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Room temperature positive magnetoresistance via charge trapping in polyaniline-iron oxide nanoparticle composites

Aigu L. Lin,^{1,2} Tom Wu,³ Wei Chen,^{1,2,4} and Andrew T. S. Wee^{1,2,a)}

¹NUS Graduate School of Integrative Sciences and Engineering, National University of Singapore, 28 Medical Drive, Singapore 117456

²Department of Physics, Faculty of Science, National University of Singapore, 2 Science Drive 3, Singapore 117542

³Division of Physics and Applied Physics, Nanyang Technological University, 21 Nanyang Link, Singapore 637371

⁴Department of Chemistry, Faculty of Science, National University of Singapore, 3 Science Drive 3, Singapore 117543

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We demonstrate a polyaniline-iron oxide nanoparticle (PANI-NP) organic hybrid composite device with room temperature positive magnetoresistance of 85.7%. Temperature dependent resistivity measurements attribute this observation to the decrease in localization length of the charge carriers in the presence of an external magnetic field which result in them being trapped within the device between the insulating PANI layer, hence allowing the device to maintain its resistive state even when the power is switched off, thus exhibiting a memory effect. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4815998>]

Spintronics^{1–3} or spin transport electronics is an emerging technology which uses the electron spin to store information. In recent years, there has been much interest in organic spintronics devices.^{4–6} Due to their very weak spin-orbit coupling, organic spintronic devices have the advantage over their inorganic counterparts, allowing for a long spin diffusion length, as well as being cheap, flexible, and easy to process. Organic electronics devices are also known to exhibit switching behaviour from a low resistive state to a high resistive state and are capable of maintaining these states⁷ just like their inorganic counterparts. Thus, they are potential candidates for non-volatile memory devices, that is, they can store information when the power is switched off. However, initial organic spintronics devices such as organic spin valves were reported to have a room temperature magnetoresistance of less than 20%, well below the limit needed for applications.^{8–12} Magnetoresistive studies of magnetic clusters embedded in a metallic matrix have been reported.¹³ Theoretical predictions showing high magnetoresistance in hybrid materials coupled with nanocarbon based materials^{14,15} have led to research on the Co-C₆₀ compound hybrid system¹⁶ and LSMO-PANI nanocomposites,¹⁷ both of which exhibit 1D variable range hopping and thus have tunneling based conductivity. In addition, room temperature tunnel magnetoresistance had been achieved in self-assembled chemically synthesized metallic iron nanoparticles surrounded by two types of organic barriers.¹⁸ Recently, a high magnetoresistance at room temperature had been accomplished with PANI/Fe₃O₄ nanocomposites,¹⁹ however, a high magnetic field of more than 4 T is needed to produce this effect, and is too high to be used for any real world applications. However, all previous work mainly involve on the conducting form of the organic materials used in the nanocomposites, and for our work, we had used the non-

conducting form of PANI to see if it is appropriate for organic spintronics device. In this letter, we report a polyaniline-iron oxide nanoparticle (PANI-NP) organic hybrid composite device which exhibits 3D variable range hopping²⁰ and has room temperature positive magnetoresistance of 85.7% which can be achieved when the external magnetic field is 0.6 T, which is much lower than previously reported as well as having a memory effect due to its ability to trap charges.

Polyaniline (PANI) belongs to a class of conducting polymers known as conjugated polymers.^{21–23} Depending on the degree of doping, PANI can either be in the insulating, semiconducting, or metallic state. The PANI used in this experiment is in its undoped emeraldine base form, hence, it is in its insulative state. The iron oxide core shell structure nanoparticles (NP) with metallic iron as the core and the oxide layer as the shell are purchased from Sigma Aldrich and come in sizes varying from 6.5 to 9.5 nm. Due to their small size, the nanoparticles exist in the superparamagnetic regime, that is, they tend to align in the same direction as the externally applied magnetic field.

0.03 g of polyaniline (emeraldine base) was dissolved in 1-methyl-2-pyrrolidone. The iron oxide nanoparticles were then added to the polyaniline solution and dispersed with the application of ultrasound for 30 s before the polyaniline-nanoparticle solution was spin coated on a silicon dioxide overlayer of thickness 200 nm on a boron-doped silicon wafer at a speed of 8000 rpm for 30 s. We repeated this spin coating process 3 times before depositing platinum electrodes on top of the polyaniline-nanoparticle composite as shown in Figure 1(a).

