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High-performance field-effect transistor-type glucose biosensor based on nanohybrids of carboxylated polypyrrole nanotube wrapped graphene sheet transducer

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ABSTRACT

We report a rapid-response and high-sensitivity field-effect transistor (FET)-based sensor with specificity towards glucose, based on reduced graphene oxide (rGO)-carboxylated polypyrrole (C-PPy) nanotube (NT) hybrids as the conductive channel. The rGO, C-PPy NTs, and rGO/C-PPy NT hybrids were characterized using Raman spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The results indicate that a well-organized structure was successfully prepared, based on specific interactions between the C-PPy NTs and the graphene sheets. Reliable electrical contacts were developed between the rGO/C-PPy NTs and the patterned-microelectrodes, which remained stable when exposed to the liquid-phase electrolyte. Liquid-ion-gated FETs composed of these rGO/C-PPy NT hybrids exhibited hole-transport behavior with higher conductivity than those of graphene sheets or C-PPy NTs because the C-PPy NTs formed a bridge between the graphene layers, resulting in effective electron transport. Glucose oxidase (GOx) was used as the capture probe, and was tightly combined with C-PPy NTs via a chemical coupling reaction, and glucose detection was performed via GOx, which catalyzes the oxidation of glucose in the rGO/C-PPy NTs hybrid FET biosensor. The FET biosensor provided a rapid response (< 1 s) with high sensitivity toward glucose with a limit of detection of 1 nM. This result is ca. 2–3 orders more sensitive than previous reported glucose sensor. The FET-type biosensor was highly reproducible and stable in air over a period of one month. Furthermore, the liquid-gated FET-type biosensor displayed specificity toward glucose in a mixed solution containing compounds found in biological fluids.

1. Introduction

Diabetes mellitus is considered to be one of the most serious diseases affecting human health in developed countries, with complications including increased risk of heart disease, kidney failure, and blindness [1]. The disease is caused when the body fails to regulate glucose levels. Therefore, accurate and sensitive glucose detection is important in the treatment and management of diabetes. Several detection methods have been proposed for glucose sensing, based on techniques including electrochemical, optical, and Raman spectroscopy [2–4]. Electrochemical sensing is particularly interesting because of the potential to create compact low-cost devices. However, such sensor devices require complicated electrode fabrication, surface modification, and/or synthesis of modifiers, including complexing agents. Thus, for using in practical application, the exploration and development of a simple, yet high performance glucose detection technology is extremely desirable.

Field-effect transistor (FET)-type biosensors are considered have attracted much recent research interest, owing to the large current amplification and relatively high signal-to-noise ratio [5,6]. To implement a high-performance FET-type biosensor, one-dimensional (1D) nanomaterials may be exploited to create highly sensitive sensors, due to high charge carrier mobility in the long-axis [7–9]. Among various 1D nanomaterials, conducting polymers (CPs) have remarkable sensing performance in biosensor applications [10], due to their several advantages, including facile control over the morphology, functionalization, and biocompatibility [11,12]. However, improvements in the response time and sensitivity are required for practical applications.

Graphene, which consists of a single layer (or a few layers) of graphitic carbon, has been extensively studied for use in many

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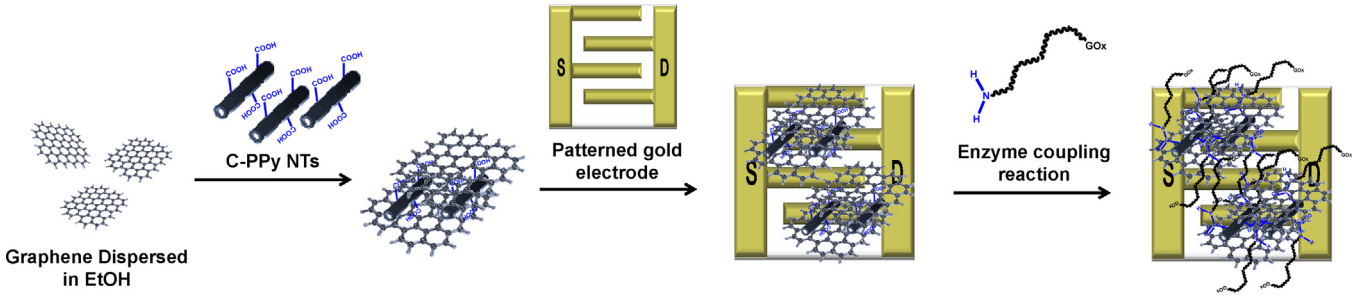

Scheme 1. Schematic illustration of the fabrication of rGO/C-PPy NT hybrid glucose sensing device.

electronics applications, due to its large theoretical surface area, good electronic conductivity, mechanical properties, and exceptional thermal stability [13–16]. In the biosensor system, the relatively low noise level property of graphene is an excellently charming point for the detection of slight signal changes caused by biological reactions. Recently, enzymatic sensor application in clinical diagnostics based on graphene-based hybrid materials has been reported. For example, graphene–metal and/or graphene–metal-oxide nanohybrid materials, including Ag, Pt, Pd, Au, CuO, SnO_2 and ZnO, have been reported for glucose detection with high sensitivity, due to their synergetic effects, including the improved large surface area and conductivity [17–22]. However, growing concerns with regard to the scarcity of many of these metals has given rise to the development of designs for new materials with high-performance detection systems for glucose.

