Electrospun polymer nanofiber sensors

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Abstract

Using the electrosprinning technique, we have prepared lithium perchlorate (LiClO\textsubscript{4}) doped-polyethylene oxide (PEO) electrospun nanofibers for humidity sensing and camphorsulfonic acid (HCSA) doped-polyaniline (PANI)/polystyrene (PS) electrosyn spun nanofibers for sensing hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and glucose. The diameters of these as-prepared polymeric nanofibers are in the range of 400-1000 nm. Owing to the large surface area and good electrical properties intrinsically associated with these nanoscale functional polymer fibers, we achieved significantly enhanced sensitivity for the nanofiber sensors in respect to their corresponding film-type counterparts. While scanning electron micrographs showed some distortions for the LiClO\textsubscript{4} doped-PEO nanofibers after the humidity measurements, no observable morphological change was seen for the HCSA doped-PANI/PS nanofiber sensors after the measurements of H\textsubscript{2}O\textsubscript{2} and/or glucose.

Keywords: Electrosyn spun nanofibers, Lithium perchlorate doped-polyethylene oxide, Camphorsulfonic acid doped-polyaniline/ polystyrene, Sensors, Humidity sensing, Glucose sensing

1. Introduction

In response to the pressing needs for cheaper, quicker, simpler, and more reliable detections, there are tremendous progresses in the development of chemical and biological sensors with high sensitivities. In this regard, the electrosprinning process has been used to produce polymeric nanofibers for sensing applications. For instance, it has recently been demonstrated that optical sensors based on certain electrosyn spun fluorescent polymer nanofibers showed a sensitivity up to three orders of magnitude higher than that obtained from thin film sensors for the detection of nitro compounds, ferric and mercury ions [1-3]. In particular, Wang et al., [4] reported a sensitive optical sensor by assembling fluorescent probes onto electrosyn cellulose acetate nanofibers, which showed fluorescence quenching upon exposure to even an extremely low concentration (ppb) of methyl viologen cytochrome in aqueous solutions.

Apart from the optical transduction, the conductivity changes of certain electrosyn conducting polymer nanowires have also been exploited for sensing chemicals, as exemplified by electrosyn polyaniline (PANI) nanowires that showed a rapid and reversible resistance change upon exposure to NH\textsubscript{3} gas at concentration as low as 0.5 ppm [5]. The unusually high sensitivities observed for these electrosyn nanofibers can be attributed to their high ratios of the surface area to volume.

Electrosprinning [6] has been widely used to generate polymer nanofibers of a large specific surface area to be attractive for a wide range of applications ranging from highly sensitive sensors to efficient catalysts. The high surface area to volume ratio, together with their excellent electrical properties, make electrosyn conducting polymer nanofibers particularly interesting for sensing applications [7]. In this paper, we present the potential use of the LiClO\textsubscript{4}-doped PEO ionically-conducting electrosyn spun nanofibers and electronically-conducting

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camphorsulfonic acid (HCSA) doped-PANI/PS nanofibers for humidity and glucose sensing, respectively. Corresponding results for the LiClO₄-doped PEO and HCSA doped-PANI/PS thin film sensors will also be discussed as appropriate.

2. Experimental

2.1. Materials

PEO (M.W. = 400,000), emeraldine base PANI (M.W. = 65,000), and polystyrene (PS, M.W. = 200,000) were purchased from Aldrich, as were LiClO₄ and HCSA. Glucose oxidase (GOX, 15,500 units/g) and dextrose glucose were purchased from Sigma. Buffer solutions of pH = 7.0 were received from Fisher Scientific.

2.2. Fabrication of PEO/LiClO₄ nanofiber humidity sensors

A predetermined amount of PEO sample was dissolved in a mixture solvent of ethanol and distilled water (EtOH/H₂O = 0.7 w/w) to produce 5 wt % PEO solution, to which 1.0 wt % LiClO₄ was added at room temperature under stirring. To construct a conductometric sensor for humidity measurements, the homogenous PEO/LiClO₄ solution was then electrosprun onto an interdigitated comb-shaped aluminum electrode supported by a glass substrate (1.25 cm²). Electrosprinning was performed at room temperature in air under a voltage of 30 kV and collected onto the comb-shaped aluminum electrode at a distance of 30 cm from the tip of the pipette electrode. As a reference, the corresponding film-type humidity sensor was prepared from the same PEO/LiClO₄ solution by spin-coating.

2.3. Fabrication of polyaniline nanofiber glucose sensors

A mixture of 2 wt % PANI, 4 wt % HCSA, and 7.5 wt % PS in chloroform was magnetically stirred overnight to produce a homogeneous solution for electrosprining under an applied voltage of 30 kV at room temperature in air. The gap distance between the tip of the pipette electrode and the collector (Al foil) was 30 cm. HCSA doped-PANI/PS non-woven mat nanofibers thus prepared were peeled off from the collector and pressed onto a sticky tape (0.5 cm × 0.5 cm). An Al clip was then used to connect the PANI nanofiber working electrode to an electrochemical unit. For comparison, a solution-cast PANI/PS film sensor was prepared from the same solution under the same conditions.

Prior to any sensing measurement, both the HCSA-PANI/PS nanofiber and film sensors were dried in a vacuum oven at 60°C for 2 hr. Thereafter, GOX was immobilized onto the HCSA-PANI/PS nanofiber and film electrodes by electrophoresis from an acetone buffer (pH=3.2) solution containing 2.5 mg/ml GOX at a potential of 0.4 V and a scan rate of 100 mV/s for 1 hr.

