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In-situ synthesis of $(Mg_{0.5}Zn_{0.5})Fe_2O_4$-graphene oxide nanocomposite for broadband microwave absorption in GHz frequency range

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Abstract

We report the in-situ synthesis of $(Mg_{0.5}Zn_{0.5})Fe_2O_4$-graphene oxide (MZF-GO) ferrite nanoparticle hybrid nanocomposite by auto-combustion technique followed by fabrication of homogeneous, structurally stable thin layer (~100-120 μm) of nanocomposite-polyurethane coating on metallic substrate (Al) and its application on the properties of broadband microwave absorption over the gigahertz (GHz) frequency range. Microstructure studies of nanocomposites depicted that small sized ferrite nanoparticles (~ 24 ± 6 nm) are grafted on and through the graphene layers, which forms a homogeneous coating. The nanocomposite-polymer coating demonstrated excellent broadband absorption properties with absorptivity of greater than 85%. The nanocomposite-polymer coating showed good absorptivity over the frequency band of 4-15 GHz, which has numerous practical applications as radar absorbing materials (RAM), stealth technology, electromagnetic shielding, and many more.

1. Introduction

The rapid growth and utilization of electrical and electronic devices in computer technology, communication devices and military applications has led to increased electromagnetic pollution which has resulted in the development of advanced electromagnetic interference shielding materials [1]. Ceramic soft ferrites are of considerable interest as EMI shielding materials due to their tunable magnetic properties, durability and cost. The microwave absorption properties in specific frequency regions of such materials depend on its coercivity, remanence, magnetization, anisotropy constants and Neel temperature. The magnetization and Neel Point can be changed by chemically substituted different size ions and thus a wide variety of soft ferrites can be synthesized which, are useful for EMI shielding purposes [2,3]. Graphene oxide, which is atomically thin monolayer graphitic allotrope and has a high surface area [4] and high dielectric permittivity [5], when added to the ferrite enhances its microwave absorption properties while enhancing the strength vs. weight ratio. It also solves the problem of reduced microwave absorption of soft ferrites due to high magnetic loss with low impedance matching and broadens the bandwidth of absorption. It is a well-known fact that the polarity of graphitic materials itself improve the broadband absorption properties in the GHz frequency range [6]. In this context, it is better idea to develop magneto dielectric hetero junctions formed by the magnetic and dielectric interface of ferrite and graphene, which may acts as center of microwave attenuation, thus, improving the absorption properties.

In this work we demonstrate the in-situ synthesis of $Mg_{0.5}Zn_{0.5}Fe_2O_4$ ferrite (MZF)-GO nanocomposite via sol-gel auto-combustion process. The structural characterization of the nanocomposite was performed using XRD and TEM. An ultra-thin coating was prepared by dispersing the as synthesized nanocomposite in thermoplastic polyurethane elastomer (TPU) and measured for microwave absorbing properties in an anechoic chamber using a vector network analyser (VNA).

2. Experimental

2.1 Preparation of Graphene oxide

Modified Hummers method was used to synthesize graphene oxide [7]. Briefly, in this process 3.0 g of flaky graphite (~150μm flakes; Merck, Germany) and 18 g of $KMnO_4$ was added to 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360 ml : 40 ml). The solution was heated for 12 h at 45 °C and cooled to room temperature followed by pouring 400 ml ice into the solution. On adding 30% H_2O_2 into the solution it turned into a yellowish orange color, which was then filtered and the filtrate washed thoroughly with de-ionized water, methanol and ethanol. The washed filtrate was dried overnight in vacuum oven at 60° C.

2.2 Preparation of $Mg_{0.5}Zn_{0.5}Fe_2O_4$-graphene oxide scaffold

The $Mg_{0.5}Zn_{0.5}Fe_2O_4$ was synthesized by sol gel auto combustion method. A solution was prepared by adding appropriate molar amount of Mg $(NO_3)_2$. $6H_2O$, Zn $(NO_3)_2$. $6H_2O$ and Fe $(NO_3)_3$. $9H_2O$ in deionized water. Citric acid (anhydrous) was added to the solution and ammonia solution was used to adjust the pH level at 6. After stirring the solutions at room temperature for 30 minutes graphene oxide was added to the solution and ultra- sonicated for 15 minutes. GO was added into the solution with the w/w ratio of MZF and GO varying as 1:1. This sample will hereby be addressed as MZF-GO50 throughout the manuscript where 50 is the percentage of graphene oxide added in the composite. The ultra-sonicated sample was evaporated at 100° C in a hot plate while continuously stirring until a thick viscous gel formed. The temperature was further increased and the gel ignited in air forming brown powder. The as burnt powder was calcined at 600° C for 2h.

