Polyaniline/Fe$_3$O$_4$-RGO Nanocomposites for Microwave Absorption

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Abstract. Fe$_3$O$_4$ nanoparticles were synthesized by co-precipitation of ferric chloride (FeCl$_3$) and ferrous chloride (FeCl$_2$). Reduced graphene oxide (RGO) was prepared by reducing the graphene oxide, which was synthesized by Hummer’s method, using hydrazine hydrate. Three nanocomposites based on sodium dodecyl benzene sulphonate (SDBS)-doped polyaniline were synthesized through in situ polymerization in the presence of the fillers (i) Fe$_3$O$_4$, (ii) reduced graphene oxide (RGO) and (iii) Fe$_3$O$_4$-decorated RGO respectively. The synthesized PANI and the composites were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and transmission electron microscopy. Their microstructures, electrical conductivities, and EMI shielding effectiveness were studied. The nanocomposite containing 10 % RGO showed the maximum electrical conductivity and the one with 10 % RGO and 10 % Fe$_3$O$_4$ showed the maximum EMI shielding effectiveness of 7.5 dB for a 1 mm thick sample.

1. Introduction

The enormous advancements in the field of electronics, including handheld electronic devices, have given rise to higher chances of electromagnetic interference (EMI), which can be disruptive to the electronic equipment. Specifically, the extensive growth in the field of gigahertz electronic equipment and communication devices has caused significant electromagnetic pollution. There are also safety concerns for humans and animals [2], which necessitate the reduction of the electromagnetic radiation from devices using EMI shielding materials [7]. EMI shielding strategies commonly use metals which tend to shield by reflecting the radiation owing to their high electrical conductivity. But the metals have drawbacks such as being heavy, prone to corrosion, and allowing very restricted tuning of their shielding effectiveness. Also, reflecting the electromagnetic radiation might not be acceptable for certain applications. [1]

Polymer-based shielding materials have been the subject of considerable research over the past few decades as they tend to absorb the radiation, are lightweight, do not get corroded and are processible.

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However, most polymers are insulating and there is a smaller variety of conductive polymers, which are often required for this application since shielding effectiveness improves with conductivity. The electrical conductivity of polymers can also be improved by adding conducting fillers like graphene, metallic fillers, graphene oxide, carbon fiber, carbon nanotubes, and so on. Shui and Chung added 7.0% volume nickel filaments into a polyether sulfone (PES) matrix, resulting in a very high EMI shielding effectiveness of 86.6 dB for a sample of thickness 1 mm [1]. Nanoparticles with the composition of Mn0.3Ni0.4Zn0.4 Fe3O4 were used as fillers to prepare PANI composites, and a high EMI SE of 49.2 dB was obtained in a sample having a thickness of 2.5 mm [2]. Polyaniline is a well-studied conductive polymer, and has been found to be suitable for this application because of its relatively easy processability, good environmental stability, easy polymerization and the convenience of adjusting its electrical conductivity by using different dopants. However, its shielding effectiveness is limited. In order to improve the shielding effectiveness, it is desirable to add conductive and magnetic fillers [7]. Nano-sized fillers are preferable due to their improved dispersability and lower percolation thresholds.

In this paper we report a three-component nanocomposite consisting of electrically conductive reduced graphene oxide and magnetic Fe3O4 nanoparticles in a matrix of doped polyaniline.

2. Experimental

2.1. Materials
Graphite with an average size <20 micrometer (Aldrich), aniline (Merck), iron(II) chloride and iron(III) chloride (Sigma Aldrich), SDBS (Loba Chemie), ammonium persulphate (Merck), sulphuric acid (Rankem), potassium permanganate (Fisher Scientific) were purchased commercially. Aniline was distilled and was kept under refrigeration before use.

2.2. Synthesis of Fe3O4 nanoparticles
Ferric chloride (FeCl3) and ferrous chloride (FeCl2) in a molar ratio of 2:1, were dissolved in deionized water to form an aqueous solution. The solution was heated for 10 minutes at 50°C. Ammonia solution was added to this drop by drop while keeping the solution under constant stirring at 70°C. Black colored particles of iron oxide were precipitated. These particles were then separated by magnetic decantation and then were washed several times with distilled water. The black colored magnetite powder was then dried in a hot air oven at 75°C for 10 hours [9].

