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Antibacterial Effect of Carbon Nanofibers Containing Ag Nanoparticles

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Abstract: Silver nanoparticles imbedded in polyacrylonitrile (PAN) nanofibers and converted into carbon nanofibers by calcination was obtained in a simple three-step process. The first step involves conversion of silver ions to metallic silver nanoparticles, through reduction of silver nitrate with dilute solution of PAN. The second step involves electrospinning of viscous PAN solution containing silver nanoparticles, thus obtaining PAN nanofibers containing silver nanoparticles. The third step was converting PAN/Ag composites into carbon nanofibers containing silver nanoparticles. Scanning electron microscopy (SEM) revealed that the diameter of the nanofibers ranged between 200 and 800 nm. Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) showed silver nanoparticles dispersed on the surface of the carbon nanofibers. The obtained fiber was fully characterized by measuring and comparing the FTIR spectra and thermogravimetric analysis (TGA) diagrams of PAN nanofiber with and without imbedded silver nanoparticles, in order to show the effect of silver nanoparticles on the electrospun fiber properties. The obtained carbon/Ag composites were tested as gram-class-independent antibacterial agent. The electrosorption of different salt solutions with the fabricated carbon/Ag composite film electrodes was studied.

Keywords: Carbon nanofiber, Electrospun, Silver nanoparticle, Water purification, Antibacterial effect

Introduction

Silver nanoparticles play a major role in the emerging field of nanotechnology in the past two decades. Colloidal silver is of particular interest because of its valuable application in life science as biosensors, labels for cells and bio-molecules, peptide probes, anti-microbial agents, wound healing agent and cancer therapeutics. The exciting and most important application of silver nanoparticles is its prominent anti-microbial activity [1-9]. Polyacrylonitrile (PAN), a well-known polymer with good stability and mechanical properties, has been widely used in producing carbon nanofibers (CNFs) as these have attracted much recent attention due to their excellent characteristics, such as spinnability, environmentally benign nature and commercial viability. Among the various precursors to produce CNFs, PAN has been extensively studied due to its high carbon yield and flexibility for tailoring the structure of the final CNFs as well as the ease of obtaining stabilized products due to the formation of a ladder structure via nitrile polymerization. In view of this, they have applications in areas such as electronics, tissue engineering, membrane filtration and high performance composites [5-7,10-19].

Adding metal nanoparticles to polymer nanofiber matrix (metal-polymer nanocomposites) has attracted a great attention due to synergic combinations of the unique optical, electrical, and catalytic properties of metal nanoparticles and excellent specific surface area of polymer nanofibers [1-8]. The incorporation of Ag nanoparticles into polyacrylonitrile (PAN) fibers exhibits excellent catalytic activity, surface-enhanced Raman scattering activity, electrical conductivity, and antimicrobial activity [2,5,6]. PAN is reported to be an important engineering polymer that has been widely used to produce a variety of synthetic fibers [2,20-33]. Zhang *et al.* [2] and Wang *et al.* [3] were succeeded to synthesis well dispersed Ag nanoparticles on the surface of the PAN nanofiber, but their method is critical in preventing nanoparticles from aggregation. Where conventional methods prepared by mechanical mixing the metal nanoparticles into dissolved polymer matrix leads to homogeneous dispersion of particles especially in the low viscous matrix [34-39].

In this paper, in situ preparation of silver nanoparticles mixed homogeneously in PAN solution to produce nanofiber film spun by electrospinning technique has been presented. Electrospinning is a process by which a suspended droplet of polymer solution is charged to high voltage to produce fibers with diameters ranging from 200 to 500 nm. When a voltage is sufficient to overcome surface tension forces, fine jets of liquid shoot out toward a grounded collector. The jet is stretched and elongated before it reaches the collector, dries and is collected as an interconnected film of nanofibers. This novel nanofiber spinning technique has been explored mainly

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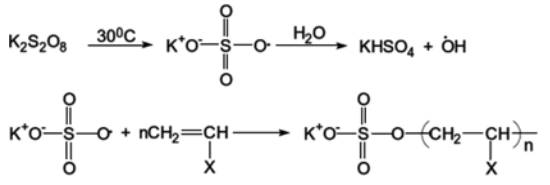
to prepare pure polymer nanofibers in past years [40-47]. We present a convenient and effective way to add Ag nanoparticles into PAN nanofiber film. UV spectrum and TEM studies have been done in order to reveal the structural properties of the Ag/PAN nanocomposite film.