2.3 Nanocomposite coating fabrication

Magnesium zinc ferrite- graphene oxide nanocomposite and TPU was taken in 1:1 w/w ratio. TPU was dissolved in Dimethylformamide (DMF) by heating it at 100° C while continuously stirring it and MZF-GO nanocomposite powders were added to the solution and sonicated in high power probe sonicator for 15 minutes. The solution was transferred to a hot plate at 100 °C and an aluminium substrate (152 mm x 152 mm) was coated with MZF-GO-polymer nanocomposite by hand brushing. Figure 1 shows an aluminium plate coated with the MZF-GO-TPU nanocomposite with diagonal distance almost ~ 9 inch.

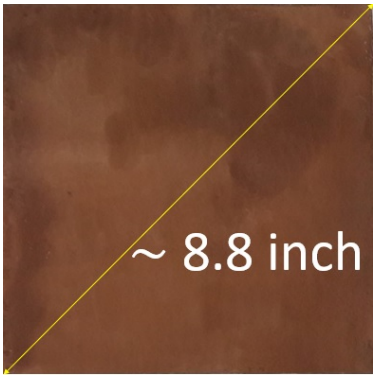

Figure 1. Shows the pictographic image of a MZF-GO-TPU coating on aluminum substrate

3. Results and Discussions

We synthesized $Mg_{0.5}Zn_{0.5}Fe_2O_4$ and GO nanocomposite by sol gel auto combustion method. Sol gel auto combustion is very fast exothermic reaction between an oxidiser and fuel. For the synthesis of $Mg_{0.5}Zn_{0.5}Fe_2O_4$ metal nitrate salts were used as oxidiser and stoichiometric amount of anhydrous citric acid as fuel and large amount of gases evolved as shown in the following reaction (1)-

0.5[Mg $(NO_3)_2.6H_2O$] +**0.5**[Zn $(NO_3)_2.6H_2O$] +2 [Fe $(NO_3)_3.9H_2O$] +**2.22**$C_6H_8O_7$ =

$Mg_{0.5}Zn_{0.5}Fe_2O_4$+**4**N_2+**13.32**CO_2+**32.88** H_2O……..... (1)

The heat of the reaction (Q) and adiabatic flame temperature (T_{ad}) were calculated using formulas (1) and (2) and enthalpy of formation and specific heat of the products and reactants from well-established thermodynamic tables were used [8,9]. Table 1 shows the heat of reaction, adiabatic temperature and moles of gases evolved during reaction.

$Q = \Delta H_j° = \sum_j n_j A_j \Delta_f H_j° - \Sigma_i n_i \Delta_f H_i°$……. (1)

Where, i and j specify reactants and products respectively and n_i and n_j are the amount of reactants and products.

$T_{ad} = T_o + Q/C_p$.....(2)

Where, $C_p = \sum_j n_j A_j$ is the average specific heat capacities of the products at room temperature

Table 1:

C/N mole ratio	Q(kJ/mol)	T_{ad} (K)	Moles of gases evolved
0.27	2065.30	1437.28	50.2

The structural and phase analysis was carried out in X-Ray diffraction (Rigaku, Japan) analysis instrument. Figure 2 shows the X-Ray diffraction profile of the synthesized samples, which were identified using standard line profile JCPDS data (#01-088-1942). MZF-GO50 shows the spinel structure with its most intense reflection at (311) plane. It can be observed that there is a significant amount of impure peaks, which are identified as Fe_2O_3 peaks, and C peaks, which are primarily owing to the presence of GO.

Figure 3 shows the data obtained from Fourier Transform Infrared spectroscopy (FTIR) (THERMO Electron Scientific, Instruments LLC, Model No: Nicolet iS5) of MZF-GO50 sample. The occurrence of C-O, C-C and O-H bonds in the spectrograph confirms the presence of graphene oxide. The characteristic peak of MZF was also found at 544 nm in the FTIR spectrum.

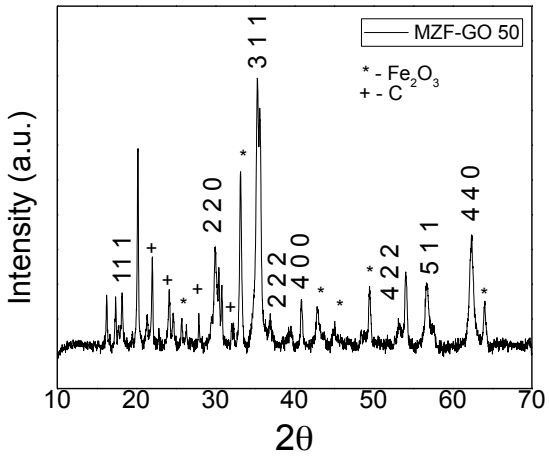

Figure 2. Shows the x-ray diffraction analysis of the MZF-GO50 sample.