2.3. Synthesis of RGO and Fe3O4 decorated RGO
Graphene oxide (GO) was synthesized by Hummers’ method from graphite flakes. Graphite (1 g) was added to 23 mL of 98% H2SO4 solution [10]. The solution was stirred for 8 hours after ultrasonication. Then 3g potassium permanganate (KMnO4) was gradually added into the above solution, and stirred at 40°C for 30 min and then at 70°C for 1 hour. Deionized water (50mL) was added into the mixture solution and stirred for 30 min at 100°C. Finally, 150 mL of distilled water and 10 mL of H2O2 were added. The product was centrifuged and washed with 5% HCl several times and later with deionized water [3].

Reduced graphene oxide (RGO) was prepared from the above synthesized GO as follows. The GO dispersion (100mL; 2mg/mL) was prepared by ultrasonication. Hydrazine hydrate (0.4 mL) was added to it and stirred at 95°C for 2 hours. The product was collected by vacuum filtration, washed with distilled water and dried at 50°C for a day.

Fe3O4-decorated RGO was prepared by adding RGO to an aqueous solution containing ferric chloride (FeCl3) and ferrous chloride (FeCl2) and ultrasonicating the solution, followed by the procedure for Fe3O4 synthesis described above.
2.4. Preparation of the nanocomposites
The PANI/Fe₃O₄ nanocomposites were prepared [4] by chemical oxidative polymerization of aniline. Fe₃O₄ (1.0g) nanoparticles synthesized above, was added to a 100ml solution containing 0.4 M aniline and 0.08 M SDBS. The solution was cooled to -5°C after ultrasonication for 15 minutes and a pre-cooled solution of ammonium persulphate (10.50g, 0.46 M) was added gradually to it. The polymerization was conducted at -5°C for 3 hours with continuous stirring. The molar ratios of aniline to SDBS and aniline to ammonium persulphate were 5:1 and 1:1.15 respectively. The reaction mixture was stirred for 1 h. The blackish green precipitate obtained was filtered, washed with double distilled water till colorless, and the filtrate obtained was dried at 75°C for 24 h under vacuum. The composites of PANI/RGO and PANI/RGO-Fe₃O₄ were similarly prepared.

2.5. Characterization
Powder X-Ray diffraction (XRD) analysis was done using Rigaku, Ultima IV diffractometer using CuKα radiation of wavelength λ=1.54 Å. Measurements were carried out in the range 2θ=10° to 100°. Average size of the Fe₃O₄ particles was found out using Scherrer’s equation.

\[ \Gamma = \frac{0.9 \lambda}{\beta \cos \theta} \]  

where β is the full width half maximum (FWHM) of the strongest peak, λ is the wavelength of the X-ray (λ = 1.5406 Å) and θ is the diffraction angle. FTIR spectra were recorded on a Nicolet iS10 instrument in the range 400-4500 cm⁻¹. An FEI Tecnai G230 HRTEM instrument, operated at 200kV was used to study the microstructure of the composite samples, which were drop casted on a carbon-coated Cu grid.

Electrical conductivity was measured using a four-point probe with a Keithley 6221 DC and AC source and Keithley 2182A nanovoltmeter. For the test the samples were pressed into pellets using a hydraulic press (PG 1055) applying a pressure of 5000 kg/cm² at room temperature.

EMI shielding test was carried out on a microwave bench in the X-band (8-11 GHz) using Scientech 4061 frequency counter, with an input power of -12.8 dB. Samples were made into films of 1mm thickness and 12cm diameter by casting from an ethanol dispersion and drying out in a petri dish at 50°C. Samples were placed equidistantly at 30cm from both the source and the receiver. A reference run was conducted without any sample (air), and an output of -17.5 dB was recorded.

