Enhanced tunneling magnetoresistance and high-spin polarization at room temperature in a polystyrene-coated Fe_3O_4 granular system

Wendong Wang,[1] Minhui Yu,[2] Matthias Batzill,[3] Jibao He,[4] Ulrike Diebold,[3] and Jinke Tang[1]

[1]*Department of Physics, University of New Orleans, New Orleans, Louisiana 70148, USA*

[2]*Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana 70148, USA*

[3]*Department of Physics, Tulane University, New Orleans, Louisiana 70118, USA*

[4]*Coordinated Instrumentation Facility, Tulane University, New Orleans, Louisiana 70118, USA*

Polystyrene-coated Fe_3O_4 nanoparticles through surface engineering exhibit an intergranular tunneling magnetoresistance (MR) ratio of 22.8% at room temperature and a maximum MR of 40.9% at 110 K. The drastic enhancement of the MR ratio clearly suggests that there is high degree of spin polarization even at room temperature for half metallic Fe_3O_4. The estimated spin polarization P is about 54% and 83% at room temperature and 110 K, respectively.

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I. INTRODUCTION

The half-metal family that includes CrO_2, Fe_3O_4, and $La_{2/3}Sr_{1/3}MnO_3$ attracts enormous attention, owing to their speculated 100% spin polarization P according to band structure calculations. They are conductors for one spin channel and insulators/semiconductors for the other spin channel and have great application potential in spin electronic devices.[1,2] On the experimental side, CrO_2 best exemplifies the half-metals with the value of P reported in the range of 85−96% at very low temperatures. However P rapidly declines with increasing temperature. Other materials fail to show high P for a variety of reasons, including disorders and defects, particularly on the surfaces.[2,3] As far as we know, clear experimental evidence showing high-spin polarization at room temperature is lacking for all known speculated half-metals.[4]

Ferrimagnetic magnetite Fe_3O_4 is a well-known half-metal with a high Curie temperature T_c of 840 K. It offers the best prospect for spintronic applications since the devices are expected to work around or above room temperature, requiring T_c above 500 K.[3] Under ordinary condition, the surface of Fe_3O_4 is oxidized and contains $Fe(3+)$-rich oxide, which is believed to be the reason for the failure to observe high-spin polarization in Fe_3O_4. To reveal the true spin polarization of Fe_3O_4, the $Fe(3+)$-rich oxide on the surface should be removed or avoided. We have selected polymers polystyrene (PS), polycarbonate (PC), and poly(methyl methacrylate) (PMMA) as the coating layer to avoid the surface oxidation of Fe_3O_4. These polymers also serve as good insulating barriers between the Fe_3O_4 nanoparticles.

II. EXPERIMENTS

Polymers (PS, PC, and PMMA) and α-Fe_2O_3 nanoparticles with various weight ratios were mixed together by first dissolving the polymer in chloroform, then adding Fe_2O_3 particles and stirring, and finally evaporating the solvent. The samples were annealed at 200 °C in pure hydrogen flow, and then pressed into pellets. The pellets were again annealed at 200 and 250 °C in pure hydrogen flow.

The structural analysis was done by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The transport properties of the samples were measured using the four-point method and in ac mode. The magnetic measurements were performed with a superconducting quantum interference device (SQUID).

III. RESULTS AND DISCUSSION

XRD spectra indicate that there is a complete phase transformation from α-Fe_2O_3 to Fe_3O_4 after annealing in hydrogen. TEM images show that the Fe_3O_4 particles are generally spherical and their size is between 10 and 30 nm [Fig. 1(a)]. They are dispersed in the polymer matrix. Some particles are close to each other but separated by the polymer [Fig. 1(b)], which provides the structure for intergranular tunneling of electrons.

The temperature dependence of the resistance (R) follows $\ln R \propto T^{-1/2}$, and the I-V curves are nonlinear (Fig. 2, insets). These results suggest that the electron transport in the samples is via intergranular tunneling, which has been broadly accepted as exhibiting $\exp(T^{-1/2})$ behavior in the resistance.[5,6] We have tested the $\exp(T^{-1/4})$ form expected for variable range hopping resistance and found that R could not be described by such a law. The data presented in Fig. 2 are reproducible. Similar behaviors are seen in other samples.

