

Rapid one-step chemical synthesis of polyaniline-manganese ferrite nanocomposites without external initiator and mechanical agitation

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ABSTRACT

We describe a rapid one-step, room temperature method to chemically synthesize bulk quantities of nanocomposites comprising specifically of manganese ferrite (MnFe_2O_4) and polyaniline (conductive form). Typically a chemical agent, for example ammonium peroxydisulfate, is used to start the polymerization of aniline in the presence of ferrites, and stirring of the reaction system for several hours is also very common. Our approach allows for the nanocomposites to be formed in less than thirty minutes without adding an external polymerization initiator and applying any form of mechanical agitation. This process affords the possibility to grow thin films of polyaniline- MnFe_2O_4 directly on device substrates. Structural, thermal, magnetic and electrical studies did reveal significant chemical interactions between MnFe_2O_4 and polyaniline matrix. The nanocomposites are magnetic semiconductors with long rod-shaped structures of average diameter in the nanometer scale range and optical properties resembling that of conductive polyaniline. They exhibit a positive magnetoresistance across all temperature ranges with a minimum at around 250 K, corresponding to the temperature for their uniform-to-irregular transition in dynamic stability behavior and likewise coinciding with a minimum in their profile of electrical conduction mechanism (one-dimensional variable range hopping below 250 K) – these complementarities are important for hybrid spintronic applications.

Keywords: organic conducting polymers, ferrites, polyaniline, manganese ferrite, magnetic, semiconductor, nanocomposites

1 INTRODUCTION

Nowadays, all attention is particularly directed towards making use of structural, optical and electrical properties of organic conducting polymers in electronic devices, where their roles could be either active or passive. Combination of members of this polymer family with magnetic materials, for example ferrites, brings forth multifunctional products that can equally serve for magnetic purposes in addition to

tunable optical and electrical functions [1-6]. The challenge to arrive at such multifunctional materials, however, is on choosing a straightforward combinatorial approach that is less time-consuming, cost-effective, and does not require too many external chemical ingredients like surfactants and initiating agents.

Polyaniline (PAni) which is amongst the most interesting conducting polymers has been blended with ferrites to produce magnetic composites: this was mainly carried out in-situ in the presence of an external initiator and/or a surfactant while stirring the reaction continuously for a prolonged period of time [1-6]. Mechanical agitation, however, does contribute to aggregation of polyaniline and can indeed be precluded during synthesis [7, 8]. Here, we demonstrate the preparation of magnetic semiconducting nanostructured composites of polyaniline and MnFe_2O_4 under a short reaction time frame and by circumventing the aforementioned conventional method of synthesis. The final characteristics of the resulting composites are evaluated.

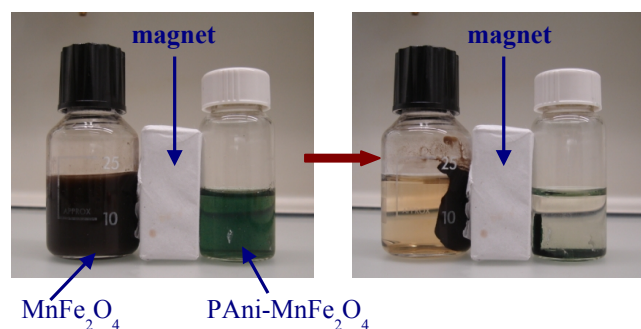


Figure 1. Response of PAni- MnFe_2O_4 nanocomposites to external magnetic field.

2 METHOD

MnFe_2O_4 was prepared by a coprecipitation method [9], and for a typical synthesis, the ratios $[\text{Fe}^{3+}]/[\text{Mn}^{2+}] = 2$ and $([\text{Fe}^{3+}]+[\text{Mn}^{2+}])/[\text{OH}^-] = 0.06$ were used. The suspension was digested at 100 °C for 90 minutes, and the magnetic nanoparticles were thereafter washed several times with water. For the preparation of polyaniline- MnFe_2O_4 nanocomposites, 0.042 M MnSO_4 + 0.084 M $\text{Fe}_2(\text{SO}_4)_3$ in

2.1 M NaOH solution was added to 0.140 M aniline in 0.5 M H₂SO₄ solution. The reaction was allowed to run for 30 minutes under room temperature conditions without mechanical stirring. Excess metal cations were removed from the green-colored suspension by repeated magnetic decantation. Figure 1 shows that the obtained composites possess magnetic properties and can respond easily to an external magnetic field, similar to MnFe₂O₄ nanoparticles.

