChemNPs (red) and PhyNPs (blue), respectively.

process. Moreover, the similarity of ChemNPs and re-bonded ChemNPs *I–V* curves reveals that the structural order and inter-particle distance are similar in these compressed nanoparticles. Obviously, the *I–V* characteristics of the ChemNPs differ dramatically from that of the PhyNPs. The current of the PhyNPs is two orders of magnitude larger than that of the ChemNPs in the entire bias-voltage range. In addition, *I–V* characteristics also have a quite different bias voltage dependence. These results clearly suggest that the resistance of PhyNPs is dominated by the physical contact between the nanoparticles and molecules rather than by the molecular resistance as in ChemNPs. In fact, the molecular junction resistance dominated by physical contact was also observed in a single molecular junction built by the scanning tunnelling microscope [20]. They showed that physical bonding can enhance the resistance of molecular junction from two to three orders of magnitude depending on the bias voltage, which is comparable to our results.

The situation for the assemblies of molecule-wrapped $Fe_3O_4$ nanoparticles is similar to that of granular giant magnetoresistive systems [21, 22]. The resistance depends on the relative orientation of the superparamagnetic moments of the neighbouring $Fe_3O_4$ nanoparticles. Under an external magnetic field, the randomly oriented superparamagnetic moments are aligned with the field to a certain degree, which depends on the field strength, resulting in a net total magnetic moment. In the meantime, a negative MR effect occurs, i.e. $\Delta\rho/\rho(0) = [\rho(H) - \rho(0)]/\rho(0) < 0$, where $\rho(0)$ and $\rho(H)$ are the resistivity in zero and applied fields, $H$, respectively. The assemblies of $Fe_3O_4$ nanoparticles chemically bonded with molecules exhibit a negative MR of $-12\%$ under a 5.8 kOe magnetic field at room temperature, as shown in figure 3. This negative MR behaviour has also been observed in $SiO_2$-coated $Fe_3O_4$ nanoparticles and polymer-coated Co nanoparticle systems, and even a few $Fe_3O_4$ nanoparticles [22–24]. In contrast, we did not observe any MR effects in PhyNPs. To rule out the alternation of $Fe_3O_4$ stoichiometry as the origin of the vanishing of MR, we performed similar measurements in the re-bonded ChemNPs, which were synthesized from the PhyNPs. We find that about $-8\%$ MR effects can be recovered after re-chemical bonding of the molecules, indicating that
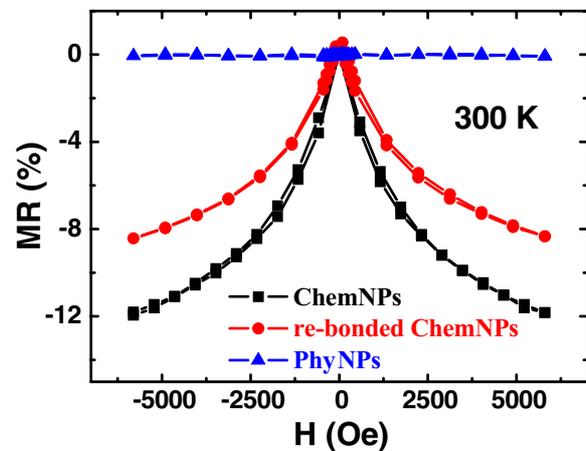
the re-bonding fabrication is successful. The MR ratio of re-bonded ChemNPs is smaller than that of the as-prepared ChemNPs, which may be due to the partial oxidation of $Fe_3O_4$.

According to the experimental results presented above, the chemical bonding between $Fe_3O_4$ and molecules is crucial to obtain MR effects. When ferromagnetic materials and molecules are brought into close proximity to form a chemical bonding, a finite magnetic moment can be induced in molecules through electronic hybridization. This proximity effect was clearly observed by spin-polarized scanning tunnelling microscopy and x-ray magnetic circular dichroism [8–10]. Furthermore, it was theoretically suggested that the magnetic proximity effect was the origin of spin-dependent tunnelling through molecules [12]. We apply this mechanism to explain the observation of strong MR effect in $Fe_3O_4$ nanoparticles chemically bonded with molecules. For PhyNPs samples, an energy barrier is present between the $Fe_3O_4$ nanoparticle and the molecule, leading to two orders of magnitude increase in resistance. Consequently, electronic hybridization at the interface is noticeably weaker than that in ChemNPs, resulting in the vanishing of proximity effect and therefore MR effect (see figure 3). Such a scenario that interface bonding plays an important role in spin-dependent tunnelling is well established in inorganic tunnelling junctions [25], whereas it is much less studied in molecular junctions.