The magnetoresistance (MR) of the samples, defined as $MR = (R_H - R_0)/R_0$, where R_0 and R_H is the resistance in zero and an applied field of H, respectively, is shown in Fig. 2. The MR of the Fe_3O_4 samples coated with PC [Fig. 2(a)] is similar to the reported data on pressed Fe_3O_4 powders and polycrystalline films,[7–10] which have a typical MR ratio of 4−7% or lower at room temperature. The Fe_3O_4 samples coated with PMMA have almost identical results with that coated with PC. On the other hand, the sample coated with PS exhibits a MR ratio of 22.8% in an applied field of 14 T at room temperature. The maximum MR of 40.9% is obtained at 110 K [Fig. 2(b)]. The MR curves show rapid change in low fields but are not completely saturated in a
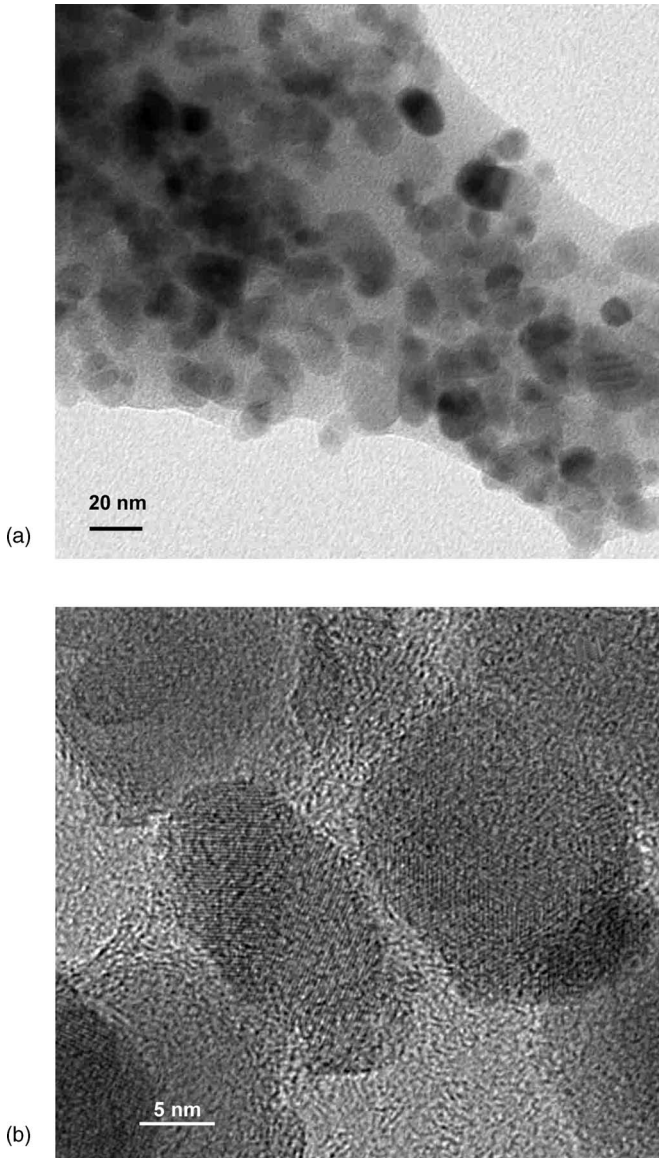
FIG. 1. (a) TEM image for the PS-coated Fe_3O_4 sample, indicating that spherical Fe_3O_4 nanoparticles are embedded in polymer matrix. (b) High-resolution TEM image showing that the Fe_3O_4 particles are separated by a thin polymer layer of a few nanometers, forming a tunnel barrier.

FIG. 2. MR ratio in an applied field of 14 T at 280 and 110 K for (a) PC-coated Fe_3O_4 and (b) PS-coated Fe_3O_4. The weight ratio of Fe_3O_4 to polymers is 1:1 for both. The MR ratio of PMMA-coated Fe_3O_4 is similar to that of PC-coated samples. (Left insets) resistance as a function of temperature: $\log R$ versus $T^{-1/2}$ curves exhibit linear relation; (Right insets) I-V curves at room temperature which have nonlinear behavior. These are consistent with the transport mechanism of intergranular tunneling. (c) Magnetic hystereses and (d) butterfly-shaped MR hystereses in low fields for PS-coated Fe_3O_4.

field of 14 T. In the low-field region, butterfly shaped hysteresis in MR curves has been observed, and the coercivities in the MR coincide with that in the magnetization curves for both low and high temperatures [Figs. 2(c) and 2(d)].