Various characterization techniques were used to investigate the chemical structure, morphology, and physical properties of the PAni-MnFe₂O₄ nanocomposites [7, 12]. To confirm the actual presence of PAni, Fourier transform infrared (FT-IR) spectra of dried samples were recorded on a Perkin-Elmer BXII spectrometer with KBr pellets, and a Cary 500 Scan was used to record the UV-vis absorption spectra of the samples dissolved in N-methyl-2 pyrrolidone (NMP). Morphology and size were studied on a LEO 1530 (FEG) microscope equipped with a cryogenic stage (Fa. Bal-Tec, Balzers, Liechtenstein). The sample was freeze-etched in a BAF 060 freeze-etching device (Fa. Bal-Tec, Balzers, Liechtenstein) and was not coated for the cryogenic scanning electron microscopy (cryo-SEM). Differential scanning calorimetry (DSC) measurements were performed in a nitrogen atmosphere using a DSC Q1000. First heating was carried out from 25 °C up to 200 °C at a rate of 10 °C min⁻¹ to remove water and to delete previous thermo-temporal history. Temperature dependence of conductivity measurements were carried out using a four-point probe method. Dried powder (20 mg) was pressed into a pellet (radius = 4 mm and thickness = 300 μm) at a load of 3 tons under vacuum for 15 minutes. The pellet was mounted on a sample puck, electrical contacts were silver glued, and puck was then inserted into the chamber of Quantum Design Physical Property Measurement System (QDPPMS). Cooling and heating cycles were performed at a constant rate within 100-343 K in a zero field and in a field of 81000 Oe (81 kOe).

3 RESULTS AND DISCUSSION

A green-colored suspension is immediately formed on addition of NaOH solution containing Fe³⁺ and Mn²⁺ ions to the acidic solution of aniline. This is the first indication that emeraldine salt which is a conductive form of polyaniline has been produced. As shown in Figure 1, response of this green suspension to the external magnetic field confirmed the successful encapsulation of MnFe₂O₄ by PAni. Concurrent precipitation of the magnetic nanoparticles and polymerization of aniline is possible due to the differences in pH as well as specific interactions between the aniline monomers and the metal cations, with likelihood of the monomers acting as ligands for the metal ions to form short-lived intermediate complexes. This leads eventually to close interactions in the composites, i.e. between the conducting polymer matrix and the insulating magnetic Mn ferrite nanoparticles whose oxygen atoms are susceptible to enter into hydrogen bonding with the PAni chains.

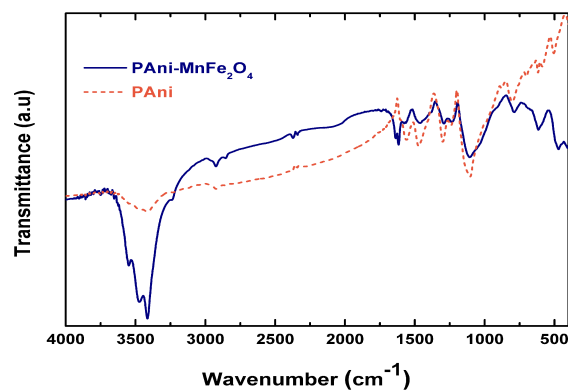


Figure 2. FTIR spectra of PAni sample and PAni-MnFe₂O₄ nanocomposites.

