Preparation and Characterization of Electrospun PVA-rGO nanofibers

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Abstract

The graphene oxide GO and reduced graphene oxide rGO were synthesized and mixed with Polyvinylalcohol (PVA) Polymer dissolved in the distilled water. The composite nanofibers were prepared with PVA-rGO solutions by electrospinning method. The size and morphology of the nanofibers were analyzed by scanning electron microscope (SEM) and optical microscope. The structural properties and the functional groups of prepared samples were analyzed by XRD, FTIR and Raman spectroscopies. The PVA-rGO nanofibers with average diameter of 330 nm has been obtained.

Keywords: reduced graphene oxide, PVA-rGO nanofibers, electrospinning

Introduction

Supercapacitors are commonly approved as one of the good alternative energy storage devices due to their excellent characteristics such as high power density, rapid charge/discharge rate, and cyclic stability. The development of advanced electrode materials with excellent energy storage properties is the major task for the fabrication of supercapacitor devices in real-world applications (Tiwari *et al.*, 2021). Carbon nanomaterials such as carbon nanofibers are the best electrode materials used for flexible devices due to their good mechanical and electrochemical properties. Carbon nanofibers are one of the most popular methods and facile tools to achieve flexible devices for various applications due to their special properties including high porosity, large liquid permeability, good electrical conductivity, flexibility and self-standing fibrous structure. Carbon nanofibers are usually prepared by the electrospinning method. The current work aims to use the nanofiber mats in capacitor electrodes (Alwan, 2016).

In manufacturing nanofibers from polymers and its composites the electrospinning is a simple and reliable method. The process is carried out in the presence of high electric field which results in stretching of polymer solution that produces fibers which are in micro/nanoscale. The working principle of the electrospinning process includes the application of an electric charge to the polymer solution, and the solution jet stretches in a high electric field to produce nanofibers (Ton Peijs, 2018). When the polymer solution flows out from the needle connected to a high-voltage DC power supply, it stretches out and elongates itself to a conical shape. The thin stretched fibers travel faster towards the collector end due to the opposite charge and accumulated on it in the form of fiber webs (Danni, 2016).

The nanofiber morphology is dependent on several parameters involved in the electrospinning process. The parameters are grouped into three different categories as follows: (a) solution parameters such as concentration, viscosity, surface tension, molecular weight, and solvent type, (b) processing parameters such as voltage, solution flow rate, needle-to-collector distance, needle tip design, collector geometry and velocity, and (c) ambient parameters which are temperature and humidity (Choo, 2016). The viscosity of the polymer solution can be regulated by varying the concentration of polymer, and it is the most important factor that affects the fiber surface morphology and diameter values (Ton Peijs, 2018).

In this work, the optimization of fiber parameters by the flow rate and the collector-to-needle distance and, the synthesis and characterization of rGO were carried out before

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preparing the composite fibers. The shape and diameters of fibers are analyzed by SEM and optical microscope.

Materials and Methods

Materials

Graphite powder, sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2, 30%) were used in the synthesis of graphene oxide. Ascorbic acid (AA) and ammonia (NH_3) were utilized for preparation of reduced graphene oxide. Polyvinyl Alcohol (PVA) (Mw 80,000) is the basic material for preparing nanofibers.

Characterization

The characterization of GO and rGO were analyzed by X-ray diffractometer (Rigaku-RINT 2000). UV–visible spectroscopy was used to observe the presence of functional groups and to determine the structure of GO and rGO. From the Raman spectra of the GO, rGO and PVA-rGO nanofibers, the chemical properties and orientation of their structures were observed. The surface morphology of the PVA-GO and PVA-rGO nanofibers were examined with Scanning Electron Microscope (SEM) (JEOL-JSM 5610LV) and Olympus BX51 Fluorescence Microscope.

Experimental

The Synthesis of Graphene Oxide and reduced Graphene Oxide

Graphene oxide (GO) was synthesized from natural graphite by Hummers method. In this reaction, graphite powder, H_2SO_4, $NaNO_3$, $KMnO_4$, is stirred together to keep the reaction temperature below 10°C. The mixture was transferred to a 40°C water bath and the distilled water was added to the mixture solution. After that, the mixture was heated up to 90°C while the distilled water and H_2O_2 was added. The color of the mixture turned gradually from dark brown to bright yellow. The warm solution was washed with diluted HCl to obtain graphite oxide. Then, the solution was centrifuged and sonicated to remove the unexfoliated graphite. Finally, the GO solution obtained was dried in oven at 40°C.