3. Results and discussion
3.1. XRD study
Fig. 1 and Fig. 2 shows the XRD patterns of the samples prepared. For PANI, peaks are found at 2θ=17°, 20° and 25° corresponding to the (0 1 1), (0 2 0) and (2 0 0) planes respectively [5]. The XRD pattern of the Fe₃O₄ synthesized, shows peaks at 35.53°, 43.45°, 57°, and 62.73° correspond to the planes (311), (400), (511), (440) (JCPDS 77-1545). The cubic lattice parameter was calculated to be 8.364 Å which matches with the literature value (a = 8.396 Å; JCPDS 19-0629). The average particle size of the Fe₃O₄ was determined to be about 11 nm using the Scherrer’s equation (Eq. 1). In the case of RGO, the diffraction peaks at 24° and 43° correspond to the (002) and (100) planes of RGO [6]. In Fe₃O₄-decorated RGO we can see that these peaks of RGO have merged with the peaks of Fe₃O₄ from around 20° to 40°. This shows that there was some interaction between the RGO and Fe₃O₄.
Fig. 1. XRD spectra of PANI, Fe$_3$O$_4$, RGO-Fe$_3$O$_4$ and RGO (anti-clockwise from bottom left)

XRD pattern of Fe$_3$O$_4$ showed sharp and strong peaks indicating its high crystallinity. In the composites, the peaks observed were consistent with those of the individual components, with reduced intensity of the crystalline peaks especially of Fe$_3$O$_4$ due to its relatively low content in the composite as opposed to the pure component.

Fig. 2. XRD spectra of PANI/RGO, PANI/Fe$_3$O$_4$ and PANI/Fe$_3$O$_4$-RGO (clockwise from top left)
Comparing the XRD spectra of PANI and PANI/RGO composite, additional peaks were found at 30° to 50° in the spectra of the composite. This includes the peak of RGO at 43° corresponding to the (100) plane. This shows that the added RGO has interacted with the PANI. Similarly in the XRD spectra of PANI/Fe₃O₄-RGO composite, we can find the characteristic peaks of both Fe₃O₄ and RGO in addition to that of PANI. It suggests that the fillers have indeed influenced the properties of the base polymer.

3.2. FTIR study
The FTIR spectra of GO, RGO, Fe₃O₄, RGO-Fe₃O₄, PANI and each composites were recorded (Fig. 6-8) PANI showed peaks of the N-H, C-N, SO₃H of SDBS, C-N+ and C=N at 3240, 1128, 503, 1300, and 1573 cm⁻¹ respectively. GO showed peaks for C-O, C=O, C-H of GO at 1056 and 1114, 1733 and 1630, and 2858 cm⁻¹ respectively. Comparing the spectra of RGO with GO, we can see that the peaks associated with the C-O group have reduced in RGO and the peak associated with the C=O has disappeared. This confirms the reduction of GO to RGO. Fe₃O₄ showed its characteristic peak at 570 cm⁻¹ due to the stretching of Fe-O bond.

In PANI/RGO, the peak of N-H was seen to have shifted by 15 cm⁻¹ to the left. While in PANI/RGO-Fe₃O₄ the shift was 30 cm⁻¹. The peak corresponding to the Fe-O bond was also found to shift in the same fashion. The greater extent of shifts in the Fe-O and N-H peaks indicates increased interactions between the components of the composite.

3.3. TEM analysis
Transmission electron microscopy images and SAED pattern of the composites were taken (Fig 3-5). The high resolution images show the Fe₃O₄ particles dispersed in the polyaniline matrix. The average particle size of Fe₃O₄ was found to be about 10nm. From these images it can be seen that the Fe₃O₄ particles have precipitated on the RGO to form Fe₃O₄-decorated RGO. The diffraction pattern of the SAED pattern matched well with the lattice planes from the XRD peaks.

![TEM images of PANI-Fe₃O₄](image)

Fig. 3. TEM images of PANI-Fe₃O₄
3.4. Electrical conductivity study
The RGO and Fe₃O₄ contents of the PANI composites affect the electrical conductivity. The addition of Fe₃O₄ reduced the electrical conductivity of the composite while RGO improved it significantly. Pure PANI (undoped) and SDBS doped PANI have been reported to have an electrical conductivity of $1.8 \times 10^{-10}$ S/cm and $1.2 \times 10^{-2}$ S/cm respectively [4]. DC electrical conductivity of the sample was measured using a four point probe.