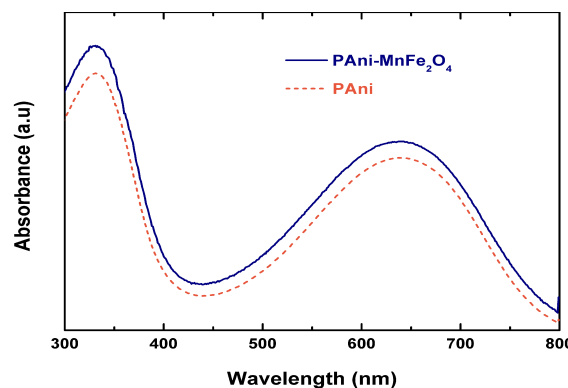


Figure 3. UV-vis spectra of PAni sample and PAni-MnFe₂O₄ nanocomposites.

Figure 2 shows the FTIR spectra of PAni and PAni-MnFe₂O₄. The presence of characteristic bands of PAni in the spectrum of the nanocomposites proves that PAni was effectively formed within the 30 minutes reaction window. The bands at 1585 cm⁻¹ and 1498 cm⁻¹ correspond to the characteristic C-C stretching of the quinoid and benzenoid rings, respectively, while the vibrations at 1302 cm⁻¹, 1146 cm⁻¹, and 825 cm⁻¹ are associated with C-N stretching modes of the benzenoid ring, modes of N=Q=N (Q refers to the quinonid-type rings), and C-H out-of-plane bending, correspondingly. The N-H stretching mode of PAni-MnFe₂O₄ located at about 3447 cm⁻¹ appears stronger in intensity than that of PAni, indicative of specific interaction between the ferrite nanoparticles and the PAni chains. Another indication of such an interaction is seen in the C-C stretching of the quinoid ring at around 1585 cm⁻¹, which is rather splitted in the spectrum of the nanocomposites. Assignments for all these bands are in accordance with those earlier reported [7, 10].

Figure 3 clearly indicates that there are no noticeable differences between the spectra of PAni and PAni-MnFe₂O₄, with only the two characteristic absorption bands of PAni present at around 329 nm and 640 nm. The band at around 329 nm is attributed to π - π^* transition of the benzenoid rings, while exciton transition from benzenoid to

quinoid segments corresponds to the absorption band at around 640 nm [7, 11]. These UV-vis and FTIR results confirm that the one-step rapid method without introduction of the conventional APS initiator yielded nanocomposites which retained the structural and optical characteristics that are distinctive of conductive polyaniline.

Representative images of PANi-MnFe₂O₄ as presented in Figure 4 reveal long rod-shaped structures of nanosized diameters. The average length of the rods is 4-6 μm, while the average diameter is in the range of 500-700 nm. MnFe₂O₄ nanoparticles produced by coprecipitation method with a $([Fe^{3+}]+[Mn^{2+}])/[OH^-]$ value akin to the ratio we used for the synthesis of these nanocomposites have average particle size of around 12 nm [9], while short rod-like structures with average diameter size of less than 100 nm are features of PANi produced from an acidic solution [7].

DSC traces of PANi and PANi-MnFe₂O₄ nanocomposites are shown in Figure 5. A broad endothermic peak due to loss of water can be observed in the first heating sequence of both samples. Melting peaks are obvious in the trace of the nanocomposites as compared to that of the PANi. Reappearance of these melting peaks during the second heating sequence suggests a crystalline nature for PANi-MnFe₂O₄ nanocomposites, which could be attributed to the presence MnFe₂O₄ nanoparticles. Absence of the melting peaks in the trace of PANi indicates a dominant amorphous structure [12]. The glass transition temperature, T_g , of the nanocomposites seems not apparent in contrast to that of PANi which is pronounced at around 20 °C.

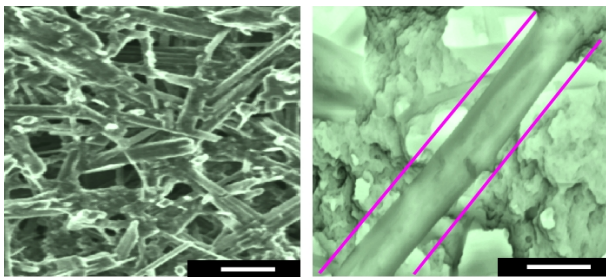


Figure 4. SEM images of PANi-MnFe₂O₄ nanocomposites (scale bars: left image = 2 μm and right image = 1 μm).

