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Electromagnetic properties of electrospun Fe_3O_4/carbon composite nanofibers

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ABSTRACT

In order to develop multifunctional nanofibers, the electrical conductivity and magnetic properties of Fe_3O_4/carbon composite nanofibers have been examined. Polyacrylonitrile (PAN) is used as a matrix to produce magnetic composite nanofibers containing different amounts of magnetite (Fe_3O_4) nanoparticles. Electrospun composite nanofibers were thermally treated to produce electrically conductive and magnetically permeable composite carbon nanofibers. The composite nanofibers were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD), Raman spectroscopy, four-point probe and Superconducting Quantum Interference Device (SQUID). Uniform nanofibers were obtained with successful transferring of magnetic properties of Fe_3O_4 into the as-spun composite nanofibers. The electromagnetic properties were tuned by adjusting the amount of Fe_3O_4 in the matrix and carbonization process. The electrical conductivity, magnetic moment and also magnetic hysteresis rise up by adding Fe_3O_4 and increasing carbonization temperature. The high surface area provided by the ultrafine fibrous structures, the flexibility and tuneable electromagnetic properties are expected to enable the expansion of the design options for a wide rage of electronic devices.

1. Introduction

Recent advances in nanotechnology have greatly expedited the development of a new generation of multifunctional materials. Multifunctional materials are materials that possess more than one physical, chemical and biological property that can be changed significantly in a controlled fashion by external stimuli such as temperature, pressure/stress, electric field, magnetic field, optical wavelength, adsorbed gas molecules and the pH value. These functionalities can be provided using different nanofillers added into an appropriate matrix. Nanotubes, nanowires and nanoparticles are promising nanofillers to produce different functionalities. Unfortunately, the discrete nature of these nanoparticles makes them difficult to create structural forms. There is a need for suitable carriers that are capable of preserving the functionalities of the nanofillers. Recently, one-dimensional (1D) nanocomposite fibers have attracted a great deal of interest due to their enhanced electronic, optical and chemical properties. Among different methods for producing 1D structures, electrospinning is one of the most attractive methods due to its simplicity which enables the assembly of the 1D structures into higher order linear, planar or 3D nanofibrous assemblies by means of electrostatic forces [1,2]. Electrospinning has been demonstrated to be a simple technique to produce multifunctional composite nanofibers by incorporating various functionalities into the polymer solution using different nanofillers with specific physical, electrochemical and biological properties [3–6]. Among various multifunctional composite materials, those with electrical and magnetic properties are suitable candidates for a wide range of applications such as magnetic transporters for biomedical applications, membrane-less bio-fuel cells, microwave absorbers and electromagnetic device applications [7–12]. In order to generate the electromagnetic properties, both electrically conductive and magnetically permeable agents are needed. One of these agents is Fe_3O_4 which can be used as a magnetic filler. In combination with polymer matrix, Fe_3O_4 can be used as microwave absorption structures and dampers [13] and medical applications [14] such as drug delivery and therapy [5]. On the other hand, electrical conductivity can also be provided by either using electrically conductive polymers like Polyaniline (PANI) and Polypyrole (PPy) or using PAN as a carbon fiber precursor. Adding magnetic nanofillers into the electrically conducting polymer matrix such as PANI and PPy have been previously investigated [15,16]. We have selected PAN which is a predominant carbon fiber precursor that can be processed by thermal stabilization and subsequent high temperature carbonization. This will lead to an improvement in electrical conductivity [1]. In order to bridge the gap between nano and macro length scales and connect the nano effect to macro performance, we propose to create composite

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fibers containing the functional nanoparticles and we specifically produce the composites in nanofiber form in order to preserve the nano effect. A major challenge for this composite nanofiber concept is to demonstrate that the unique functional properties of the nanoparticles can be translated to the composite nanofibrous structure. Electromagnetic multifunctional composite nanofibers can be produced by using Fe_3O_4 precursor dissolved in PAN followed by electrospinning and carbonization to fabricate magnetic composites which are electrically conductive [17–19]. These electromagnetic composite nanofibers have been reported to be used as anode materials for high performance lithium ion-batteries [19]. The idea of direct dispersing of Fe_3O_4 nanoparticles in PAN matrix is proposed in this study. The morphology of electrospun magnetic Fe_3O_4/PAN nanofibers with direct dispersion of Fe_3O_4 nanoparticles into the polymer solution has also been studied by others [3,21]. However, these studies focused mainly on the morphology and magnetic properties of the as-spun magnetic nanofibers leaving the carbonization process unexplored and missing the opportunity to examine and cultivate the multifunctionality of these composite nanofibers. In this study, we illustrate the creation of electromagnetic composite nanofibers using Fe_3O_4 nanoparticles in a carbon matrix thus combining the magnetic properties of Fe_3O_4 with the electrical conductivity derived from the carbon nanofiber matrix. To demonstrate the multifunctional composite nanofiber concept, we begin by dispersing Fe_3O_4 nanoparticles into PAN/N,N-Dimethylformamide (DMF) to form the spinning dope solution for electrospinning. The electrospun composite nanofibers were subsequently pyrolized at elevated temperatures. The electromagnetic properties of the composite nanofibers were characterized by systematic examination of the effect of Fe_3O_4 content and carbonization temperature on the electrical conductivity, degree of graphitization and magnetic properties.

