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Preparation and characterization of poly(vinyl alcohol)/graphene nanofibers synthesized by electrospinning

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ABSTRACT

We report on the synthesis and characterization of electrospun polyvinyl alcohol (PVA)/graphene nanofibers. The samples produced were characterized by Raman spectroscopy for structural and defect density analysis, scanning electron microscopy (SEM) for morphological analysis, and thermogravimetric (TGA) for thermal analysis. SEM measurements show uniform hollow PVA fibers formation and excellent graphene dispersion within the fibers, while TGA measurements show the improved thermal stability of PVA in the presence of graphene. The synthesized polymer reinforced nanofibers have potential to serve in many different applications such as thermal management, supercapacitor electrodes and biomedical materials for drug delivery.

1. Introduction

Fibers have become attractive due to their high length to diameter ratio at the nanoscale and have several potential industrial and commercial applications [1]. The properties of the nanofibers which makes them commercially important includes small diameter, large surface area and small pore size; which are ideal industrial requirements for filtration, catalysis and adsorption [2,3]. There are several techniques for production of nanofibers such as drawing, template synthesis, phase separation, self-assembly and electrospinning [1,4]. Amongst this techniques electrospinning is versatile for production of continuous fibers from microscale to nanometer range [5] by the application of electrostatic forces to a jetting polymer solution [6,7]. Mechanical reinforcement of fibers by the incorporation of nanofillers has been shown as a method for enhancement of the fibers' properties for a number of particular applications. Materials mostly used as nanofillers include zero dimensional (0D) nanoparticles [8], one dimensional (1D) nanotubes [9–11] and two dimensional (2D) layered materials [8,12,13]. The incorporation of these materials into the matrix generally improves the mechanical, electrical, thermal, and optical properties of the fiber. Examples of 2D-layered nanofillers used include graphene and graphene oxide (GO) [14,15] owing to their relatively high mechanical strength, and thermal and electrical conductivities [16] which make them promising candidates as nanofillers for enhancement of the fiber properties. It has been shown that the addition of these materials into polymer matrix can greatly improve the mechanical [17,18], electrical [19] and thermal stability [20] of the polymer fibers.

In most cases, electrospinning polymer matrix (TiO_2–PVP) gives rise to hollow fibers which are usually stabilized with sol–gel as reported by McCann et al. [21]. This sol–gel serves as nanofillers and hence an increase in the morphological homogeneity of the resulting nanofibers. Recently graphitic material such as graphene derived from expanded graphite (EG) have been used as fillers by centrifuge and ultrasonication in polyvinylpyrrolidone (PVP)/PVA polymer matrix, but PVP leads to fragile fiber when electrospun [22]. This may be due to the fact that electrospinning of polymer/graphene composite matrix solution requires a homogeneous well dispersed graphene sheets in the polymer matrix solution [2] which is not easily achievable using EG and could also be due to the aggregation or agglomeration of the graphene sheets due to the dispersion forces (van der Waals and Casimir interactions) [23]. In this study, we explore the prospects of uniform dispersion of graphene foam and graphene derived from expanded graphite in hollow PVA polymer matrix nanofibers achieved by just optimizing growth parameters to enhance and/or modify their properties via electrospinning.

2. Experimental

Nickel foam (Alantum Innovation, Munich, Germany), expandable graphite (grade ES 250 B5 from Qingdao Kropfmuehi

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Graphite), polyvinyl alcohol (PVA) (M_w 89,000–98,000 g mol^{-1} Sigma Aldrich) were used as received for the preparation of materials to be used in the synthesis of fibers.

2.1. Materials preparation

Graphene foam (GF) was synthesized on nickel foam template with 420 g/m^2 in area density and 1.6 mm in thickness, using CVD technique as previously reported [24,25]. Briefly the nickel foam was annealed at 800 °C in the presence of H_2:Ar flow ratio of 10:300 sccm for 20 min to remove impurities, before the introduction of the CH_4 gas at 1000 °C. The flow rates of the gases (CH_4:H_2:Ar) were 10:10:300 sccm, respectively. After 15 min of deposition, the sample was rapidly cooled by pushing the quartz tube to a lower temperature region. After growth, the nickel template was removed by chemical means as follows: polymethylmethacrylate (PMMA) was drop-coated on the sample and baked at 180 °C for 30 min to provide mechanical support for the GF during etching of the nickel. The samples were then placed in 3 M HCl solution at 80 °C, left overnight to ensure complete removal of the nickel template. The resulting GF sample was placed in acetone at 50 °C for 30 min to remove the PMMA and subsequently placed in isopropanol at 80 °C for 1 h to remove the acetone and finally rinsed in deionized water to remove the isopropanol. A subsequent annealing was performed at 400 °C in argon. After annealing, the sample was again rinsed with deionized water and dried at 50 °C in an electric oven. The EG samples were synthesized by exfoliation of expandable graphite in a quartz boat using a microwave oven at 300 W irradiated for 5 min.