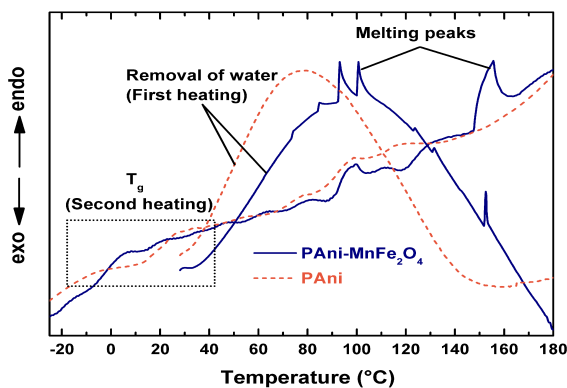


Figure 5. DSC traces of PANi sample and PANi-MnFe₂O₄ nanocomposites for first and second heating cycles.

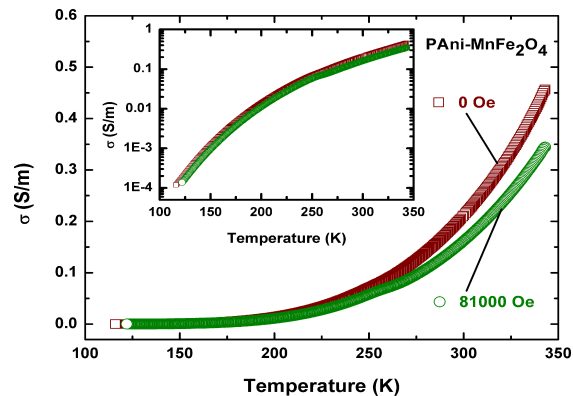


Figure 6. Electrical conductivity of PANi-MnFe₂O₄ as a function of temperature with (81 kOe) and without (0 Oe) applied magnetic field. (Inset = Log conductivity plot).

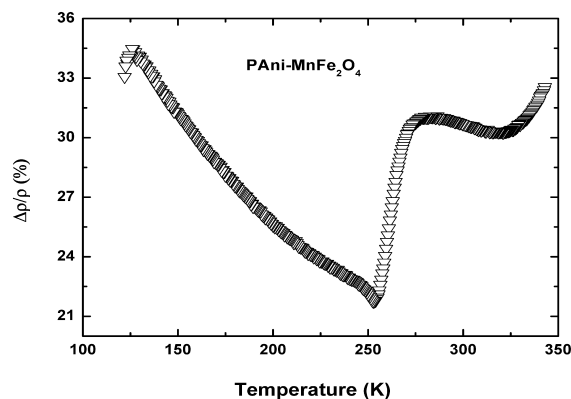


Figure 7. Magnetoresistance ($\Delta\rho/\rho$) of PANi-MnFe₂O₄.

Figure 6 substantiates our earlier contention that the green-colored magnetic suspension (Figure 1) obtained within a short time frame without an external initiator (e.g. APS) is composed of emeraldine salt, a conductive form of PANi. It can be observed that the nanocomposites exhibit intrinsic semiconducting properties despite the presence of the insulating magnetic ferrite nanoparticles, which have close interaction with the PANi matrix. This semiconducting behavior is comparable with that of PANi [7, 12]. Figure 6 further indicates that the value of resistivity (reciprocal of conductivity, $\rho = 1/\sigma$) clearly increased on application of a magnetic field of 81 kOe, and thus gave rise to a positive magnetoresistance, $\Delta\rho/\rho = [\{\rho(81 \text{ kOe}) - \rho(0 \text{ Oe})\}/\rho(0 \text{ Oe})] \%$, across all the temperature ranges as depicted in Figure 7. Spin fluctuations due to the applied field could possibly explain this positive magnetoresistance. It could also be that the strong magnetic forces somewhat altered the mechanical connectivity of the structures. Figure 7 shows that the magnetoresistance exhibits a minimum at around 250 K, which is coincident with the temperature for the uniform-to-irregular transition in dynamic stability behavior (Figure 8). Thermally-activated asynchronous motions in such a polymer system do play a major role in irregular dynamic stability at elevated temperatures [12].