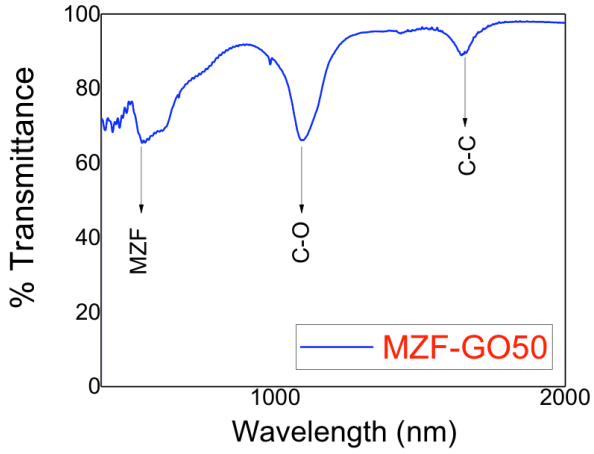

Figure 3. Fourier transform infrared spectrograph of NZF-GO nanocomposites with various ratios of NZF and GO.

Figure 4a shows the morphology of MZF-GO50 nanocomposite, which was characterized using a scanning electron microscope (SEM) (NOVA FESEM 450, FEI USA). Figure 4a illustrates the topology of as synthesized MZF-GO nanocomposite where small Mg-Zn ferrite nanoparticles were found to be grafted on GO layers. Some of the nanoparticles are also found to be intercalated through the GO layers as depicted in Figure 4a. Furthermore, the particle size and morphology of MZF-GO50 nanocomposite was characterized using a TECNAI G2 20 TWIN (FEI, USA) transmission electron microscope (TEM) where the as-synthesized nanocomposite sample was dispersed in methanol and drop casted onto a TEM grid. Figure 4b demonstrates the homogeneously dispersed MZF over GO sheet is observed for MZF-GO50 thereby creates large interfacial contact between NZF nanoparticles and GO.

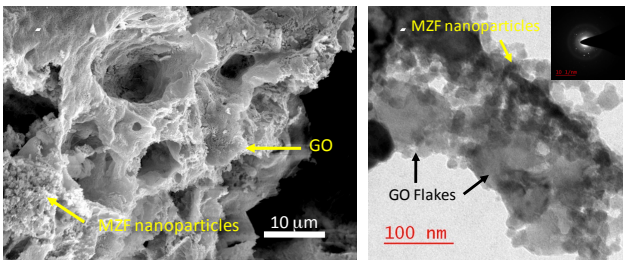

Figure 4: (a) Illustrates the scanning electron micrograph of the MZF-GO50 nanocomposite sample; (b) demonstrate the transmission electron micrograph of MZF-GO50 sample and selected area electron diffraction (SAED) image of the samples are shown in inset of Figure 4b.

The magnetic properties were measured by a vibrating sample magnetometer (VSM) (Microsense EZ9, USA). Figure 5 shows magnetization (M) vs. applied field (H) for the MZF-GO50 sample and the slim hysteris curve demonstrates that is a soft magnetic material. From the M-H curve (Figure 5), the saturation magnetisation and coercivity is obtained as 8 emu/g and 20 Oe, respectively.

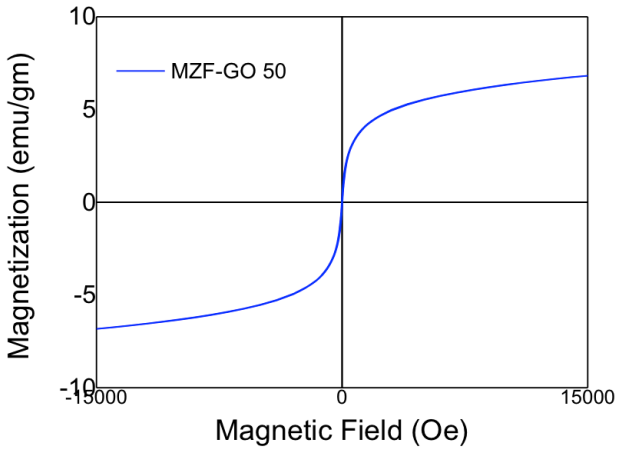

Figure 5. Demonstrates the magnetization (M_S) vs. Magnetic field measurement data for MZF-GO50 nanocomposite.

The reflection coefficients (S_{11}) of as-prepared nanocomposite coating sample was tested under free space measurement technique. Initially, the reflection was taken directly from the aluminum substrate (i.e. bare substrate) of identical dimension. A pair of horn antennas are used for measuring the reflection coefficient where one of them act as the transmitting antenna while the other one act as receiving antenna for reflected signals. Furthermore, the metal plate was replaced by the as-prepared sample coated on the metal substrate. Thus, the exact reflection coefficient of the sample was measured. The measured reflection coefficient is shown in Figure 6. It has been observed from Figure 6 that the sample offers selective absorption over the frequency range of 4-15 GHz. The surface impedance pertaining to the MZF-GO 50 sample are close to 377 ohm and 0 ohm, respectively; thereby providing perfect matching at those selected bands as provided in Figure 7.