There are several models that can be used to calculate the spin polarization P from the MR data. Inomura and Maekawa have derived a simple relationship between MR and P for intergranular tunneling,[6]

$$MR = P^2 m^2 / (1 + P^2 m^2), \qquad (1)$$

where m is the relative magnetization of the system and $m^2 = \langle \cos \theta \rangle$. In saturated state, $m = 1$, then
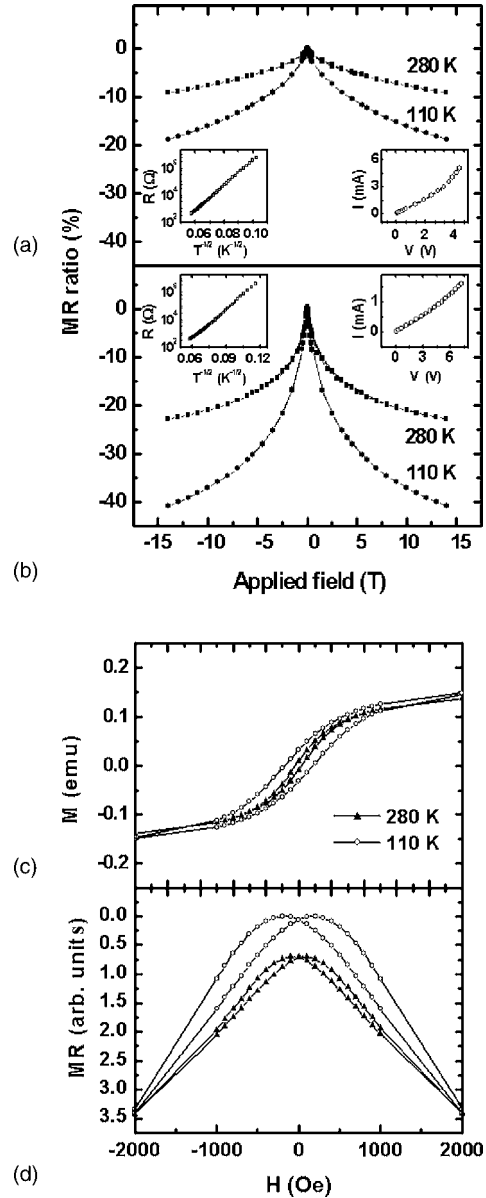
$$P = [MR_s / (1 - MR_s)]^{1/2}, \qquad (2)$$

where MR_s is the saturated MR ratio. A modification of the model is to consider a serial connection of the grains in addition to parallel connections used in the model.[11–13] The difference between these models becomes very small when three-dimensional (3D) nature of the network of grains is considered. This is true even for relatively high-spin polar-

ization $P > 0.5$.[12,13] Our composite pellet samples fall well within the 3D regime, and Eq. (2) was used to calculate the spin polarization. It should be mentioned that the models proposed by Slonczewski[14] and MacLaren[15] suggest the nature of the barrier is a factor influencing the effective spin polarization. Such effect diminishes with increasing barrier height. The polymer barriers used here are in general of very large band gap (~ 7 eV); therefore, we believe the effect of the barrier on the spin polarization is small in this case. More importantly, as long as one understands that the P obtained from Eq. (2) is the effective spin polarization, the result is valid.

The spin polarization P of Fe_3O_4 estimated from the MR values according to Eq. (2) is 83% at low temperature and 54% at room temperature. These values are much higher than the reported experimental results[16–18] and higher than a recent theoretical calculation after taking into the consideration of modified surface state.[19] Fe_3O_4 indeed belongs to the category of highly spin polarized half-metals. The more than 50% value for spin polarization at room temperature is significant in that this is the first time that such a high-spin polarization has been observed in Fe_3O_4 at room temperature, which has both practical and scientific implications. Coulomb blockade effect is believed to be another factor to sometimes contribute to the enhancement of MR; however, it occurs only at very low temperature[20,21] and should not play a significant role here. We believe these P values only set lower limits for Fe_3O_4 and its actual values can be higher, especially at room temperature, because

(1) There may exist spin-independent conductance channels owing to the imperfections, defects, and impurities in the barrier in our samples, which reduces the tunneling MR ratio.[22]

(2) Bulk magnons and surface magnons will reduce the MR via magnon-assisted tunneling.[23] Although they may also reduce the spin polarization itself,[4] theoretical studies indicate that the MR ratio will decrease more rapidly with temperature than P.[24]

(3) Even an applied field of 14 T may not be high enough to completely align the magnetic moments of the Fe_3O_4 particles of 10–30 nm in size in our samples, especially those on the surface. It should be noted that using MR data taken at 14 T to calculate P is justified because the intrinsic magnetoresistance of Fe_3O_4 is very small in such a field.[7]

(4) We have assumed that the relative magnetization $m = 1$ in the calculation of P using Eq. (2), but it takes a reduced value at high temperatures.