Figure 4 shows the temperature dependence of the MR ratio under 5.8 kOe field with a constant current of 0.1 $\mu$A for ChemNPs and re-bonded ChemNPs. The MR ratio of both samples increases with decreasing temperature in a similar trend. The MR ratio of re-bonded ChemNPs is smaller than that of the as-prepared ChemNPs in the entire temperature range. In order to study the origin of the MR effect, we analyse the data with Juilliere's formula. The spin polarization, $P$, of the $Fe_3O_4$ nanoparticles is estimated from the formula: $\Delta\rho/\rho(0) = -P^2/(1 + P^2)$ [26], where the MR ratio $\Delta\rho/\rho$ is the resistance change between the random ($H = 0$) and completely ordered configurations ($H = \infty$). In figure 3, the MR curves are not completely saturated at 5.8 kOe, which is likely caused by loose surface spins due to the broken exchange bonds [27]. Therefore, spin polarization would
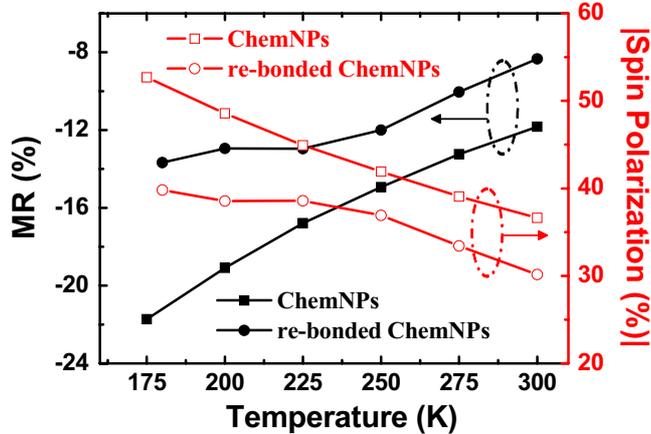
**Figure 4.** MR ratio (left) and deduced spin polarization (right) of ChemNPs (square) and re-bonded ChemNPs (circle) as a function of temperature.

## 4. Conclusions

In summary, we performed a comparative spin injection study of $Fe_3O_4$ nanoparticles chemically bonded with molecules and $Fe_3O_4$ nanoparticles with physically absorbed molecules. Up to 22% MR is achieved in $Fe_3O_4$ nanoparticles chemically bonded with C18. $Fe_3O_4$ nanoparticles with physically absorbed C18 molecules, however, show no MR effect and two orders of magnitude higher resistance. This sharp contrast clearly demonstrated the importance of chemical bonding between molecules and FM electrodes for spin-dependent injection into molecules. This high value of MR for $Fe_3O_4$ nanoparticles chemically bonded with C18 may be attributed to an enhanced spin polarization of the $Fe_3O_4$/molecule interface, which results from the induced magnetic moment in molecules and improved stoichiometry of the $Fe_3O_4$ surface. Our results provide a new possibility to tailor FM/molecule interface and therefore spin injection into molecules.

## Acknowledgments

be inevitably underestimated. Here, although the sign of $Fe_3O_4$ spin polarization cannot be determined in the transport measurements, spin-resolved photoemission spectroscopy has revealed that it is negative [28]. Nevertheless, if we use the unsaturated MR ratio of −12%, we obtain $P = -37\%$ at room temperature. As shown in figure 4, when the temperature is decreased from 300 to 175 K, the MR ratio magnitude steadily increases to −22%, corresponding to a spin polarization of −53%. This spin polarization value is much larger than the reported value obtained from bare $Fe_3O_4$ nanoparticles, $SiO_2$-coated $Fe_3O_4$ nanoparticles and planar magnetic tunnel junctions based on $Fe_3O_4$ films [22, 29, 30], but it is smaller than the value obtained by spin-resolved photoemissions [28].

Recently, Barraud *et al* proposed that the induced spin polarization of the molecules, which chemically bond with ferromagnetic electrodes, can be much larger than that of contacted ferromagnetic electrodes, and even reversed the sign [7]. The spin-dependent tunnelling is dominated by molecular polarization, resulting in an MR effect as high as 300%. The much larger spin polarization extracted from our data could have originated from C18 molecules due to the magnetic proximity effect. In addition, the stoichiometry of bare $Fe_3O_4$ is expected to be oxygen deficiency at the surface. In ChemNPs, FTIR spectra show that the surface Fe ions of $Fe_3O_4$ are symmetrically bonded with two oxygen atoms (see figure 1). Therefore, the stoichiometry of $Fe_3O_4$ at the surface could be stabilized through the bonding. This could improve the $Fe_3O_4$/molecule interfacial states and yield a better surface magnetism. This may give an additional mechanism to enhance the spin polarization. In addition, Pauly *et al* recently reported that co-tunnelling between a few $Fe_3O_4$ nanoparticles enhanced the MR value up to ∼60% at 100 K [24]. The co-tunnelling process involves only a small number of nanoparticles. However, in our system, the separation of electrodes is about 1 mm, which results in the electrons tunnelling through about $10^5$ nanoparticles, indicating that the co-tunnelling process is not responsible for the larger spin polarization.

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F J Yue *et al*

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