In the reduction of GO through a chemical treatment process, ascorbic acid (0.7 g) and the GO suspension (250 ml, 0.3 g/ml) were mixed. Then, ammonia solution (60 µl) was added to adjust the pH level between 8 and10. After that the suspension was stirred at 90ºC for 2 hrs. The reaction mixture was centrifuged at 3000 rpm and washed with ethanol and distilled water. Finally, rGO precipitate was dried in the oven at 40°C.

Preparation of Reduced Graphene Oxide (PVA-rGO) Solutions

Polyvinyl Alcohol (PVA) 10 wt % solutions were prepared by dissolving PVA powder 10 g in 100 ml of deionized water. PVA powder was stirred into the deionized water at room temperature for 30 min. Then the temperature was gradually raised to 80 °C while the mixture was constantly stirred for 5 hrs to homogenize the solution. The solutions were placed in a refrigerator overnight to obtain transparent solutions.

To prepare PVA-rGO solutions, firstly, 4.2 mg of rGO was mixed and sonicated with 10 ml of distilled water. Then rGO solution was added to the 30 ml of PVA solution. The mixture was stirred for 3 hrs in order to make rGO suspension to disperse completely in the polymer solution. After that, the mixture was sonicated at room temperature for 15 min to form a homogeneous solution before the electrospinning process.

Preparation of the Electrospun PVA-rGO Nanofibers

PVA-rGO solution was loaded into the syringe which is connected to a needle via a flexible tube. The needle was connected to a positive high-voltage DC power supply. The syringe was loaded to the syringe pump to control the flow rate of the solution. After switching on the power supply and syringe pump, PVA-rGO nanofibers were collected to the rotating collector which is covered by aluminum foils. The processing parameter are given in the table 1.The fiber collection time was set to 45 mins. Finally, PVA-rGO nanofibers were found on the aluminum foils.

Table 1 Processing parameters for electrospinning

voltage	15 kV
flow rate	0.2 mL/hr
needle-to-collector distance	15 cm
collector geometry and velocity	Cylinder,.8 m/s
Needle diameter	0.2 mm
Temperature	31 ºC
Humidity	42 %

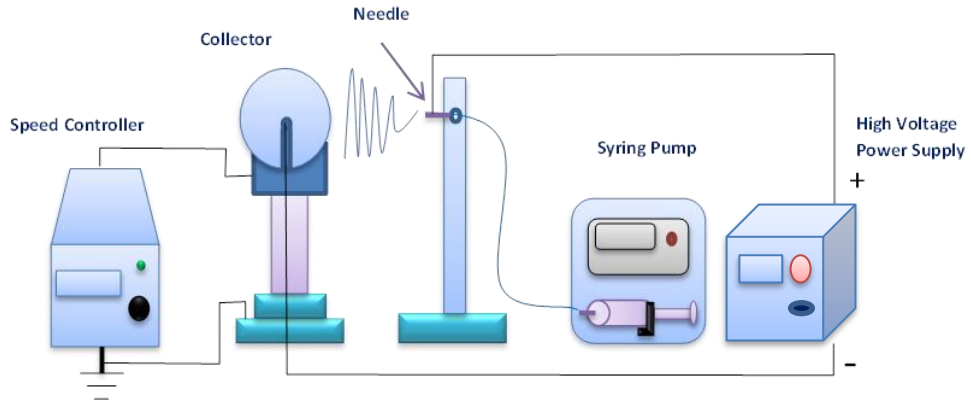


Figure1 Schematic diagram of electrospinning setup

Results and Discussion

XRD Analysis

The XRD pattern of GO and rGO shown in figure 2 were obtained from X-ray diffraction analysis. A sharp peak at 2θ~11.72° corresponded to the reflection from the (100) plane was observed in XRD spectrum of GO. The pattern revealed that the phase precipitated out in the sample was hexagonal structure (Cao, 2015)**.** The larger interlayer distance of GO is the formation of oxygen-containing functional groups, such as hydroxyl, epoxyl and carboxyl. Thus, the XRD pattern of GO was inferred that the original graphite powders had almost been completely oxidized.

The inter planner d spacing (002) plane between individual graphene layers was an indicator of the degree of graphitization. Reduced graphene oxide has a peak at around 2θ value of 24.15º. This peak position was indicated by the exfoliation of rGO sheets after the removal of the intercalated carboxylic groups (oxygenated functional group) and the

appearance of hydrophobic properties. These XRD results indicate the exfoliation and reduction processes of graphene oxide.

