Synthetic Metals 160 (2010) 1136–1142

Contents lists available at ScienceDirect

Synthetic Metals

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

Preparation of one-dimensional (1D) polyaniline–polypyrrole coaxial nanofibers and their application in gas sensor

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ARTICLE INFO

Article history:
Received 12 October 2009
Received in revised form 16 February 2010
Accepted 23 February 2010
Available online 25 March 2010

Keywords:
Polyaniline–polypyrrole
Coaxial nanofibers
Gas sensor
TEA

ABSTRACT

A facile and low-cost method has been developed to prepare one-dimensional (1D) polyaniline–polypyrrole (PANI–PPy) coaxial nanofibers (PPCF). The morphology and molecular structure of PPCF were proved by scanning electron microscopy, transmission electron microscopy, EDX, UV–vis, FTIR and Raman spectroscopy. A possible synthetic scheme for the synthesis of PPCF has been proposed. The electrical responses of PPCF to triethylamine (TEA) vapor were measured at room temperature. It was found that PPCF showed a rapid, sensitive and reversible conductance change upon exposure to TEA vapor at concentrations ranging from 1 to 1000 ppm. The results suggested that the comprehensive performance of the gas sensor using PPCF was better than the results obtained using PANI nanofibers and PPy separately. In addition, a sensing mechanism was proposed.

1. Introduction

Conducting polymers have been widely investigated in the past two decades due to their facile synthesis, environmental stability, high conductivity and various applications in optical, nanoelectronic devices, batteries and sensors [1–4]. Among the conducting polymers, polyaniline (PANI) and polypyrrole (PPy) both exhibit stable doping/dedoping chemistries and have been the most extensively studied conducting polymers by far. To date, one-dimensional (1D) conducting polymers have received much attention due to their potential for improving the results of applications performed using the corresponding bulk conducting polymers [4]. Recently, the reported techniques for fabricating 1D PANI and PPy include hard and soft templates [5–7], and some "template-less" method [8–10]. Such 1D PANI (PPy) possessing high aspect ratios and high surface area are potentially applied in various fields such as sensors [11–13]. Meanwhile, conducting polymers based on composites especially with 1D morphology have attracted great interest owing to their better catalytic and sensing properties compared with the neat conducting polymers [14–18]. Currently, some studies have demonstrated the composites of two conducting polymers which exhibit superior electrochemical activity compared with the neat one [15,18].

1D PANI and PPy have been widely studied in the development of gas sensors due to their high surface area, enhanced gas sensor performance, room temperature operation, and their rich structural modification chemistry [1,16]. Craighead and co-workers [12] used a non-lithographic deposition process to form single PANI nanowire chemical sensors, which exhibited high sensitivity to low concentration NH_3. A similar result was gained with a single PPy nanowire gas sensor [13]. The gas sensing response rate and sensitivity of nanostructured PANI or PPy to special target gases has been improved considerably. However, the regeneration of gas sensors based on nanostructured conducting polymers is still somewhat difficult [19–22]. For example, when PANI is exposed to a relatively high concentrations of NH_3, the PANI need to react with HCl or heat the sensor to regenerate the sensor [22,21]. It is necessary to develop the repeatability of conducting polymer materials for gas sensor applications. As is known, the applications of conducting polymer based composite materials in gas sensors have attracted the interest of some researchers. It is considered that composite polymers will improve the property of gas sensors due to their synergistic and hybrid capabilities. Li et al. [23] fabricated a composite of PANI/MWNT, which showed high sensitivity and fast response to low concentrations of TEA vapor of ppb level. Airoudj et al. [20] developed an optical NH_3 sensor based on a PANI/SU-8 composite, which displayed a rapid response time and strong regeneration capacity. However, the synthesis of 1D nanostructures of conducting polymer based composites with a high sensitivity, rapid response time and good recoverability in gas sensor applications still remains a scientific challenge. As has been reported, PANI and PPy have been widely researched as positive materials in

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doi:10.1016/j.synthmet.2010.02.037

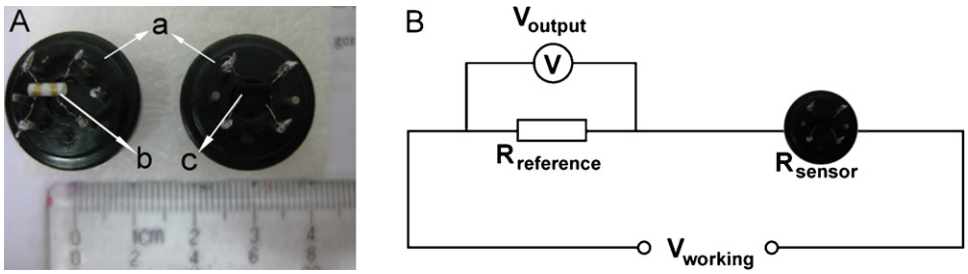

Fig. 1. (A) Digital image of hexagonal base (a), ceramic tube (b) and ceramic tube with conducting polymer (c) and (B) schematic of gas sensing measurement device. The change of the resistance of the R_{sensor} can be monitored via V_{output}, which is the voltage at the two ends of the reference resistor $R_{reference}$.

sensor applications. It is possible that the combination of PANI and PPy with 1D nanostructures will lead to a synergy effect and help to improve the general properties of gas sensors.