2. Experimental

2.1. Materials

The materials used in this study are PAN with 150,000 average molecular weight purchased from Scientific Polymer Products, Inc.; DMF (99.9%) purchased from Fisher Scientific; Fe_3O_4 magnetite nanoparticles purchased from Nanostructured and Amorphous Materials Inc. and Triton X-100 (contains less than 3% Polyethylene glycol) purchased from Sigma–Aldrich.

2.2. Polymer solution preparation

Pure 10 wt.% PAN/DMF and composite Fe_3O_4/PAN/DMF solutions were prepared in this work. To make composite solutions, 1, 5 and 10 wt.% Fe_3O_4 to the PAN were dispersed in 10 wt.% PAN/DMF solution. The solutions were prepared using Triton X-100 as surfactant and DMF as solvent for PAN. The Fe_3O_4 nanoparticles were first bath sonicated in DMF for 9 h. Then, Triton X-100 (with the same weight as Fe_3O_4) was added to the solution and solution was bath sonicated for another 9 h to obtain uniform dispersion of Fe_3O_4 nanoparticles in the solvent. In the final step, an appropriate amount of PAN was added to the previously prepared Fe_3O_4/Triton X-100/DMF solution and the sample was then bath sonicated for 9 h.

2.3. Composite nanofiber fabrication

An electrospinning unit (KATO TECH CO. LTD.) was used to prepare the nanofibrous samples from the solutions containing different amounts of Fe_3O_4 nanoparticles. The prepared pure PAN or Fe_3O_4/PAN solutions were first loaded into a plastic syringe with G18 needle. A collector at 17 cm distance from the needle tip was placed as a grounded counter electrode. A constant volume of the Fe_3O_4/PAN solution was delivered to the needle at a flow rate of 2 ml/h and a high potential of 11–12 kV was applied to the polymer solution as they exit the needle. The non-woven fibers were collected on the aluminum foil connected to the ground. Fig. 1 shows the schematic of the electrospinner unit used to fabricate nanofibers.

2.4. Pristine and composite carbon nanofiber preparation

The electrospun pure PAN nanofibers or composite Fe_3O_4/carbon nanofibers were heat treated according to the procedure shown in Fig. 2 using a tube furnace (79,400 Thermolyne). The as-spun nanofibers were first weighed and placed in the furnace. They were then heated to 250 °C at a ramping rate of 5 °C/min and then stabilized for 100 min under air atmosphere. The stabilized samples were then exposed to nitrogen at 250 °C for 20 min and heated to 700 °C or 900 °C with the ramping rate of 5 °C/min. The samples were kept at each of these processing temperatures for 60 min to be carbonized. Carbon fibers were then cooled down to the room temperature under nitrogen atmosphere and weighed to measure the carbon yielding during the carbonization process. Fig. 3 illustrates a flowchart explaining the detail design of the experiments. A summary of sample designation code for the different samples used in this study is shown in Table 1.

2.5. Characterization methods

Fiber morphologies and nanoparticles distribution of pristine carbon nanofibers and Fe_3O_4/carbon composite nanofibers were studied using SEM (Hitachi S-2300) and TEM (Hitachi H-800). X-ray diffraction (XRD) with Rigaku Multiflex diffractometer using Cu-K_α radiation was used to verify the chemical composition of nanofibers after carbonization. The 2θ angle was varied from 10° to 90° with the scanning speed of 2°/min. The prepared pristine and composite carbon nanofibers were also subjected to Renishaw InVia Raman microscope, using He–Ne laser at 633 nm excitation. The electrical conductivity was measured using the four-point probe method. Electrical conductivity, σ, was calculated by the expression, $\sigma\ (\mathrm{S/cm}) = L/(t \times R)$, where R is electrical resistance in Ω, t is thickness of the specimen in cm and L is the distance between electrodes in cm. The magnetization versus magnetic field (M–H curves or hysteresis loops) were plotted using SQUID (Quantum Design, CA, USA) which was used to measure the magnetic moment (emu) as a function of applied magnetic field (Oe) at room temperature (300 K). The information related to sample size used for four-point probe and SQUID measurements has been summarized in Table 2.

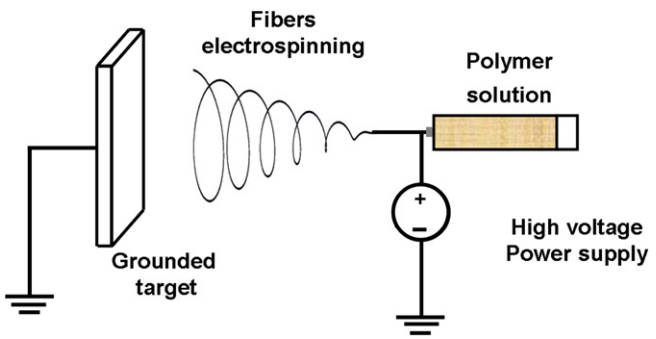

Fig. 1. The electrospinner unit used to make electrospun nanofibers.