2.4. Characterization

Both PEO/LiClO₄ nanofiber and film-type sensors were dried in a vacuum oven at 30°C for 1 hr, followed by measuring their humidity-resistance characteristics over a humidity range from 25 to 65% controlled by a humidifier (Lasko) at 25°C.

The GOX-containing HCSA-PANI/PS nanofiber and film sensors were used to monitor concentration changes of H₂O₂ released from the glucose oxidation reaction, by measuring redox current at the oxidative potential of H₂O₂ (i.e. the amperometric method) on an AD Instruments Power Lab 4SP electrochemical unit. Prior to the glucose sensing measurements, however, the HCSA-PANI/PS nanofiber and film sensors were tested with the pristine H₂O₂. In both cases, a single compartment cell with a working volume of 2 ml was used. The three-electrode system consisted of a working electrode, platinum counter electrode, and Ag/AgCl reference electrode.

SEM images were taken on a Hitachi S-2150 SEM unit under 20 kV for the PEO/LiClO₄ and HCSA-PANI/PS nanofiber sensors before and after the humidity, H₂O₂ and glucose measurements, respectively.

3. Results and Discussion

3.1. PEO/LiClO₄ nanofiber humidity sensors

Figs. 1 (a,b) represent changes of the resistance in the logarithm scale as a function of % humidity for PEO/LiClO₄ nanofiber and film sensor, respectively. A linearly inverse proportional relationship between the resistance and the % humidity was observed in both cases. However, the rate of resistance reduction with the % humidity is much higher for the PEO/LiClO₄ nanofiber sensor than that of the corresponding PEO/LiClO₄ film sensor, as indicated by the different values of the slopes of the two lines. The greater absolute value of the slope for the nanofiber sensor (0.06 vs. 0.01) indicates a higher sensitivity, presumably due to the larger surface area.
As also seen in Fig. 1, the initial resistance of the electrospun nonwoven mats was lower than the cast film, although they have been made from the same starting solution. The lower conductivity values for the electrospun nanofibers than those of the cast films can be attributed to the porous nature of the non-woven mat nanofibers, as the present method measures the volume resistivity rather than the conductivity of an individual fiber.

3.2. HCSA-PANI/PS nanofiber glucose sensors

Fig. 3 shows typical SEM image of the as-spun HCSA-PANI/PS nanofibers, in which fiber-like structures of diameters in the ranges of 800-1000 nm are clearly evident.

The cyclic voltammetric (CV) spectra measured at various H$_2$O$_2$ concentrations for the HCSA doped-PANI/PS nanofiber electrode are given in Fig. 4 (a). Also included in Fig. 4 are the current responses, recorded at the H$_2$O$_2$ redox potential, to the H$_2$O$_2$ concentrations for the nanofiber (Fig. 4a) and the thin film (Fig. 4b) sensors measured under the same conditions. As expected, the film sensor shows a much weaker current response than those of the nanofiber device. Although a linear response of the redox current to the H$_2$O$_2$ concentrations was obtained for both the HCSA doped-PANI/PS nanofiber and film sensors, the nanofiber sensor shows a much higher sensitivity, as evidenced by a greater value for the slope.

As expected, the film sensor shows much weaker current signals than those of the nanofiber device, though a linear response of the redox current to the H$_2$O$_2$ concentrations was obtained for both the HCSA doped-PANI/PS nanofiber and film sensors. The nanofiber sensor shows a much higher sensitivity, as indicated by a much greater slope value for the corresponding curve in Fig. 4b.

The above results obtained from the measurements of pure H$_2$O$_2$ prompted us to carry out the sensing measurements for glucose using the GOX-immobilized HCSA-PANI/PS electrospun nanofibers. The redox current at the oxidative potential of H$_2$O$_2$ from the GOX-immobilized HCSA-PANI/PS nanofibers for glucose sensing was also found to increase with increasing glucose concentrations (Fig. 5a). The amperometric response from the GOX-immobilized HCSA-PANI/PS nanofiber sensor is much higher than
that of the HCSA-PANI/PS film sensor, as shown in Fig. 5b. Since nanofibers contain a large specific surface area, therefore the amount of GOX immobilized on the nanofiber sensor was much higher than that for the film sensor, leading to a higher sensitivity for the current response. Thus, the HCSA-PANI/PS electrospun nanofibers could be promising for fabricating novel glucose sensors with a higher sensitivity.

Fig. 4. (a) CVs for the HCSA-PANI/PS nanofiber sensors at different H2O2 concentrations, and (b) The current response for HCSA-PANI/PS nanofiber and film sensors to various H2O2 concentrations. Note that the current response has been scaled by the weight of the polymeric material deposited on the electrodes.

Unlike the PEO/LiClO4 nanofiber sensor, there is no obvious deformation observed for the water insoluble HCSA-PANI/PS nanofiber sensors as illustrated in Fig. 6, suggesting reusability for the HCSA-PANI/PS nanofiber sensor.

Fig. 5. (a) CVs for the GOX-immobilized HCSA-PANI/PS nanofiber sensors at different glucose concentrations, and (b) The current response of the GOX-immobilized HCSA-PANI/PS nanofiber and film sensors to various glucose concentrations. Note the current response has been scaled by the weight of the polymeric material deposited on the electrodes.

4. Conclusion

We have demonstrated the use of the electrospun PEO/LiClO4 and HCSA doped-PANI/PS nanofibers for humidity and glucose sensing, respectively. The large surface area, together with the good electrical properties, made these conducting polymer nanofibers promising materials for sensing applications, especially comparing with their corresponding film-type sensors.

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References