Materials Letters 68 (2012) 133–136

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Electrospun carbon nano-felt surface-attached with Pd nanoparticles for hydrogen sensing application

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ARTICLE INFO

Article history:
Received 22 March 2011
Accepted 20 October 2011
Available online 26 October 2011

Keywords:
Nanomaterials
Electrospinning
Fiber technology
Palladium nanoparticle
Hydrogen sensors

ABSTRACT

Carbon nanofibrous mat (nano-felt) surface-attached with Pd nanoparticles was prepared from electrospun polyacrylonitrile nano-felt surface-functionalized with amidoxime groups, and its application for hydrogen sensing was explored. The material consisted of relatively uniform and randomly overlaid carbon nanofibers with diameters of ~300 nm, while the attached Pd nanoparticles had sizes in the range from a few to tens of nanometers. The electrospun carbon nano-felt was mechanically flexible/resilient, and the resistance of the material varied upon exposure to H_2 at room temperature. The study suggested that electrospun carbon nano-felts surface-attached with metal nanoparticles could be a material of choice for the fabrication of gas- and/or bio-sensors, and the amidoxime-functionalization of electrospun polyacrylonitrile nano-felt could be a general approach for the development of various carbon nano-felts surface-attached with different metal nanoparticles.

1. Introduction

Carbon nanotubes/nanofibers have been studied for gas- and/or bio-sensing applications in recent years [1]. The sensitivity and selectivity of these sensors can be further enhanced via deposition of metal nanoparticles on the surface of the nanotubes/nanofibers through wet-chemical reduction or electrochemical deposition [2]. Nonetheless, chemical reactions during the deposition may introduce impurities and/or have adverse effect on electrical properties of carbon nanotubes/nanofibers [3]. Unlike carbon nanotubes/nanofibers that are produced by bottom-up synthetic methods, electrospun carbon nanofibers are fabricated through a top-down nano-manufacturing process of electrospinning followed by thermal treatments of stabilization and carbonization [4]; this results in low-cost and continuous carbon nanofibers that are easy to align, assemble, and process into applications. The aim of this study is to develop and evaluate the nanofibrous mat (nano-felt) of electrospun carbon nanofibers surface-attached with palladium (Pd) nanoparticles (as electric signal transducer) for the hydrogen sensing application.

The functional group of amidoxime [$-C(NH_2)=N(OH)$], which can be readily generated via the reaction between nitrile group ($-C\equiv N$) and hydroxylamine (NH_2OH), possesses high capability for adsorption of metal ions due to its coordinating/chelating property [5,6]. Polymers with amidoxime groups, such as amidoxime-functionalized polyacrylonitrile (PAN), have been used for removal and/or recovery of metal ions from aqueous media [7]. With the development of electrospinning technique [8], PAN nanofibers surface-functionalized with amidoxime groups have attracted growing attention for adsorption of metal ions due to large surface-to-mass ratio and porosity [9]. Research endeavors have indicated that, metal ions (*e.g.*, Ag^+) coordinated/chelated on amidoxime-functionalized PAN fibers (including both conventional microfibers and electrospun nanofibers) can be converted into uniformly distributed and immobilized metal nanoparticles; and the resulting materials possess excellent photo-catalytic and/or antimicrobial functionalities [10,11]. Since PAN is a common precursor for making carbon fibers, electrospun PAN nano-felt surface functionalized with amidoxime groups could be used to prepare various carbon nano-felts surface-attached with different metal (*e.g.*, Pd) nanoparticles.

Hydrogen sensing is important for safety and other practical concerns in the proposed hydrogen economy [12]; Pd nanoparticle is of particular interest for hydrogen sensing because it selectively adsorbs H_2 and forms a reversible compound of palladium hydride, and the process is accompanied with measurable variations of electrical properties. During this study, the felt of relatively uniform and randomly overlaid PAN nanofibers with diameters of ~350 nm was prepared by electrospinning; subsequently, amidoxime groups were introduced onto fiber surfaces through immersion of PAN nano-felt into NH_2OH aqueous solution. The generated amidoxime functional groups were then utilized for coordinating/chelating of Pd^{2+} ions, which were further reduced by hydrazine (NH_2NH_2) into Pd nanoparticles. Finally, the amidoxime-functionalized PAN nano-felt with Pd nanoparticles attached on fiber surface (ASFPAN-PdNP) was stabilized and carbonized to convert PAN into carbon; and the prepared material was evaluated for hydrogen sensing application. For comparison, carbon nano-felts without Pd nanoparticles were also prepared from electrospun PAN nano-felts (ESPAN) and ESPAN surface-functionalized with amidoxime groups (ASFPAN). The study revealed that the carbon nano-felt made of ASFPAN-PdNP possessed excellent hydrogen sensing capability at room temperature, and

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doi:10.1016/j.matlet.2011.10.064

the material was mechanically flexible/resilient. It is envisioned that electrospun carbon nano-felts surface-attached with metal nanoparticles could be a material of choice for the fabrication of gas- and/or biosensors, and the amidoxime-functionalization of electrospun PAN nano-felt could be a general approach for the preparation of various carbon nano-felts surface-attached with different metal nanoparticles.

2. Materials and methods

2.1. Materials

The PAN used in this study was the Special Acrylic Fibers (S.A.F. 3E) provided by the Courtaulds, Ltd. (Nottingham, UK). Acetone, *N*, *N*-dimethylformamide (DMF), NH_2OH, $Pd(NO_3)_2$, and NH_2NH_2 were purchased from the Sigma-Aldrich Chemical Co. (St. Louis, MO) and used without further purifications.