Experimental

Materials

PAN was prepared with a redox system in aqueous solution (precipitation polymerization). The procedure can be summarized as following; In 250 m*l* round-bottomed flask, acrylonitrile (AN) (I) (15 m*l*, 230.30 mmol) was mixed with distilled water (175 m*l*) at room temperature with stirring under nitrogen atmosphere. Then, sodium disulfite solution (5 %, 0.5 m*l*, 0.13 mmol) and ferrous sulfate solution (2.5 m*l*, 9.10 mmol), were added followed by potassium proxodisulfate solution (5 %, 2.5 m*l*, 0.46 mmol). The turbidity was noted after 5 min and stirring was continuing for more 20 min. The precipitated polymer was flittered and was washed with distilled water (300 m*l*) and then finally washed with methanol (100 m*l*). The product was dried in oven under vacuum at 50 °C overnight to yield 7.9 g (65.83 % yields).



Preparation of PAN Nanofiber Film by Electrospinning

PANNF film was prepared by electrospinning (Figure 1). PAN (5 wt.%) was dissolved in DMF, and stirred until homogenous at room temperature. After that, the solution obtained was added into a plastic syringe, the internal diameter of plastic was 20 cm, the pinhead was connected to a 20-kV high-voltage, and aluminum foil served as counter electrode. The distance between the capillary and electrode was 21 cm, the feed rate of the solution was adjusted to 0.1 m*l*/h through a syringe pump. The electrospinning was performed at room temperature.

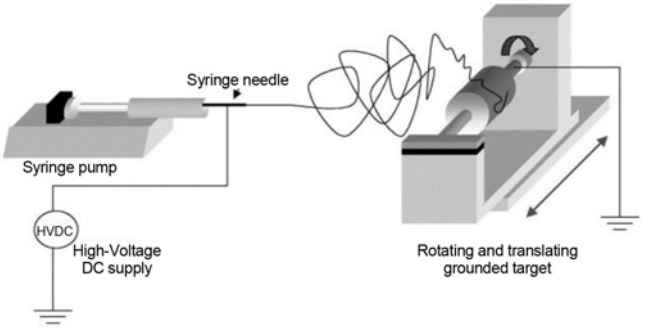


Figure 1. Schematic for electrospinning system.

Preparation of PAN Solution Containing Ag Particles

0.03 mg $AgNO_3$ (99.99 %, Sigma-Aldrich Co., USA) dissolved in 70 m*l* DMF with stirring at 30 min (the weight percentage of $AgNO_3$ in the solution and the time of stirring for optimum reduction was investigated by UV/vis spectrometer), 5 wt % PAN was then added to the solutions followed by stirring for 24 h at room temperature. The solution obtained was added into a plastic syringe with 20 mm internal diameter and 0.5 mm needle, the pinhead was connected to a (20 kV) high-voltage, and aluminum foil served as counter electrode. The distance between the capillary and electrode was 21 cm. the feed rate of the solution was adjusted to (0.1, 0.2, 0.3 and 0.4 m*l*/h) through a syringe pump. The electrospinning was performed at room temperature.

Treatment of PAN/Ag Composite Nanofiber (Stabilization, Carbonization)

The PAN/Ag nanofibers were stabilized in an air atmosphere at 270 °C for 2 h (at a heating rate of 2 °C/min) and followed by carbonization at 600, 650, 700, 750, 1000 °C for 1 h (at a heating rate of 4.5 °C/min) under an inert nitrogen atmosphere to yield carbonized. Stabilization is necessary to form a ladder structure that can withstand high temperatures during carbonization. During stabilization and carbonization, calcination of Ag also occurs and it is important because it increases the crystallinity of the nanoparticles which enhances photocatalytic activity. Using a programmable tube furnace, the nanofibers mats produced from electrospinning were heated at a rate of 2 °C/min up to 270 °C and maintained at this temperature for 2 hours (Figure 2). After the stabilization process, nitrogen gas was purged into the furnace to remove unwanted air or oxygen. This was done to prevent oxidation of fibers at high temperatures. The nanofibers were then heated at a rate of 4.5 °C/min up to 600, 650, 700, 750, 1000 °C in a nitrogen environment. The resulting carbon nanofibres were cooled down to room temperature in an inert gas atmosphere before

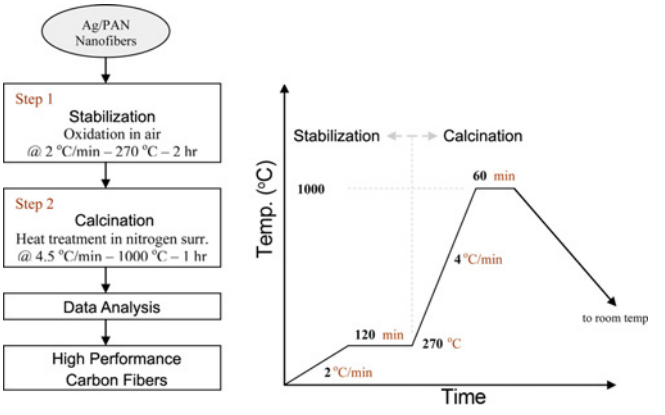


Figure 2. Stabilization and carbonization processes.