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Graphene and MWCNT based bi-functional polymer nanocomposites with enhanced microwave absorption and supercapacitor property

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ABSTRACT

Development of multifunctional nanocomposites, which are able to serve many purposes effectively in different fields of applications, is an eminent topic to the modern researchers. We have prepared a novel hybrid networking nanostructure with bi-functionality based on graphene (Gr), TiO_2 coated multi wall carbon nanotube (Ti@CNT), Fe_3O_4 and polyaniline (PANI) for its use in microwave absorption and electrochemical devices. The structural and morphological properties of the prepared nanocomposites were determined through different spectral and microscopy techniques. Electrical, magnetic and thermal property was also evaluated for these nanocomposites. The prepared bi-functional nanocomposites showed excellent microwave absorption and the electrochemical property. The addition of PANI also enhanced its performance in both these field of applications due to the formation of conducting network structure. Finally, these nanocomposites can be used separately as broadband microwave absorber and electrode material for supercapacitor applications.

1. Introduction

The applications of microwave absorbing materials (which allow the electromagnetic wave to penetrate into a region where the electric and/or magnetic fields experience loss) are widely known in various fields including telecommunications, defense, aerospace, medical equipment, consumer electronics, computers etc. [1–3]. The electromagnetic interference problems arising from the wireless electronic devices can be reduced by using noise suppression sheets made of microwave absorbing materials [4]. The stealth technology is an impressive technique used in the defense sector since the Second World War. The microwave absorber can be used in stealth technology to stealth an object by reducing its radar cross section [5]. Hence, the demand of microwave absorbing material is huge for the applications in the modern fields of science and technology. Generally, the microwave absorber consists of dielectric and magnetic material, and the complementarity between them is essential for good microwave absorption. A good quality absorber should be lighter, cost effective, and flexible with the absorbing ability in wide frequency region. The single component system shows deficient and narrow band absorption property which is not desirable for many high frequency applications. Multicomponent based nanocomposites can serve this purpose effectively [6]. Hence, there is always a scope to design a better microwave absorbing material with remarkable wider-band microwave absorption property. The ability of an effective microwave absorber depends upon many factors such as material's permeability, permittivity, conductivity, surface area etc. The proper combination of these parameters can make an absorber as an excellent candidate for many microwave absorbing applications. In the work carried over by Maiti et al., the conductive network structure made of graphite nanoplate and MWCNT helps to enhance the electromagnetic shielding effectiveness of the prepared nanocomposites [7]. Conventionally, the primary mechanism of shielding is reflection from the surface of the shield. This high reflection can be achieved from the material with high conductivity. On the contrary, a microwave absorber should have minimum reflection and maximum absorption and so an optimum conductivity is required for good absorption. Hence, the tuning of conductivity can be a good technique to enhance the absorption of a microwave absorbing materials. In a report, Chen et al. have reported the synthesis of nanocomposites with different conductivity based on expanded graphite, polyaniline and $CoFe_2O_4$ [8]. They showed that the microwave absorption property has been changed with the percentage of aniline used to prepare the composite. Conducting polymers are important candidates in this field, because they have tuneable electrical conductivity, dielectric properties, facile processing technique, low cost, availability etc.

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[9]. Conducting polymers are known for both reflection and absorption of microwave. To prepare a microwave absorber, reflection should be as low as possible. The reduction of reflection and enhancement of absorption can be done by the use of proper dielectric and magnetic fillers which interact with the electromagnetic radiation. Therefore, several attempts have been made to incorporate various dielectric ($BaTiO_3$, TiO_2 etc.) and magnetic materials (γ-Fe_2O_3, Fe_3O_4, $BaFe_{12}O_{19}$ etc.) into the conducting polymers for the synthesis of effective microwave absorber [10,11]. The traditional microwave absorber includes ferroelectric ceramics (ferrites and ferromagnetic materials, barium and lead zirconate titanate etc.) and carbonaceous material (Gr, carbon nanotube, carbonyl iron etc.). Among the carbon nanomaterials, the invention of Gr and CNT has set a promising platform for the development of research in various fields of applications such as microwave absorption, energy storage device, fuel cells, biosensors, drug delivery etc. [7,12–14]. Gr and CNT is a superior candidate for microwave absorption because of their excellent response in the microwave region. Che et al. described the enhanced microwave absorption property for CNT–$CoFe_2O_4$ nanocomposite compared to that of pristine CNT and $CoFe_2O_4$ [15]. Yi et al. reported the microwave absorption properties of MWCNT/Co/resin composites which showed the reflection loss of −10 dB [16]. Zhao et al. have prepared Gr coated Fe nanocomposites and established its ability as an excellent microwave absorber [17]. Except Gr and CNT only, the hybrid of Gr and CNT is a promising microwave absorber because the accumulation of different functions of Gr and CNT in one single system may help to get better properties than that of individual Gr and CNT [18]. So, the nanocomposites based on Gr and CNT hybrid is highly demandable for modern microwave absorbing applications.

