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The woven fiber organic electrochemical transistors based on polypyrrole nanowires/reduced graphene oxide composites for glucose sensing

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ABSTRACT

Novel woven fiber organic electrochemical transistors based on polypyrrole (PPy) nanowires and reduced graphene oxide (rGO) have been prepared. SEM revealed that the introduction of rGO nanosheets could induce the growth and increase the amount of PPy nanowires. Moreover, it could enhance the electrical performance of fiber transistors. The hybrid transistors showed high on/off ratio of 10^2, fast switch speed, and long cycling stability. The glucose sensors based on the fiber organic electrochemical transistors have also been investigated, which exhibited outstanding sensitivity, as high as 0.773 NCR/decade, with a response time as fast as 0.5 s, a linear range of 1 nM to 5 μM, a low detection concentration as well as good repeatability. In addition, the glucose could be selectively detected in the presence of ascorbic acid and uric acid interferences. The reliability of the proposed glucose sensor was evaluated in real samples of rabbit blood. All the results indicate that the novel fiber transistors pave the way for portable and wearable electronics devices, which have a promising future for healthcare and biological applications.

1. Introduction

Serum glucose real-time measurement have important meaning for the therapy of diabetics, prevention of gestational diabetes, reducing the incidence risk of health complications and controlling the spread of sickness (Reach and Wilson, 1992; Wang Joseph, 2001). Early, many researchers monitored glucose concentrations in blood samples by using an enzyme-coated oxygen electrode (Clark and Lyons, 1962; Kang et al., 2009). Then, organic thin film transistors (OTFTs) are attracting considerable scientific attention for sensor applications, including low cost, inherent amplification characteristic, compatibility for miniaturization, and favorable integrated into circuits (Dimitrakopoulos and Malenfant, 2002; Sekitani et al., 2007; Sirringhaus et al., 2001). Among OTFTs, organic electrochemical transistors (OECTs) possess the advantage of the electrical parameters do not relate to the geometrical constraints, integration into portable electronic devices, and operate in liquid environment at low voltages, which make them more suitable for chemical and biological sensing (Lin and Yan, 2012; Lin et al., 2010; Tang et al., 2011b). The operating mechanism of OECTs depends on the doping and dedoping of the conducting polymer, which results in variation of its conductivity. Macaya et al. (Macaya et al., 2007) reported a simple glucose biosensor using poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT: PSS) as active layer, and the enzyme glucose oxidase to confer specificity. The sensor with sensitivity in the micromolar region was demonstrated. Bernards et al.(Bernards et al., 2008) investigated the behavior of OECT-based glucose oxide's sensors. The results demonstrated underlying device physics and established the relationship between sensor response and glucose concentration. An all PEDOT: PSS OECT for glucose sensing was investigated by Shim et al.(Shim et al., 2009) To improve the catalytic properties of enzymatic reaction, a ferrocene mediator was introduced for the electron transfer. The glucose can detect down to the micromolar region, which is capable for sensing in human saliva. Yan Feng et al. (Liao et al., 2013) developed a glucose sensing OECT that can measure glucose concentration in a broad concentration from 10 nm to 1 μm, which use the co-modifying graphene or reduced graphene oxide (rGO) and glucose oxidase on the gate electrodes. In addition, the sensor exhibits excellent selectivity. Liao et al. (2015) reported TiO_2 nanotube arrays was used as the gate electrode of the OECT device for glucose

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sensing, the device exhibited a linear response to the logarithm of glucose concentration (100 nM–5 mM), and the detection limit down to 100 nM was obtained. Furthermore, the device presents specificity, superior reproducibility and stability. Elizabeth Welch et al. (Welch et al., 2015) developed a glucose-sensing OECT using a polymer brush of poly(glycidyl methacrylate) and poly(2-hydroxyethyl methacrylate), which showed remarkable sensitivity and long-term stability.

Many progresses have been made in improving the performance of OECTs. However, it should be noted that most public papers about the OECT-based glucose sensors are equipped with solution electrolyte and planar configuration, which is not compatible with miniaturization and wearable devices for real time measurements. Therefore, it is expected that the devices can integrated with fabrics, which are preferable to portable detection for future applications. Fiber-based devices have attracted many attentions because of flexible geometry, facile woven into fabrics, and high degree of integration of the devices. Moreover, fiber-based devices have superior sensitivity due to their high specific areas and surface-dependent morphology. In our previously work, the fiber thin film transistors based nanofiber and polypyrrole for ion sensing exhibited good performances (Wang Yuedan et al., 2016). Polypyrrole nanowires with high aspect ratio were proved to be more effective in enhancing the electric properties. Many papers reported that PPy nanotube and rGO composites exhibited high surface area (Park et al., 2014; Sheng et al., 2016), which provided outstanding sensing performance in biosensor application. In this paper, we have incorporated polypyrrole into rGO sheets by a facile in-situ polymerization, and reported the hybrid fabrication of polypyrrole nanowires/graphene active layer for fiber organic thin-film transistors. To the best of our knowledge, this is the first example of fiber organic thin-film transistors sensor based on polypyrrole nanowires/graphene composites as active layer. A detailed study concerning the influence of rGO sheet on the PPy nanowires structure, electric properties and electrical performance has been presented. Our results suggest that the introduction of rGO sheets could be a facile and efficient way to enhance the device performance of low-voltage organic TFTs. Sensitivity, selectivity as well as reproducibility were further investigated by using FECTs. This work also indicates that the FECTs can be used as many other types of biosensors with high sensitivity and selectivity.