I-V measurements were done after connecting two probes onto two platinum electrodes using a KEITHLEY Semiconductor Characterization System with voltage varying from 0 to 5 V. When pure PANI is used without nanoparticles, the current magnitude remains constant at the background level of 1 pA even when we increase the voltage

^{a)} Author to whom correspondence should be addressed. Electronic mail: phyweats@nus.edu.sg.

FIG. 1. Schematics of the device and conductivity of the nanocomposite. (a) Platinum electrodes were deposited on the polyaniline-Iron Oxide nanoparticles composite after it is spin coated on a silicon oxide substrate. The direction of the applied magnetic field is either parallel or anti-parallel to the direction of current flow. (b) Conductivity dependence on the iron oxide nanoparticles percentage by volume. Pure PANI (no nanoparticles) has a very low current flow of the order of 1 pA and thus demonstrates an insulating behavior. As the iron oxide nanoparticles concentration is increased the magnitude of the current flow increases thus showing better conductivity.

to 30 V as expected due to the insulating nature of the undoped PANI thin film. Upon addition of the nanoparticles to form the PANI-NP nanocomposite, it becomes semiconducting and allows current to flow through the network.^{21,22} The magnitude of the current flow increases with increasing nanoparticle concentration as seen in Figure 1(b). This shows that the main mode of charge transport in the nanocomposite is via the hopping or tunnelling of charge carriers from one nanoparticle to the other and as the concentration of the nanoparticles increase and percolation of the system improves, it allows for better conductivity within the nanocomposite network. Structural analysis of as-deposited films was performed in a FEI Titan 80/300 S/TEM equipped with a High-Angle Annular Dark-Field (HAADF) detector, an Energy Dispersive X-ray spectroscopy detector, a monochromator and a Gatan spectrometer. The TEM was operated at 80 keV to minimize the electron beam damage to the organic films. The PANI matrix isolates the nanoparticle clusters from each other and as the nanoparticle concentration increases, their cluster size increases and their separation distances decreases as can be seen in the TEM images in Figures 2(a)–2(c).

The magnetic field was generated using a DEXTER Adjustable Pole Electromagnet (Model # 1607037) and was varied from 0 T to 0.6 T for each I-V measurement. Figures 2(a)–2(c) show the magnetoresistance data and corresponding TEM images for samples with 2%, 6%, and 10% nanoparticles by volume, respectively. Samples with low nanoparticle concentrations (1% to 2% by volume) show

FIG. 2. Magnetic field dependence of the magnetoresistance for different nanoparticle concentrations together with their TEM images with some of the top layer of PANI scrapped off to reveal the iron oxide nanoparticles distribution beneath it. The insulative nature of PANI leads to a poor transmission of electrons and hence leading to a lower resolution of the images. (a) Maximum magnetoresistance of 9.15% is obtained when the nanoparticles are 2% by volume. (b) Maximum magnetoresistance of 32.2% is obtained when the voltage is around 0.8 V and the nanoparticles are 6% by volume. (c) Maximum magnetoresistance of 85.7% is obtained when the nanoparticles are 10% by volume. (d) When the magnetic field is switched off, the magnitude of the resistance remains approximately constant, thus exhibiting a memory effect. The concentration of the iron oxide nanoparticles for this sample is 10% by volume.

poor distribution within the nanocomposite as seen in the TEM image of Figure 2(a) which forms a poor percolation network and there are very few pathways for which the charge carriers could get transported along. This leads to poor conductivity within the sample. For the sample used in Figure 2(a), the magnetoresistance measured is $6.15\% \pm 3\%$ which is low due to poor charge transport within the system.