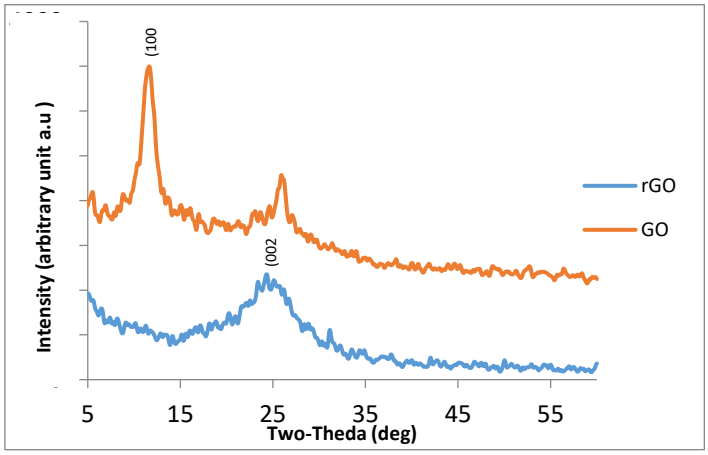


Figure 2 XRD patterns of graphene oxide (GO) and reduced graphene oxide (rGO)

UV-visible spectroscopy Analysis

The optical absorbance spectra of GO and rGO solutions are shown in figure 3. Graphene oxide exhibits a strong absorption edge in a wavelength range of 230.4 nm which is attributed to π-π* the transition of the aromatic C=C bond. A shoulder peak at 302.13 nm corresponds to n-π* the transition of the carbonyl group. In the absorbance spectrum of rGO, only one peak at a wavelength of 293.6 nm is appeared. This peak is correlated to the π-π* orbital transition and shows the characteristic peak of rGO absorbance spectrum (Eluyemi, 2016).

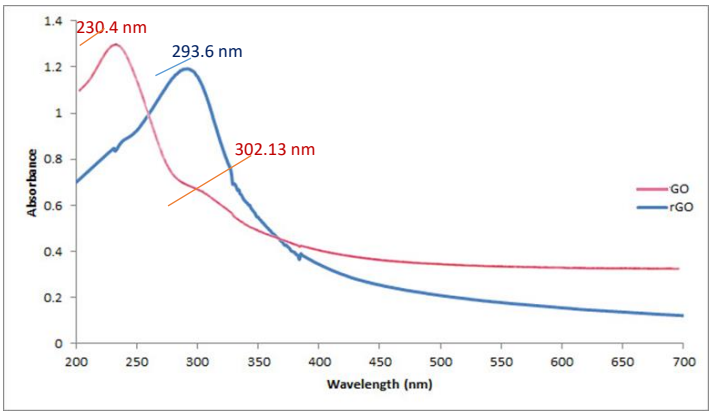


Figure 3 UV-visible absorption spectra of GO and rGO

FTIR Analysis

Fourier Transform Infrared spectroscopy (FTIR) spectra provides information about the functional groups in a sample. Figure 4 shows the FTIR spectra of GO and rGO. The GO spectrum showing the peak at 1049 cm^{-1} is attributed as C-O stretching. The peak at 1217 cm^{-1} was confirmed as C-O-C bending and C-OH bending is observed at 1419 cm^{-1}. The carbonyl groups were also shown at 1716 cm^{-1} as C=O stretching and a broad peak at 3425 cm^{-1} was attributed as O-H stretching vibration of the C-OH groups and water content in the material. The rGO peaks at 1217 cm^{-1}, 1716 cm^{-1}, 1049 cm^{-1} and 3425 cm^{-1} decrease and this is an indication of the removal of oxygen-containing functional groups in GO. These rGO spectra observations confirmed that most oxygen containing functional groups in the GO were removed although some residual oxygen-functionalities on GO were still present on the rGO

surface with weaker intensity after the reduction. The peak at 1643 cm^{-1} (C=C aromatic stretching) in rGO shows a strong band, which suggested the recovery of sp^2 lattice (Habte, 2019).