Here, we demonstrate a high-performance FET-type glucose biosensor based on the hybrid nanomaterials formed of carboxylated-polypyrrole nanotubes (C-PPy NTs) wrapped in graphene sheets. The syntheses of rGO/C-PPy NTs were described in Scheme 1. The synergetic effects of graphene and C-PPy NTs led to very great sensing performance (limit of detection (LOD) = 1 nM). The real-time response of liquid-ion-gated FET sensors to glucose, on was very fast (< 1 s). Compared with non-hybrid C-PPy NTs, the rGO/C-PPy NT hybrids showed an improvement in the sensing performance of 5 orders of magnitude, with a high degree of specificity toward glucose. This detection limit is ca. 2–3 orders of magnitude more sensitive than previous reported glucose sensor. Furthermore, the results obtained using the FET-type biosensor was highly reproducible, and the devices were stable in air.

2. Experimental

2.1. Materials

Pyrrole (98%), Pyrrole-3-carboxylic acid (P3CA), hydrogen peroxide (30%), uric acid (UA), ascorbic acid (AA), glucose, glucose oxidase (GOx) enzyme, graphite flakes, methyl orange (MO), 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpho-liniumchloride (DMT-MM) and ferric chloride ($FeCl_3$, 97%) were purchased from Aldrich Chemical Co. and used without further purification.

2.2. Synthesis of 1D C-PPy nanomaterials

The C-PPy NTs were prepared using a self-degraded template method,[23] whereby 0.243 g of 1.5-mM $FeCl_3$ solution was added to a 5-mM solution of sodium 4-[4′-(dimethylamino)phenyldiazo] phenylsulfonate, $(CH_3)2NC_6H_4$-N = $NC_6H_4SO_3Na$ in deionized water. After a flocculent precipitate appeared, 0.006 g of 0.05-mM P3CA and 0.1 g of 1.5-mM pyrrole monomer solution were added, and the mixture was stirred at room temperature for 24 h. The resulting precipitate was purified by washing it with deionized water and methanol several times until the filtrate was colorless and had a neutral pH. The powdered C-PPy NTs, weighing 0.08 g, and with 79.5% purity, were then dried under vacuum at 60 °C for 24 hours.

2.3. Synthesis of graphene-C-PPy NT composites

Graphene oxide (GO) was obtained from graphite powder using a modified Hummers and Offeman method [24]. Graphene was obtained by reduction process of GO with 5 μL hydrazine (35 wt %) treatment at 95 °C for 1 h. A 4-mg/mL suspension of graphene was dispersed in 5.1-mL of a 50:1 mixture of water and EtOH, and then mixed with 4 mg of the C-PPy NTs. The mixtures were ultrasonicated for 1 h, and the final product was a 6.3 mg of 78.8% purity graphene-C-PPy NT hybrid material, which was obtained via filtration, purified using water, and dried in a vacuum oven at 25 °C for 24 h.

2.4. Fabrication of graphene-C-PPy NT composites FET sensor

A photolithographic process was used to pattern a microarray of 80 pairs of gold interdigitated microelectrodes on a glass substrate using a 50-nm-thick Cr adhesion layer. The resulting electrodes, formed on a 50-nm-thick gold layer, were 10-μm-wide and 4-mm-long, with an interelectrode spacing of 10 μm. The microelectrode substrate was cleaned using distilled water and ethanol. An aliquot of 0.1 mL of the ethanol solution containing 0.1-wt% rGO/C-PPy NT hybrid was dropped onto the interdigitated electrodes. A coupling reaction between enzyme and graphene-nanohybrid material was conducted by a modified previous our method [10]. In brief, the coupling reaction was then carried out by exposing the substrate to a mixed solution of GOx and 10 μL of 1-wt% aqueous DMT-MM for 12 h to attach the GOx to the surface of the rGO/C-PPy NTs. The substrate was then rinsed with distilled water and dried under vacuum at room temperature for 12 h. A 10-mL solution chamber was employed for all solution-based measurements. The FET sensor substrate based on liquid-ion gate was fabricated with phosphate-buffered solution (PBS), which had a pH of 7.5. The current was monitored at room temperature using a source meter.

2.5. Instrumentation

The TEM images were taken with a JEOL JEM-2100 microscope at the National Center for Inter-university Research Facilities (NCIRF) at Seoul National University. For TEM observation, the samples were diluted with in ethanol and then the diluted solution was deposited on a copper grid coated with a carbon film. The FE-SEM images were obtained with a JEOL JSM-6700 F microscope. A specimen was coated with a thin layer of gold to eliminate charging effects. Raman spectra were recorded with a T64000 (Horiba Jobin Yvon). ATR-FTIR spectra were collected with a Thermo Scientific Nicolet 6700 FTIR spectrophotometer. X-ray diffraction (XRD) patterns were carried out with a New D8 Advance (Bruker). All