Fig. 4. TEM images of PANI-RGO
Electrical conductivity of the synthesized PANI measured to be $1.18 \times 10^{-2}$ S/cm. The addition of 10% Fe$_3$O$_4$ decreased the electrical conductivity of the nanocomposite to $0.64 \times 10^{-2}$ S/cm due to the low electrical conductivity of Fe$_3$O$_4$. Similar results were reported by S.S. Umare, et al.[4] The composite prepared with 10% RGO in the present study, led to a five-fold increase electrical conductivity to $6.5 \times 10^{-2}$ S/cm. The composite having 10% of both Fe$_3$O$_4$ and RGO exhibited a conductivity of $4.9 \times 10^{-2}$ S/cm which is intermediate to that of the other composites. This is due to the Fe$_3$O$_4$ particles, around the RGO particles partially blocking the conductive paths provided by RGO.
Fig. 6. FTIR spectra of RGO, GO and Fe$_3$O$_4$

Fig. 7. FTIR spectra of the composites
3.5. EMI shielding effectiveness test

Table 1 shows the output power and shielding effectiveness of the samples. A glass sample was run as a reference. It can be understood from these results that the fillers Fe$_3$O$_4$ and RGO can greatly improve the EMI shielding effectiveness of the conducting polymer polyaniline. Fe$_3$O$_4$ alone could increase the shielding effectiveness of the polymer by six times while RGO alone could only improve the shielding effectiveness by three times. PANI/RGO-Fe$_3$O$_4$ showed a shielding capacity far superior to both the other composites. The magnetic susceptibility of Fe$_3$O$_4$, in combination with the high electrical conductivity of RGO, are responsible for the enhancement in the shielding effectiveness.

Table 1. Output power and shielding effectiveness of PANI/RGO-Fe$_3$O$_4$ composites.

| Sample            | Glass | PANI | PANI/Fe$_3$O$_4$ | PANI/RGO | PANI/RGO-Fe$_3$O$_4$ |
|-------------------|-------|------|-----------------|----------|---------------------|
| Output Power      | -18   | -18.5| -21             | -19.5    | -25.5               |
| SE (dB)           | -     | 0.5  | 3               | 1.4      | 7.5                 |

4. Conclusion

Polyaniline-based nanocomposites containing Fe$_3$O$_4$ and reduced graphene oxide (RGO) were investigated for their microwave absorption behaviour. The nanocomposites consisted of Fe$_3$O$_4$, RGO and Fe$_3$O$_4$-decorated RGO in a polyaniline matrix. XRD studies showed that the Fe$_3$O$_4$ nanoparticles are highly crystalline and FTIR studies indicated good interaction between the Fe$_3$O$_4$ and the N-H groups of polyaniline (PANI).

With the addition of 10% RGO, the DC electrical conductivity of PANI increased almost five times and the shielding effectiveness increased by 2.5 times to 1.4 dB. Even though the addition of 10% Fe$_3$O$_4$ reduced the conductivity of PANI by 50%, it increased its shielding effectiveness to 3 dB, which was almost 6 times that of pure PANI. The nanocomposite with 10% Fe$_3$O$_4$ and 10% RGO had an electrical conductivity of 4.9x10$^{-2}$ S/cm and it showed the highest shielding effectiveness of 7.5 dB. Thus, we see that although Fe$_3$O$_4$ decreased PANI conductivity drastically, it improved the composite’s shielding effectiveness significantly due to its magnetic properties. Similarly, RGO improved the nanocomposites electrical conductivity dramatically but falls short of Fe$_3$O$_4$ in improving shielding effectiveness of the composite. The combination of the two fillers provides a synergistic enhancement of the shielding effectiveness. Further studies to optimize the proportions of the fillers to suit different applications are likely to yield further improvements in the shielding effectiveness of the composites.

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