2. Experimental section

2.1. Materials

Poly (vinyl alcohol) (PVA), glucose, ascorbic acid (AA), uric acid (UA), lithium perchlorate, pyrrole, 5-sulfosalicylic acid dihydrate, iron (III) nitrate nonahydrate, and sodium anthraquinone-2-sulfonate were purchased from Aladdin Reagent Database Inc. Glucose oxidase (GOx) (10 kU g^{-1}) was also obtained from Aladdin Reagent Database Inc. and stored at −20 °C for future use. Propylene carbonate (PC) was purchased from Sigma-aldrich. Nafion (D520) was supplied from Shanghai River's electric Co., Ltd and stored at 4 °C. GOx stocking solution (5.0 mg/mL) in phosphate buffered saline (PBS, pH 7) was stored at 4 °C in a refrigerator. All the reagents used in this study are analytical grade.

2.2. Preparation of PPy nanowires/rGO/PA filament

The 133.3D (D represents denier) PA6 filament was sequentially ultrasonicated with alcohol and acetone for 10 min in order to remove the surface residue and improve its hydrophilicity, then the preprocessed filament was soaked in the DI water and dried completely in the fume hood. The above PA6 filament was immersed in 0.5% (wt%) graphene oxide (GO) solution at room temperature for 1.5 h on the shaking table. The GO solution was prepared according to chemical oxidation of microcrystalline graphite flakes using a modified Hummers method (Hummers Jr and Offeman, 1958; Li et al., 2008). In order to prepare the rGO/PA6 filament, GO/PA6 filament was suspended and sealed in a reaction kettle, then reduced by the hydrazine hydrate (HHA) for 4 h at 80 °C, finally rinsed with DI water to remove the unattached rGO. Subsequently, the obtained rGO/PA filament was immersed in the solution A, which consists of pyrrole, sodium anthraquinone-2-sulfonate (1 g/100 mL) and water, and then put the solution with rGO/PA filament in the refrigerator for 10–15 min before use. Meanwhile, the same volume of solution B also put into refrigerator for 10 min 5-sulfosalicylic acid dihydrate and iron (III) nitrate nonahydrate (mole ratio 1:1) were dissolved into DI water (named solution B). Finally the solution B was added dropwise to the solution A in 5–10 min, which contained the PA/rGO filament. The polymerization was implemented in an ice bath for 4 h under continued stirring. The obtained PPy/rGO/PA6 was successively washed with running water, ethyl alcohol and DI water, and then dried completely in the fume hood. The PPy/PA6 was obtained according to the same polymerization process.

2.3. Immobilization of the Enzymes

The as-prepared 133.3D PPy/rGO/PA6 filament was first immersed in the 5.0 mg/mL GOx PBS solution and conserved in the refrigerator at 4 °C for 12 h. After rinsed by DI water, the filament was soaked in the Nafion solution (1 wt%) at 4 °C for another 12 h, finally took out and dried at 4 °C for future use.

2.4. Device fabrication and characterization

Fig. 1a. shows the schematic diagram of a FECTs-based glucose sensor with the active layer of PPy/rGO composites. The source/drain and the gate electrode filament were made of 133.3D PPy/rGO/PA6 and PPy/rGO/PA6/GOx/Nafion respectively. The GOx and Nafion processed gate electrode filament was rinsed in the PBS solution utterly to eliminate the undesired residues before the assembly of the device. The gap between the two non-contacted fibers was connected by drops of electrolyte gel, which was prepared following the protocol described by Chodankar et al. (Chodankar, 2015) The simple protocol was PVA and DMSO by weight of 1:8 dissolved at 80 °C under stirring, and then added the lithium perchlorate and PC by weight of 1:9 at room temperature, the solution was left to stir and form the electrolyte gel. All FECTs were characterized with a semiconductor parameter analyzer (Keithley 4200) at room temperature. The response of sensor to the addition of glucose was measured at a constant V_g and V_{ds} as a function of time.

3. Results and discussion

3.1. Glucose sensor based on FECTs

Fig. 1 shows the schematic diagram of glucose sensor of fiber organic electrochemical transistors, which based on cruciform cross-junction geometry and PPy/rGO acted as the active layer. While two monofilaments consist of PA6 fiber acted as substrates, then modified by rGO, and in-situ polymerized by pyrrole. For the transistors assembly, the source/drain and gate were composed of PPy/rGO/PA6 filaments, which was in a simple cross-junction configuration with electrolyte gel contact at the junction of filaments. For the preparation of glucose sensor based on transistor, the PPy/rGO/PA6 filaments were coated with nafion and glucose oxidase as gate, then creating a fiber crossbar with PPy/rGO/PA6 monofilaments, and dropping electrolyte at the crossbar junctions. Large-area textile based on sensors could be woven by functionalized coated filaments.

3.2. SEM image and IR spectroscopy

The different surface morphology of raw and functionalized PA6 filaments were characterized by SEM, as shown in Fig. 2. The raw PA6