It ought to be noted that there are different ways to define spin polarization.[3] Some measure the spin polarization of the density of states and some measure that of the transport current density. The spin polarization obtained from our intergranular tunneling experiments is the spin polarization of the tunneling current. We would like to argue that the spin polarization of density of states is also high for Fe_3O_4. The difference between the two definitions becomes significant when there are "heavy" (e.g., d electrons) and "light" electrons (e.g., s electrons) coexisting at the Fermi level, which is not the case for Fe_3O_4. For Fe_3O_4, t_{2g}(Fe) electrons form small polarons and hop among the B sites of the inverse spinel structure in a fully spin-polarized spin-down band.
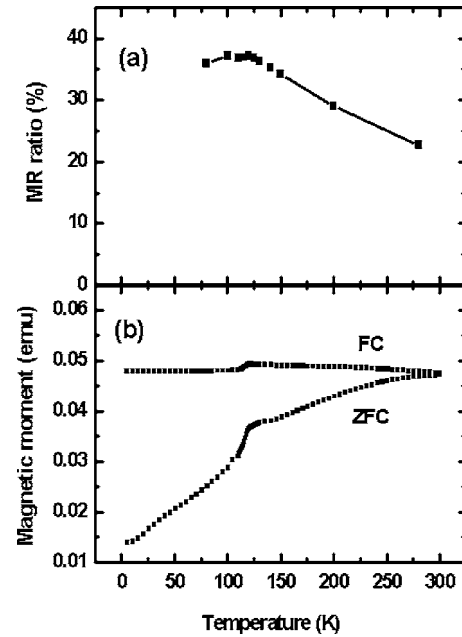

FIG. 3. (a) Temperature dependence of MR ratio in an applied field of 14 T for a PS-coated sample. (b) ZFC-FC curves with an applied field $H = 200$ Oe, which shows sharp Vervey transition in the range of 110–120 K in our samples.

Therefore, we believe the two numbers, 54% and 83%, may also represent the approximate values for the lower limits of the spin polarization of the density of states at room temperature and 110 K, respectively.

It is necessary to study the temperature dependence of MR since Fe_3O_4 undergoes a Verwey transition, which is characterized by an increase in the resistivity by about two orders of magnitude at the transition temperature $Tv \sim 120$ K. This transition is associated with an order-disorder transition from a charge-ordered state of the Fe ion on the B sites at low temperature to a statistical distribution at high temperature. A sharp narrow negative MR peak is normally observed at the Verwey point in single crystal Fe_3O_4.[25,26] In our samples, the MR ratio continuously increases with decreasing temperature before the Verwey transition [Fig. 3(a)]. After the transition, the MR ratio exhibits a plateau between 80 and 120 K. We cannot acquire MR data below 80 K because the resistance of the samples becomes too high to measure with our setup. According to the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves [Fig. 3(b)], the Verwey transition is quite sharp and occurs in a relative narrow temperature range of 110–120 K in our samples. This suggests that MR observed in our samples can be used to calculate the spin polarization because it is not part of the sharp peak ordinarily associated with the Verwey transition. The latter does not arise from the spin polarization but is a critical phenomenon at the phase transition and thus cannot be used for deriving spin polarization. The Verwey transition does not significantly change the tunneling MR and the spin polarization, consistent with reported results.[16,17] To understand the temperature dependence of MR ratio in our samples, we propose the following model. We think there exist two channels of conductance.
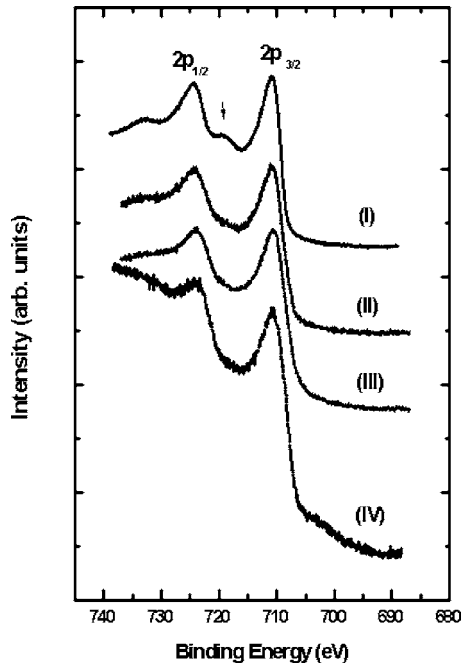
FIG. 4. Al Kα-exited Fe $2p$ core-level photo emission spectra for (I) pure Fe_3O_4 powder sample, (II) PC-coated Fe_3O_4, (III) PMMA-coated Fe_3O_4, and (IV) PS-coated Fe_3O_4. The arrow indicates the characteristic shake-up satellite associated with Fe(3+) ion photoemission at a binding energy of ~719 eV.