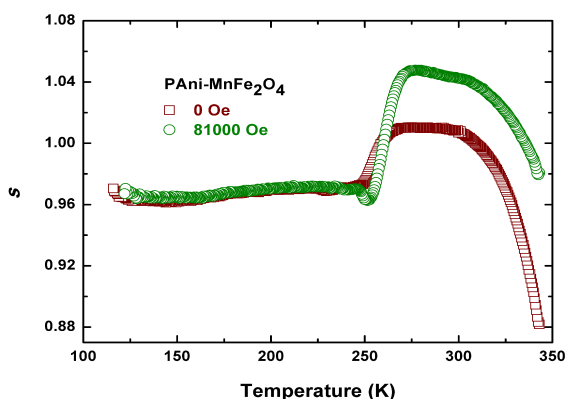


Figure 8. Dynamic stability of PANi-MnFe₂O₄ in zero field and in applied field of 81 kOe.

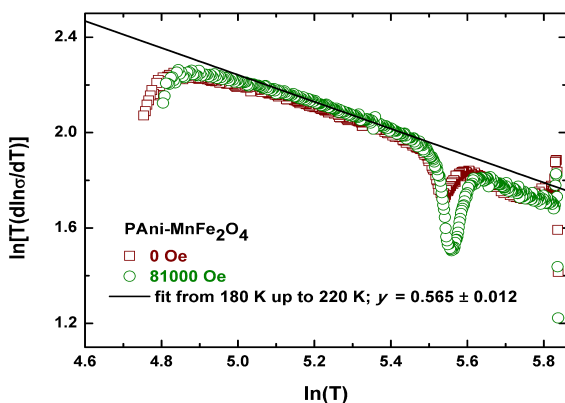


Figure 9. Electrical conduction mechanism of PANi-MnFe₂O₄ in zero field and in applied field of 81 kOe. Symbols represent data, while line is fit to the data.

Below 250 K, the positive magnetoresistance (Figure 7) displays a consistent pattern while the dynamic stability profiles in zero field and in 81 kOe (Figure 8) also exhibit uniform behaviors which are relatively overlapped. The magnetoresistance appears irregular above 250 K, mirroring the irregular dynamic stability behavior at elevated temperatures. This transition temperature may be a critical point at which the thermally-induced asynchronous motions of the system become suppressed, leading to reduced spin motions which are then synchronized with the entire motion of the magnetic semiconducting polymer system at lower temperatures – that is, these observed uniform behaviors below 250 K for both magnetoresistance and dynamic stability (0 and 81 kOe). This scenario is also evident in the electrical conduction mechanism of the nanocomposites (Figure 9), where ill-defined behavior dominates above 250 K. Dynamic stability of a semiconducting polymer system typically reflects in its electrical conduction mechanism [12], hence the corresponding minimum at around 250 K in Figure 9. Below 250 K, PANi-MnFe₂O₄ nanocomposites follow a one-dimensional variable range hopping (1D VRH; for $\gamma=1/[1+Dimension\ of\ VRH]$), which is consistent with the typical 1D VRH process in PANi [12].

4 CONCLUSION

We produced magnetic semiconducting nanocomposites composed of polyaniline and manganese ferrite by an effective one-step chemical method without introducing an external initiating chemical agent and/or surfactant to start the polymerization. Under room temperature conditions and without mechanical agitation, the product was obtained in less than thirty minutes. Evidence of strong interaction between the ferrite and polyaniline was provided by various characterization techniques. The nanocomposites exhibit a positive magnetoresistance which has behavior patterns mimicking those of dynamic stability and electrical conduction mechanism, and their relationships can find potential applications in hybrid spintronic devices.

5 ACKNOWLEDGEMENT

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