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Electrospun polymer nanofiber sensors

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Abstract

Using the electrospinning technique, we have prepared lithium perchlorate ($LiClO_4$) doped-polyethylene oxide (PEO) electrospun nanofibers for humidity sensing and camphosulfonic acid (HCSA) doped-polyaniline (PANI)/polystyrene (PS) electrospun nanofibers for sensing hydrogen peroxide (H_2O_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 $LiClO_4$ 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_2O_2 and/or glucose.

Keywords: Electrospun nanofibers, Lithium perchlorate doped-polyethylene oxide, Camphosulfonic 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 electrospinning process has been used to produce polymeric nanofibers for sensing applications. For instance, it has recently been demonstrated that optical sensors based on certain electrospun 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 electrospun 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 electrospun conducting polymer nanowires have also been exploited for sensing chemicals, as exemplified by electrospun polyaniline (PANI) nanowires that showed a rapid and reversible resistance change upon exposure to NH_3 gas at concentration as low as 0.5 ppm [5]. The unusually high sensitivities observed for these electrospun nanofibers can be attributed to their high ratios of the surface area to volume.

Electrospinning [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 electrospun conducting polymer nanofibers particularly interesting for sensing applications [7]. In this paper, we present the potential use of the $LiClO_4$-doped PEO ionically-conducting electrospun nanofibers and electronically-conducting

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camphosulfonic acid (HCSA) doped-PANI/PS nanofibers for humidity and glucose sensing, respectively. Corresponding results for the LiClO$_4$-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 LiClO$_4$ 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/LiClO$_4$ nanofiber humidity sensors

A predetermined amount of PEO sample was dissolved in a mixture solvent of ethanol and distilled water (EtOH/H$_2$O = 0.7 w/w) to produce 5 wt % PEO solution, to which 1.0 wt % LiClO$_4$ was added at room temperature under stirring. To construct a conductometric sensor for humidity measurements, the homogenous PEO/LiClO$_4$ solution was then electrospun onto an interdigited comb-shaped aluminum electrode supported by a glass substrate (1.25 cm^2). Electrospinning 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/LiClO$_4$ solution by spin-casting.

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 over night to produce a homogeneous solution for electrospining 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 electrodeposition from an acetate buffer (pH=5.2) 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. Charaterization

Both PEO/LiClO$_4$ nanofiber and film-type sensors were dried in a vacuum oven at 30°C for 1 h, 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 H$_2$O$_2$, released from the glucose oxidation reaction, by measuring redox current at the oxidative potential of H$_2$O$_2$ (*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 H$_2$O$_2$. 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/LiClO$_4$ and HCSA-PANI/PS nanofiber sensors before and after the humidity, H$_2$O$_2$ and glucose measurements, respectively.

3. Results and Discussion

3.1. PEO/LiClO$_4$ nanofiber humidity sensors

Figs. 1 (a&b) represent changes of the resistance in the logarithm scale as a function of % humidity for PEO/LiClO$_4$ 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/LiClO$_4$ nanofiber sensor than that of the corresponding PEO/LiClO$_4$ 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 nanofiber mat was higher than that of 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.
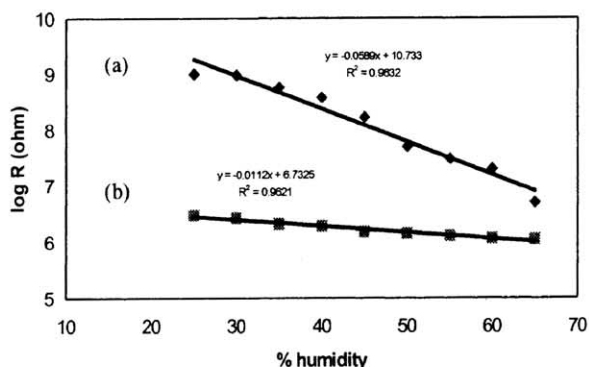

Fig. 1. Humidity dependence of resistivity for PEO/LiClO₄ sensors: (a) the nanofiber sensor and (b) the film sensor.

Although the measured conductivity for the electrospun nanofibers is relatively low, their porous structures together with the high surface area to volume ratio and good electrical properties, have been demonstrated to be significant benefits for the development of advanced humidity sensors with a high sensitivity.