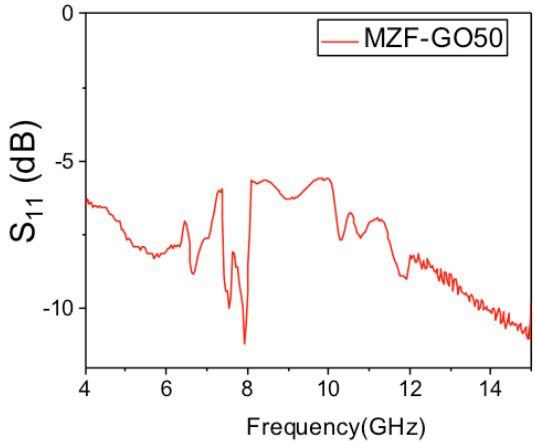

Figure 6. Demonstrates the plots of the reflection coefficients of the MZF-GO50-TPU coated sample in 4-15 GHz range.

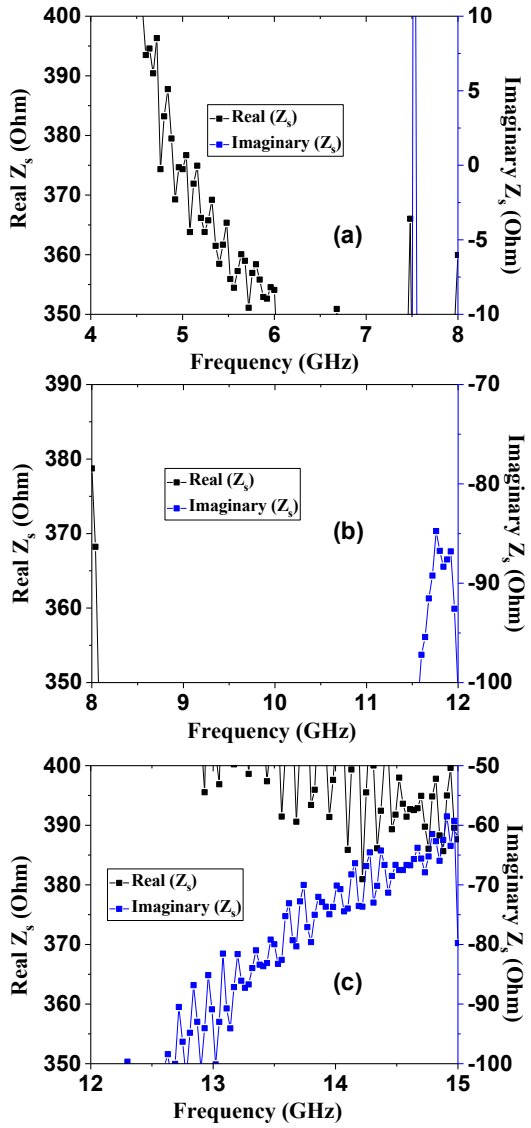

Figure 7. Shows the surface impedance profile of MZF-GO50-TPU coated sample in (a) C-band, (b) X-band and (c) Ku-band (i.e. from 4GHz to 15 GHz).

4. Conclusions

In conclusion, we have successfully demonstrated the in-situ synthesis of $(Mg_{0.5}Zn_{0.5})Fe_2O_4$ nanoparticle-graphene oxide hybrid nanocomposite as broadband microwave absorber material. The morphology of the material was unique as it exhibits MZF nanoparticles grafted on GO membrane, which forms during the in-situ gel combustion process. It was also obtained from TEM that various heterogeneous interfaces are formed between MZF particles and GO membranes with distinct lattice structures and bonding. The magnetic data delineates that the MZF-GO50 nanocomposite exhibits soft ferrimagnetic properties. Furthermore, the nanocomposite-polymer coating showed excellent broadband absorption properties throughout the microwave frequency range (4-15 GHz) with absorptivity greater than 85%. The real and imaginary components of the surface impedance values of the coatings are found to be close to 377Ω and 0Ω, respectively, over the significant region of the frequency band (i.e. 4-15 GHz). This implies minimum reflection from the coating over the frequency band of interest, thus, producing approximately ~ 85% broadband absorption in the range through the 4-15 GHz. These types of graphene oxide nanocomposite-polymer coating on metal substrates will find enormous possibilities for applications as radar absorbing materials, electromagnetic shielding, stealth technology etc.

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