One is the intergranular spin-dependent channel and the other is a spin-independent channel due to thermal excitation or inelastic hopping through localized states due to imperfections in the barrier, etc. Above the Verwey transition, the current of the spin-independent channel rapidly decreases with decreasing temperature, whereas the current of the spin-dependent channel decreases relatively slower. This results in the enhancement of tunneling MR ratio with the decrease of temperature. Below the transition, the resistance of Fe_3O_4 increases rapidly with decreasing temperature. The number of carriers available for tunneling decreases accordingly, which greatly diminishes the spin-dependent tunneling current. At the same time, the spin-independent current decreases with temperature as well. The plateau in the MR ratio below the Verwey point is the combined effects of these two channels.

It is widely accepted that the surface state of Fe_3O_4 plays a key role in magnetotransport properties, and x-ray photoelectron spectroscopy (XPS) is one of the most powerful tools to obtain information about the electronic structure of a solid's surface. Figure 4 shows the XPS Fe $2p$ core-level spectra for pure Fe_3O_4 powders and PS-, PMMA-, and PC-coated Fe_3O_4 samples, which contain contributions from the top 15 layers of the surface. Different from the polymer-coated Fe_3O_4 samples, the lineshape of the pure Fe_3O_4 sample exhibits shake-up satellite at a binding energy of ~719 eV and a little narrow peak of the Fe $2p_{3/2}$ peak, which is characteristic of Fe(3+) oxide.[27,28] This clearly demonstrates that the surface of Fe_3O_4 is Fe(3+) oxide once it is exposed to air. The lineshapes of PS-, PMMA-, and PC-coated samples reveal the characteristics of Fe_3O_4 and there is no obvious difference among them, suggesting that the coating prevented the oxygen infusion into the Fe_3O_4 particles. However, the very top layers of the surface may be different from the top 15 layers, the latter of which are probed by XPS, depending on the coating materials. Studies have indicated that the top two layers of the surface are rich in Fe(3+) compared to the top 15 layers in Fe_3O_4 films molecular-beam epitaxy (MBE) grown in ultrahigh vacuum.[29,30] Polymer PMMA and PC contain oxygen whereas PS is oxygen free. For the PMMA- and PC-coated samples, it is possible to form bonding between the oxygen in polymer and Fe(2+) ion on the surface, which will result in the presence of Fe(3+)-rich oxide on the top one or two layers of Fe_3O_4 surface, which will greatly diminish the spin polarization as it does in pure Fe_3O_4 powders or polycrystalline film. Since PS contains no oxygen element, the Fe_3O_4 state can be preserved and the high-spin polarization can survive on the surface. This greatly enhances the spin-dependent tunneling MR.

IV. CONCLUSIONS

Drastic enhancement of the MR ratio suggests that there is a high degree of spin polarization at both low and room temperatures for half-metallic Fe_3O_4. The improvement was achieved by controlling the surface of Fe_3O_4 through surface engineering using oxygen-free insulating barriers. Based on our result, it is possible that a simple tunnel junction made of Fe_3O_4 exhibits large MR in a relatively small field. Fe_3O_4 may also be used as an effective spin injector. Knowing that our results provided only a lower limit on the spin polarization of Fe_3O_4, it has the potential to play an important role in spintronic devices.

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