Herein, we demonstrate first the preparation of 1D PANI–PPy coaxial nanofibers (PPCF) by a facile method. At first, PANI nanofibers were synthesized by interfacial polymerization, and then PPy was in situ polymerized onto the surface of the PANI nanofibers in the presence of SDS surfactant. The product was characterized by scanning electronic microscopy (SEM), transmission electronic microscopy (TEM), UV–vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and conductivity measurement. The results confirmed the structure and molecular characteristics of the PANI–PPy coaxial nanofibers. Furthermore, the gas sensing properties of the PANI–PPy coaxial nanofibers to triethylamine (TEA) vapor, an important toxic gas in the biological field and food industry, were also studied. The obtained result showed that PPCF exhibited high sensitivity, fast response and good recovery. The gas sensing mechanism was also explored.

2. Experimental part

2.1. Materials

Aniline (ANI), pyrrole (Py), hydrochloric acid (HCl), ammonium persulfate ($(NH_4)_2S_2O_8$, APS), dichloromethane (CH_2Cl_2), iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and triethylamine (TEA) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium dodecyl sulfate (SDS) was obtained from Shanghai Sangon Biological Engineering Technology & Services Co., Ltd. Aniline and pyrrole were distilled under reduced pressure before use. All of the solutions and the dispersions were prepared with Milli-Q water (resistivity was 18.2 MΩ cm).

2.2. Preparation of PANI–PPy coaxial nanofibers (PPCF)

PANI nanofibers were prepared by interfacial polymerization in accordance with the literature method [9]. In a typical procedure, 145 μl aniline was dissolved in 5 ml dichloromethane (CH_2Cl_2) (solution a) and 91 mg APS was dissolved in 5 ml 1 M HCl solution (solution b). The solution b was then carefully transferred to the solution a, generating an interface and then triggering the polymerization of PANI. After 6 h, the entire aqueous phase (comprising of PANI nanofibers) was collected. Then, the by-products were removed from the PANI nanofibers by centrifugation method with ethanol and water respectively several times. The synthesis of the PPCF was according to the references [24,25] with some modifications. The prepared PANI nanofibers were all dispersed in 25 ml water using ultrasound for 1 h, and then 80 mg of SDS was added to the dispersion and stirred for another 2.5 h. After stirring, 40 μl of pyrrole monomer was dropwise added into the dispersion with continuous stirring. Approximately 1.5 h later, 1.45 ml of 0.4 M $FeCl_3$ solution was added into the PANI/pyrrole solution. The polymerization of pyrrole on the surface of the PANI nanofibers was carried out for 12 h. Then, PPCF was obtained by repeated centrifugation and redispersion of the product in ethanol and water, respectively. The product was then dried in vacuum (40 °C) for 24 h.

For comparison, the PANI nanofibers were also prepared by interfacial polymerization, which is the same as the above-mentioned process for preparing of PANI nanofibers.

Pure PPy was synthesized as follows. In a 150 ml flask, 690 μl Py was dissolved in 50 ml 1 M HCl solution, 50 ml of 0.4 M $FeCl_3$ solution was added into the Py solution with stirring. The reaction was carried out for 12 h at room temperature to complete the polymerization. As-prepared PPy was obtained after filtrating and repeated washing with ethanol and water, dried for 24 h at 40 °C in vacuum.

2.3. Characterizations

TEM images were obtained with a JEOL JEM-2100 electron microscope operating at 200 kV. SEM images were obtained on a LEO-1530 SEM system operating at 20 kV. The conductivities of compressed pellets of PANI nanofibers, PPCF and PPy, respectively, at room temperature were measured by the standard four-probe method on an SX1934 (SZ-82) digital four-probe testing instrument operating at an applied voltage of 20 mV. UV–vis absorption spectra were recorded on a Varian Cary-5000 spectrometer. FTIR measurements were performed on a Nicolet Avatar 360 spectrometer using KBr pressed pellets. Raman spectra were obtained using a LabRam I Raman spectrometer using the excitation line at 632.8 nm of a He–Ne laser at room temperature.

2.4. Gas sensing characteristic measurements

Gas sensing tests were performed using a WS-30A Gas Sensing Measurement System (Zhengzhou Winsen Electronics Technology Co., Ltd). As shown in Fig. 1A, the gas sensing device was fabricated from a ceramic tube and hexagonal base (Zhengzhou Winsen Electronics Technology Co., Ltd). 10 mg samples (PANI nanofibers, PPCF and PPy) were thoroughly dispersed in 1 ml ethanol, then 10 μl of the dispersion was sucked and dropped onto the ceramic tube, and the tube was carefully rotated above an electric heater to evaporate the ethanol. Finally, the ceramic tube was welded onto the hexagonal base. The prepared device was placed into an air-tight test box (18 l). TEA vapor was obtained following injecting a certain quantity of TEA liquid into the sealed test box. The gas sensitivities of the PANI nanofibers, PPCF and PPy were investigated by online recording their electrical responses when exposed separately to TEA vapor and air at room temperature using the WS-30A gas sensing device. The schematics of the gas sensing device and the operating principles are shown in Fig. 1B. The room temperature and relative humidity were 15 °C and 60%, respectively. The applied voltage of the measurement was 5 V. The sensitivity of the sensor (S) is defined as $S = \Delta R/R$, $\Delta R = R_{TEA} - R$, where R_{TEA} and R