The new generation of supercapacitor becomes popular as hybrid capacitor which is made of the hybridization of double layer capacitor (non-faradaic process) and pseudocapacitor (faradaic process). The supercapacitor (hybrid capacitor) is known for its use in many high power application demands such as electric vehicles, hybrid electric vehicles, mobile electronic devices, off-peak energy back-up systems etc. [19,20]. Supercapacitor is also a suitable replacement of batteries and conventional capacitors over the last few years. Therefore, the demand of supercapacitor with high energy and power density and longer cycle life is indispensable. Gr, CNT and their hybrid nanocomposites have already left a broad signature on the field of supercapacitor [21–24]. Considerable effort has also been paid to the electronically conducting polymers such as PANI, polypyrrole, polythiophene etc. for the development of supercapacitors [25,26]. According to the previous literatures, various materials with the combination of dielectric and conducting component can be used separately for two different applications i.e. microwave absorption and supercapacitor. Also the spinel ferrites are already known for both these fields of applications. Therefore, we realize that one single material containing all these components i.e. dielectric, magnetic and conducting components will be able to serve these two different applications separately. Zhang et al. have prepared a composite of reduced graphene oxide for the electromagnetic wave absorbent and supercapacitor applications together [27]. In the present work, we have prepared a networking structure with different conductivity based on Gr, Ti@CNT, Fe_3O_4 and PANI by a facile synthetic procedure and investigated their impact on the two modern field of research i.e. microwave absorption and supercapacitor. Though, there is no such device where both the applications can be operated at the same time but our aim is to elaborate the dual role of the prepared material. The final fabrication of the prepared nanocomposites was carried out in thermoplastic polyurethane (TPU) matrix. To the best of our knowledge, the formation of a networking structure based on both Gr and Ti@CNT for these two particular fields of applications is not reported elsewhere till date.

2. Experimental work

2.1. Preparation

2.1.1. Synthesis of Gr/Ti@CNT/Fe_3O_4 and Gr/Ti@CNT/Fe_3O_4/PANI hybrid

Prior to the synthesis of the proposed hybrid nanocomposites, we have synthesized Ti@CNT through the sol–gel technique. The detail procedure was reported in our previous report [28]. For the better dispersion of Gr in water, Gr was modified [29] by acid mixture (HNO_3 and H_2SO_4), and then 0.1 g of acid modified Gr (i.e. —OH, —COOH functionalised) in water was sonicated for 1 h in presence of CTAB. Previously prepared Ti@CNT (0.1 g) was added to the aqueous solution of well dispersed Gr, and the sonication was continued for next 1 h. Then the mixture was stirred for overnight at room temperature. Aqueous solution of $FeSO_4 \cdot 7H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (molar ratio is 1:2) was added to the above mentioned mixture for the decoration of Fe_3O_4 particles on Gr/Ti@CNT hybrid. The whole solution was heated up to 50 °C and then stirred vigorously for some time under the nitrogen atmosphere. Now to initiate the precipitation process, we have added NaOH solution until the pH of the mixture becomes nine. The as formed solution was stirred for 2 h at 50 °C to complete the precipitation process. After that, the mixture was cooled to room temperature and filtered to obtain the precipitate in presence of Gr/Ti@CNT hybrid. The obtained product was washed several times by distilled water and ethanol. Then the sample was kept overnight at 100 °C for the preparation of Gr/Ti@CNT/Fe_3O_4 hybrid.

The synthesis of Gr/Ti@CNT/Fe_3O_4/PANI composite was achieved by the in-situ chemical oxidation polymerization of aniline in presence of Gr/Ti@CNT/Fe_3O_4. The process is simple and according to the previous report [30]. Briefly, the prepared Gr/Ti@CNT/Fe_3O_4 composite (0.1 g) was taken and sonicated in H_2O for quite some time. Then the aniline in 1.5 M HCl solution was added to the aqueous solution of Gr/Ti@CNT/Fe_3O_4 composite, and sonicated for 10 min with 15 min stirring. After that the oxidant (ammonium persulfate) was added to start the polymerization process (weight ratio of monomer to the oxidant is 1:2). The stirring was continued at a constant rpm for the next 5 h at room temperature, and finally the obtained product was washed, dried at 60 °C and pouched. The preparation procedure of Gr based nanocomposites is shown schematically in Fig. 1.

2.1.2. Preparation of TPU based nanocomposites

The microwave absorption property of the prepared nanocomposites was measured in the X-band (8.2–12.4 GHz) region.

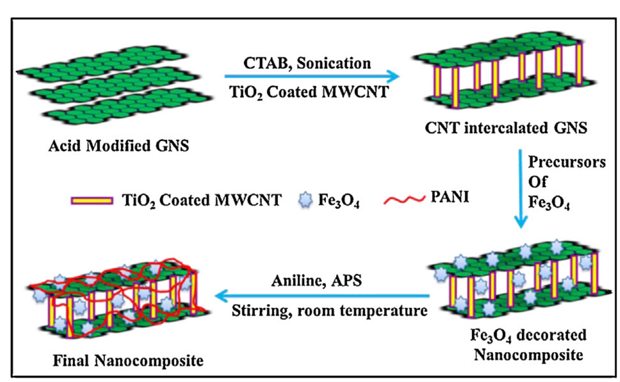

Fig. 1. Schematic representation of the preparation of the nanocomposites. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)