The composites solutions were prepared by ultrasonication (Eumax sonicator (ud100sh)) for both GF and EG in 100 ml of 10 wt% PVA solution for 5 h at 40 °C with varying mass ratios of the starting materials ranging from 20 to 80 mg in order to obtain a good homogeneous dispersion of graphene sheets. The solution was then centrifuged at 5000 rpm for 3 min to remove aggregates from the GF and EG. The ultrasonication step for EG in the PVA solution may lead to exfoliation of the graphite to graphene sheets [2]. The composite solution was also centrifuged to remove the non-exfoliated graphite aggregates.

2.2. Electrospinning

The homogeneous dispersed solutions were electrospun using a standard NaBond electrospinning machine (NaBond Technologies SN-50F6). Before production of the nanofibers the various parameters such as the flow rates, the voltage and the speed were optimized to get the best fibers without beads and these values were further used to perform the subsequent experiments. The solution was loaded into a hypodermic syringe (10 ml) and a flexible tube was used to connect the syringe to the blunt needles (Gauge 6). A syringe pump was used to control the flow rate of the solution which was varied between 3 and 7 ml/h. The applied voltage between the needle and the collector was adjusted between 10 and 30 kV and the fibers were collected on a glass (18 × 18 mm^2) substrate mounted on the rotating collector by conductive tape with speed varying between 500 and 1000 rpm. The distance between the needle and the collector was varied between 10 and 14 cm and the growth time between 30 and 180 s. Fig. 1 shows the schematic diagram of the fiber growth process.

2.3. Characterization

Raman spectroscopic analysis of the graphene and composite materials were performed using a T64000 micro-Raman spectrometer from HORIBA Scientific, Jobin Yvon Technology equipped with a triple monochromator system to eliminate contributions from the Rayleigh line. All the samples were analyzed with a 514 nm argon excitation laser with a power of 12 mW at laser exit to avoid thermal effects. The surface morphology of all samples was investigated using a Zeiss Ultra Plus 55 field emission scanning electron microscope (FE-SEM). Thermogravimetric Analysis (TGA) was carried out using TA Instruments Q600 Simultaneous DSC/TG which measures the weight change in a material as a function of temperature or time under a controlled atmosphere. TGA samples were heated from room temperature to 1000 °C at a rate of 10 °C min^{-1} in air.

3. Results and discussion

3.1. Raman analysis

Raman spectroscopy is an important tool for characterization of carbon materials. Fig. 2(a) and (b) shows Raman spectra of PVA, GF and EG before and after dispersed in water respectively. The dispersed GF and EG spectra show prominent peaks at around 1580 cm^{-1} (G-Peak) and 2700 cm^{-1} (2D-Peak). G-Peak have been assigned to graphitic carbons with sp^2 hybridization [26,27]. In particular, the 2D peak of the EG dispersed in water and ultrasonicated matches the wavenumber of the shoulder of the 2D mode in the EG before sonication. This shift of the 2D to lower wavelength is generally observed for graphene [26]. This evidences the exfoliation of graphite to graphene after dispersion in solvent by ultrasonication. In addition, in the case of disordered sample EG after dispersion, the peak at around 1350 cm^{-1} (D-Peak) is observed which corresponds to defect in the graphene sample. The full width at half maximum (FWHM) of the 2D peak for dispersed GF and EG are 54 and 76, respectively while the I_{2D}:I_G

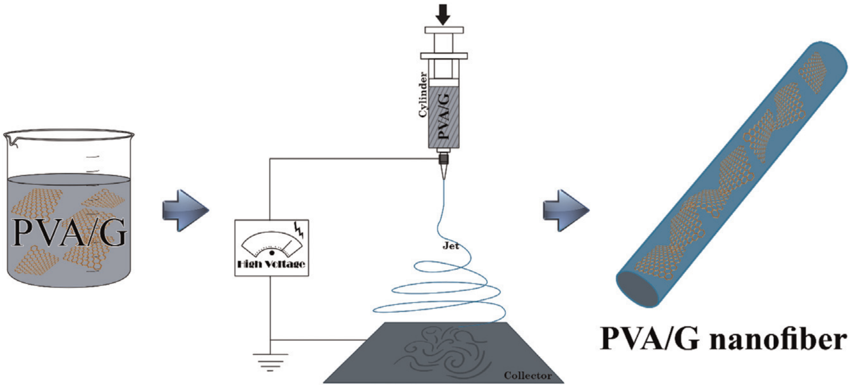

Fig. 1. Schematic illustration of the fabrication of graphene/polymer nanofiber composite by electrospinning.