After the humidity sensing measurements, some deformation of the nanofibers was observed, as shown by the SEM images given in Fig. 2. The observed morphological changes in Fig. 2a and Fig. 2b resulted from the swelling effect of water-soluble PEO/LiClO₄ nanofibers during the humidity measurements. Consequently, the as-prepared PEO/LiClO₄ nanofiber sensors might be utilized only as a disposable humidity sensor. However, further modification of the material/ device design could circumvent this problem.
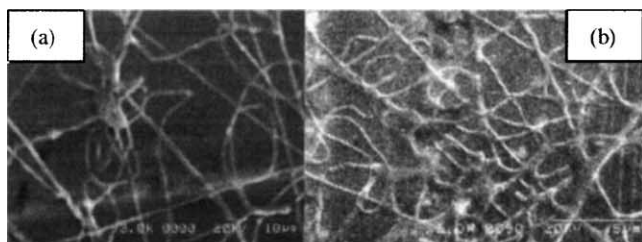

Fig. 2. SEM images of PEO/LiClO₄ nanofibers; (a) before and (b) after the humidity measurement.

3.2. HCSA-PANI/PS nanofiber glucose sensors

Fig. 3 shows typical SEM image of the as-spun HSCA-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_2O_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_2O_2 redox potential, to the H_2O_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 enormously weaker current signals than those of the nanofiber device. Although a linear response of the redox current to the H_2O_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_2O_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.
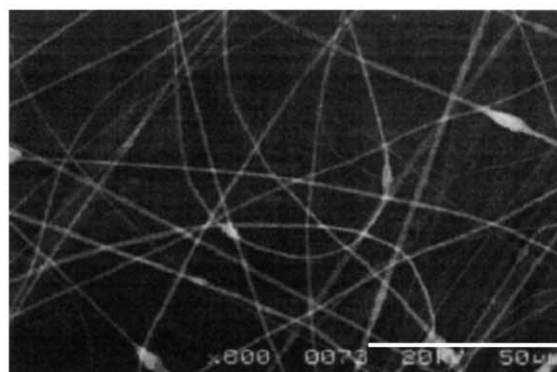

Fig. 3. A typical scanning electron micrograph of HCSA doped-PANI/PS nanofibers.

The above results obtained from the measurements of pure H_2O_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_2O_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.
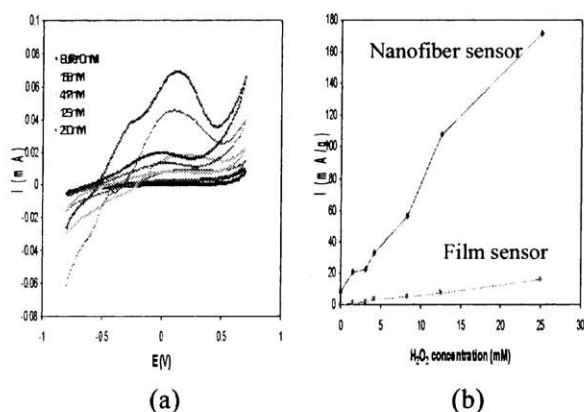

(a)   (b)

Fig. 4. (a) CVs for the HCSA-PANI/PS nanofiber sensors at different H_2O_2 concentrations, and (b) The current response for HCSA-PANI/PS nanofiber and film sensors to various H_2O_2 concentrations. Note that the current response has been scaled by the weight of the polymeric material deposited on the electrodes.
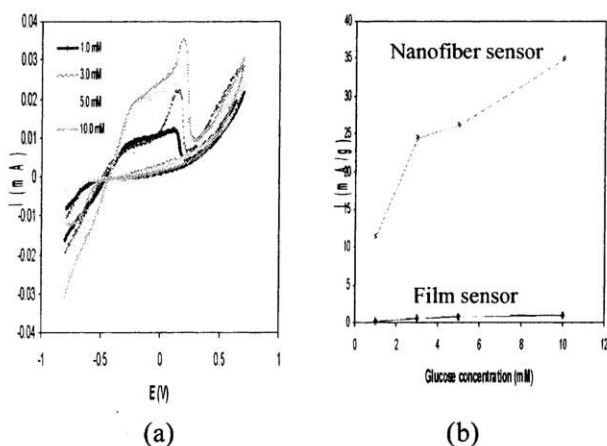

(a)   (b)

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.

Unlike the PEO/LiClO$_4$ 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.
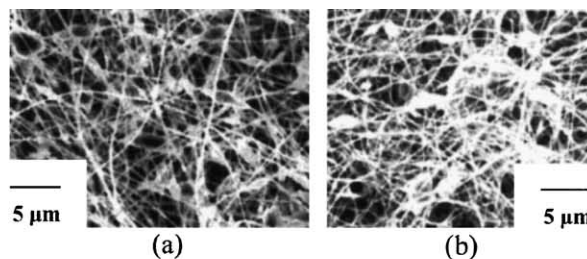

(a)   (b)

Fig. 6. Scanning electron micrographs of the HCSA-PANI/PS nanofibers; (a) before the sensing measurement, and (b) after the glucose sensing measurements.

4. Conclusion

We have demonstrated the use of the electrospun PEO/LiClO$_4$ 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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