As the concentration of the nanoparticles is increased, the magnetoresistance values increase very quickly to $32.2\% \pm 3\%$ when the nanoparticle concentration is 6% by volume, as shown in Figure 2(b). This continues until the maximum value of the magnetoresistance of $85.7\% \pm 5\%$ is attained at nanoparticle concentration of 10% by volume as seen in Figure 2(c). However, when the nanoparticle concentration is increased beyond 12%, the magnetoresistance decreases and falls to a value of $10\% \pm 6\%$ at 18% nanoparticle concentration by volume due to too much nanoparticles being present causing stress to the PANI matrix as well as additional defects leading to poor functionality of the device. For nanoparticle concentrations greater than 2%, the magnitude of the current remains approximately constant even after the magnetic field is switched off, exhibiting a memory effect (Figs. 2(b) and 2(c)). For samples with 2% nanoparticle concentration, the resistance of the device remains approximately 3.5% higher than its initial value at the start of the experiment when the magnetic field is switched off at 0.6 T. This shows that it exhibits some memory effect but is not as efficient as when the nanoparticles concentrations are 6%–10% by volume. For instance, as seen in Figure 2(a), when the magnetic field of 0.6 T is switched off, the I-V curve almost traces out the one where the magnetic field was at 0.3 T. In order to verify this, the samples are loaded onto a Quantum Design Physical Property Measurement System (PPMS) and their electrical resistance is measured as the magnetic field is gradually increased from 0 T to 0.6 T. The magnitude of the electrical resistance remains at approximately the same value with small fluctuations between $7.1\text{ M}\Omega$ and $7.3\text{ M}\Omega$ as the magnetic field is gradually decreased from 0.6 T to 0 T as seen in Figure 2(d). Hence, the device exhibits a memory effect.

To reveal that variable range hopping is indeed the dominant mode of transport in this sample which is characteristic of highly disordered systems, we measured the electrical

resistance of the device from 298 K to 80 K using the PPMS without applying any external magnetic field. The formulae of the variable range hopping is given as^{23–25}

$$\rho(T) = \rho_0 e^{\left(\frac{T_{\text{Mott}}}{T}\right)^{\frac{1}{d+1}}}, \quad (1)$$

where $\rho(T)$ is the resistivity at temperature T , ρ_0 is the resistivity at infinite temperature, T_{Mott} is the characteristic Mott temperature which tells us the energy separation between the localized states and d is the dimensionality of charge transport. The best fit is obtained when $\rho(T)$ is plotted against $T^{-1/4}$ as seen in Figure 3(a), indicating 3D charge transport, that is the charge carriers can hop to any iron oxide nanoparticle within the matrix as long as it is within range. The localization length, L_{Loc} of the sample under the effects of different magnetic field strength can be determined from the following formula which is valid under the weak field regime:²⁶

$$\ln\left(\frac{\rho(H)}{\rho(0)}\right) = \frac{5}{2016} \left(\sqrt{\frac{eH}{\hbar}} L_{\text{loc}}\right)^4 \left(\frac{T_{\text{Mott}}}{T}\right)^{\frac{3}{4}}, \quad (2)$$

where $\rho(H)$ is the resistivity when the magnetic field, H is being applied and $\rho(0)$ is the resistivity of the nanocomposite in the absence of any external magnetic field. PPMS measurements were performed by varying the temperature T from 180 K to 298 K and repeated at different external magnetic fields, H . The plots of $\ln(\rho(H)/\rho(0))$ vs $T^{-3/4}$ for the different samples under different magnetic field strengths are shown in Figures 3(b)–3(d). As T_{Mott} remains unchanged under the application of an external magnetic field, the different slopes obtained is attributed to the change in the localization length as the magnetic field strength is varied. The various parameters are computed and summarized in Tables I and II. Table I shows that as the concentration of

FIG. 3. Plots used to determine the dimensionality of the VRH as well the localization length under different magnetic field strengths. (a) A linear plot is obtained when $\ln(\rho/\rho_0)$ is plotted against $T^{-1/4}$ which characterizes a 3D VRH. For this plot, the NP concentration is 6% by volume. (b) Plot of $\ln(\rho(H)/\rho(0))$ vs $T^{-3/4}$ for the different samples under different magnetic field strengths when the NP concentration is 2% by volume. The different slopes are due to the change of the localization lengths in the presence of an external magnetic field. (c) Plot of $\ln(\rho(H)/\rho(0))$ vs $T^{-3/4}$ when the NP concentration is 6% by volume. (d) Plot of $\ln(\rho(H)/\rho(0))$ vs $T^{-3/4}$ when the NP concentration is 10% by volume.

TABLE I. The values of T_{Mott} with different iron oxide nanoparticle concentrations.