2.2. Electrospinning

The PAN of S.A.F. 3K was first immersed in acetone to remove the surface oil, and then was used to prepare a 14 wt.% solution in DMF. Subsequently, the solution was filled in a 30 ml BD Luer-Lok™ tip plastic syringe having an 18 gauge stainless-steel needle with 90° blunt end. The electrospinning setup included an ES30P high voltage power supply, purchased from the Gamma High Voltage Research, Inc. (Ormond Beach, FL), and a nanofiber collector of electrically grounded aluminum foil that covered a roller with the diameter of 25 cm. The collector was placed at 22 cm below the tip of needle. During electrospinning, a positive high voltage of 25 kV was applied to the needle; and the solution feed rate of 1.3 ml/h was maintained using a KDS200 syringe pump purchased from the KD Scientific Inc. (Holliston, MA). The electrospun PAN nano-felt could be readily peeled off from the aluminum foil, and it was stored in a desiccator before the subsequent surface functionalization.

2.3. Surface functionalization

The surface functionalization was carried out by immersion of electrospun PAN nano-felt (ESPAN) in 1 M NH_2OH aqueous solution at 70 °C for 15 min. The amidoxime-functionalized nano-felt (ASFPAN) was then immersed in 0.01 M $Pd(NO_3)_2$ aqueous solution at 25 °C for 6 h to allow amidoxime groups to coordinate/chelate with Pd^{2+} ions. The nano-felt was further treated in 0.001 M NH_2NH_2 aqueous solution at 25 °C for 24 h to prepare the nano-felt surface-attached with Pd nanoparticles (ASFPAN-PdNP). All of the nano-felts were thoroughly rinsed with distilled water after each step followed by being dried in an oven at 70 °C for 6 h.

2.4. Stabilization and carbonization

Each nano-felt of ESPAN, ASFPAN, and ASFPAN-PdNP was first sandwiched between two graphite plates, and then heated to 280 °C at 1 °C/min in a Lindberg 54453 heavy duty tube furnace; this was followed by holding the temperature at 280 °C for 6 h during the stabilization. The stabilized nano-felts were further heated to 700 °C at 5 °C/min in argon followed by holding the temperature at 700 °C for 1 h during the carbonization.

2.5. Characterization

The nano-felts were examined with a Zeiss Supra 40VP field-emission scanning electron microscope (SEM) equipped with a PGT energy-dispersive X-ray spectrometer (EDS), a Hitachi H-7000 FA transmission electron microscope (TEM), and a Rigaku Ultima Plus X-Ray diffractometer (XRD). The Fourier transform infrared (FT-IR) spectra of the nano-felts were obtained from a Bruker Tensor-27 FT-IR spectrometer.

2.6. Hydrogen sensing test

Prior to hydrogen sensing test, a piece of each carbon nano-felt with length, width, and thickness being 10, 7, and 0.05 mm was cut and placed across two electrodes in a sealed chamber with inlet and outlet of H_2. All experiments were conducted with the flow rate of H_2 being 500 sccm. The current of each device at 5 V was recorded as a function of time using the Keithley 2612 Sourcemeter. During each test, a nano-felt sensor was first purged with air for 10 min, then with H_2 for 25 min, and finally in vacuum for 25 min; thereafter, the H_2 and vacuum cycle was repeated for three times to evaluate the sensing performance and reproducibility.

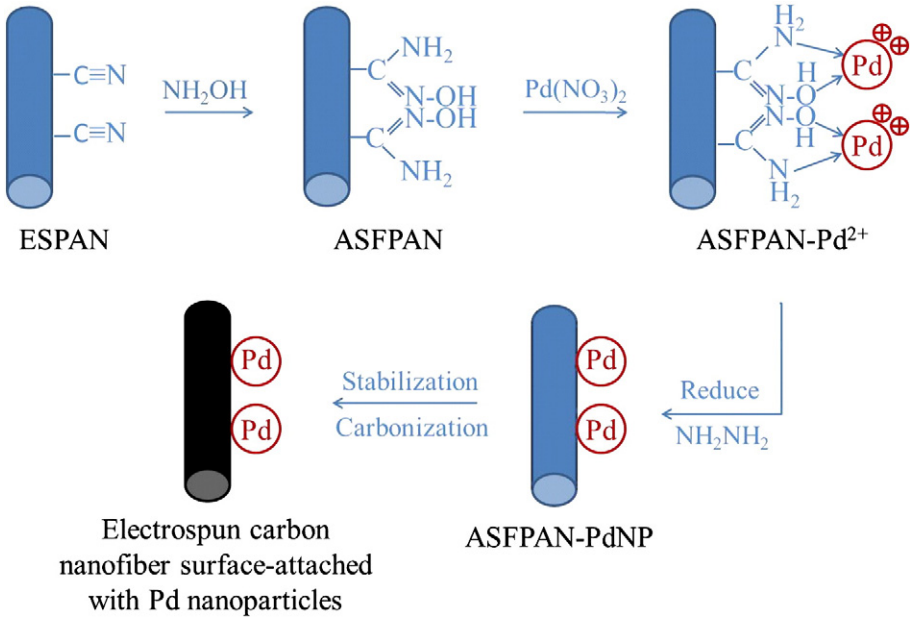

Fig. 1. A schematic representation showing all of the steps for the preparation of electrospun carbon nano-felt surface-attached with Pd nanoparticles.