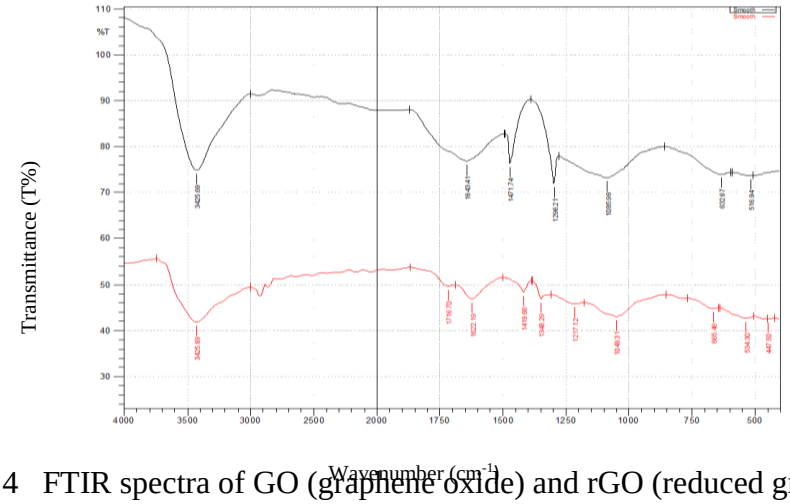


Figure 4 FTIR spectra of GO (graphene oxide) and rGO (reduced graphene oxide

Raman Spectroscopy Analysis

Raman spectroscopy is an effective tool to analyze the relative contributions of ordered and disordered regions in carbonaceous structures. Raman spectra of synthesized GO, rGO and PVA-rGO nanofibers were presented in figure 5. The graphite lattice of GO, rGO and PVA-rGO exhibits G band at 1594 cm^{-1}, 1570 cm^{-1} and 1573 cm^{-1} respectively which are generally assigned to C=C stretching vibrations common to all sp^2 bonded carbon atoms, whereas D band at 1350 cm^{-1}, 1358 cm^{-1} and 1339 cm^{-1} originates from phonon modes coming from sp^2 bonded carbon atoms that reside near local lattice distortions (defects) of the graphitic network (Khan, 2017). The intensity ratio of D and G bands (I_D/I_G) was used to determine defects of graphene materials. The intensity ratio(I_D/I_G) of GO is 0.95. After reduction reaction, intensity ratio (I_D/I_G) of rGO is increased to 1.1. The peak at 2926 cm^{-1} in PVA-rGO spectrum shows the C-H stretching in PVA.

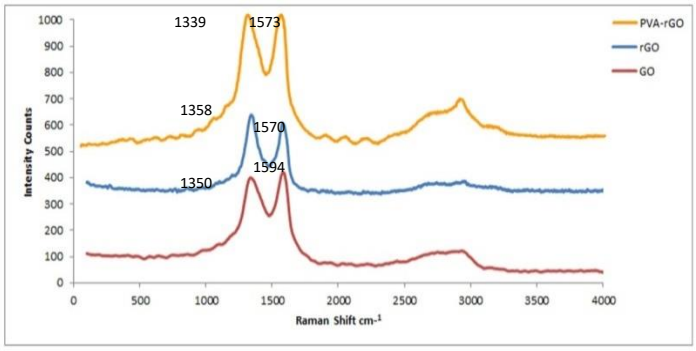
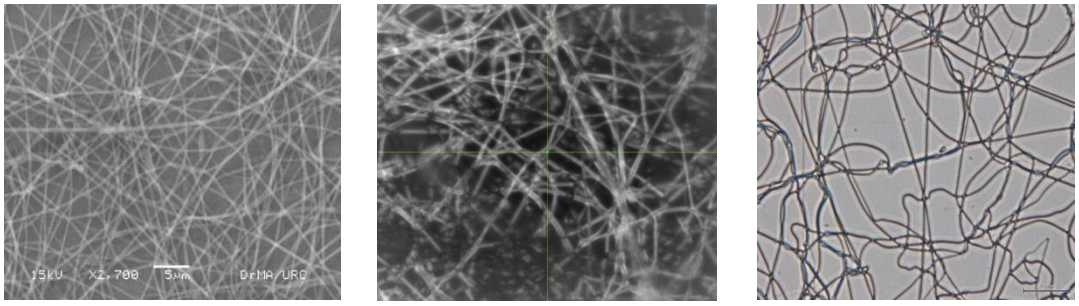


Figure 5 Raman spectra of GO, rGO and PVA-rGO nanofibers

Morphology Analysis by SEM and Optical Microscope

The size and formation of PVA-rGO samples were analyzed by SEM. For the flow rates of 0.2 ml/hr, the diameter of PVA-rGO nanofibers was found 330nm as shown in figure 6(a) which looks like the bird-nests. In this work, the morphology of PVA-rGO samples was also checked by optical microscope for pre-analysis before observing with SEM. The optical image of the PVA-rGO obtained in figure 6(b), (c) shows thread-like fiber texture.



(a) (b) (c)

Figure 6 (a) SEM image of PVA-rGO nanofibers, (b) Reflected light microscope image and (c) transmitted light microscope image of PVA-rGO nanofibers

Conclusion

In this study, GO and rGO was synthesized by Hummer's Method. PVA-rGO solution was prepared and PVA-rGO nanofibers were successfully produced using the electrospinning technique. The structural properties, optical properties, functional group and morphology were analyzed. The random distribution of fine PVA-rGO nanofibers with average diameter of 330 nm has been obtained. . The electrospun composite nanofiber techniques affords the possibility to fabricate flexible electronic devices, providing potential applications in various new energy storage such as supercapacitors.

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