Nanoparticles concentration by volume (%)	T_{Mott} (K)
2	7720
6	33 300
10	987 000

the nanoparticles increase, the value of T_{Mott} increases, corresponding to an increase in the energy barrier for hopping from one localized site to another. Thus, T_{Mott} is also a measure of how localized the charge carriers in the system are. For systems with a high degree of localization and a low overlapping of the wavefunctions, the magnitude of T_{Mott} is high.^{23,26} In order for the charge carrier to minimize the energy cost, it would be preferable for them to hop at a further distance. Equation (2) is also known as the wave function shrinkage model and what it means is that the localization length decreases in the presence of an external magnetic field due to lesser extent of overlapping of the wavefunction under the effect of stronger magnetic field strengths as seen in Table II. As the PANI layer separates the iron oxide clusters from one another, the charge carriers have to tunnel from one cluster to the other, and due to the decrease in their localization length, this means that more charge are hopping into each isolated cluster than the rate of charge exiting it. Eventually, it leads to a charge build up and as the concentration of charge carriers inside each cluster increases, the coulombic repulsion force it creates lowers the probability of a charge being able to tunnel into it. This in turn leads to a high resistance state within the nanocomposite. Also, as the system does not show any ferromagnetic transition but instead remains superparamagnetic as seen in Figure 4(a), it is evident that the memory effect is due to this charge trapping effect within the nanocomposite. In order to verify the increase in the extent of localization of charge carriers under the presence of an external magnetic field is further supported by capacitance measurements as shown in Figure 4(b). In the absence of an applied magnetic field, there is minimal capacitance as indicated in the almost flat curve. As the magnetic field strength is increased to 0.6 T, the sample capacitance increases to 4.57 nF from 2.0 nF when the magnetic field strength is 0.2 T, suggesting increased charge trapping. Also, due to the insulative nature of PANI, it helps to prevent the trapped charges from

TABLE II. The change in localization lengths of the different nanocomposites with different iron oxide nanoparticle concentrations under the influence of an external magnetic field from 0.1 T to 0.6 T.

Magnetic field strength	(L_{loc} (2%) (nm))	L_{loc} (6%) (nm)	L_{loc} (10%) (nm)
0.1	82.3	53.7	46.6
0.2	69.9	43.7	36.8
0.3	61.6	36.4	33.6
0.4	55.0	35.0	32.9
0.5	49.6	32.7	30.0
0.6	46.7	30.9	28.6

FIG. 4. SQUID measurement on the magnetization of the nanocomposite and magnetocapacitance measurements under varying magnetic field strength. (a) The nanocomposite exhibit a superparamagnetic response due to the iron oxide nanoparticles and does not exhibit any ferromagnetic behavior, thus suggesting that the memory effect is not due to ferromagnetic transition of the sample. (b) There is minimal capacitance when in the absence of an external magnetic field and the value of the capacitance increases with increasing magnetic field strength. This shows that the charge carriers are trapped in the nanocomposite which probably is the origin of the memory effect in this device.

“leaking out” of the system even when the current is switched off, and hence retaining the memory effect.

In the report on LSMO-PANI nanocomposites,¹⁷ the negative magnetoresistance at room temperature is attributed to the weak localization effect. In the absence of a magnetic field, constructive interference leads to localization of the charge carriers; when a magnetic field is applied, an additional phase term is gained via the vector potential which destroys the constructive interference and hence the localization effects, thus decreasing the electrical resistance. For the Co-C₆₀ compound hybrid system where tunnelling leads to the magnetoresistive effects,¹⁶ the magnetoresistive effects are destroyed at room temperature due to scattering of the electrons’ spin by magnons. In this work, the positive magnetoresistance is attributed to a decrease in localization of the charge carriers in the presence of an external magnetic field, leading to the accumulation of charges within the insulative PANI matrix which is not affected even if the spins are scattered by the magnons since the process is not spin dependent. A similar work on PANI/Fe₃O₄ nanocomposites¹⁹ suggests that the non-insulating form of PANI seem to be important since they require a much higher magnetic field strength of 4 T to get a magnetoresistance above 85% when

the PANI used is semiconducting in nature. In addition, they also did not report any memory effect due to their semiconducting PANI being unable to trap the charge carriers from leaking out.

In summary, this work reports room temperature magnetoresistance as high as 85.7% for a PANI-NP nanocomposite device and have good potential to be used in memory devices since they can retain the trapped charges for a long time. The advantage of such hybrid organic devices over their inorganic counterparts is their ease of fabrication using chemical solution methods, the ability to utilize flexible substrates, lower power consumption, and cost. By further optimizing the fabrication process, it should be possible to create a practical working device which can be used in our day to day applications without the need to use such a high external magnetic field strength at room temperature.

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