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Metalloid polymer nanoparticle functionalized graphene oxide working electrode for durable glucose sensing

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ABSTRACT

A new class of functionalized graphene oxide (FGO) nanosheet based amperometric glucose biosensor platform has been fabricated. FGO nanosheet comprises of chemically bound metalloid polymer hybrid (MPH) nanoparticles (average size of 12.5 ±2 nm) on the surface of a graphene oxide (GO) nanosheet. Spectroscopic characterization indicated that MPHs are well distributed, with a strong binding affinity between the GO nanosheets. The synergistic features of the metalloid polymer and the GO resulted in a unique three-dimensional nano-architecture on a gold-printed circuit board electrode (Au-PCB). The electrocatalytic response against a glucose sample is predominant, with a characteristic response time of 7 s, correlation co-efficient of 0.9981 and a wide linear range of up to 55.5 mM. The stability of the nano-architecture modified on the electrode substrate is suitably durable for long-term application. The practical applicability of the fabricated electrode system was evaluated using a hyperglycemic clinical samples, and was compared with a commercial glucose biosensor. The obtained amperometric results were in good agreement with those of the commercial biosensor, and are promising for further clinical applications.

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1. Introduction

Self-monitoring of metabolic disorders through novel biosensors is regarded as vital methodology for a more complete understanding of many health issues [1]. Among metabolic disorders, diabetes mellitus is quoted as the "*global burden*" according to the International Diabetes Federation (IDF). IDF world-wide statistics reported that 366 million people are found to have diabetes in 2011 and it is expected to become 552 million by 2030. Furthermore, diabetes caused 4.6 million deaths in 2011. Proper health care awareness, including physical exercises and dietary management can enable a healthy life style. On the other hand, monitoring of hyperglycemic serum and/or urine glucose level can identify the issues and possibly assists an individual to maintain their healthy life style. Although there are several biosensing methods available for monitoring the relevant bioanalytes, electrochemical-based monitoring devices are predominate in practical applications than other biosensor methods due to their low fabrication cost, high sensitivity, superior selectivity and simple integration [2–4].

Even though significant electrochemical based analysis have been applied to the development of blood glucose [5–9] and urine glucose sensors [1,10–12], there are further valuable optimizations required for bio-diagnostics in this field. For instance, reusable self-monitoring devices, with amplified analytical performance, the capacity to resist interference, and self-contained multiplex features are highly desirable for such applications. Furthermore, the development of new, high-performance and durable enzymatic electrochemical biosensors with appropriate supporting matrices for promoting direct electron transfer (DET) behaviors is of potential interest for device applications [13]. The chemical modification of electrodes, especially with nanoscale materials such as carbon nanostructures [14,15], noble metal nanoparticles [16,17] and metal oxides [18], provide significant microenvironments for the immobilization of enzymes. Such hybrid nanostructured electrodes have not only retained the biological activity of surface immobilized enzymes but also enhance electron transfer kinetics between biomolecules and the electrode.

Graphene, graphene oxide (GO) and reduced graphene oxide (rGO) are different types of thin carbon nanosheet materials, with different surface chemical functionality on their edges and basal

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planes [19,20]. Among these materials, GO nanosheets possess additional features for biomedical applications, including large surface-to-volume ratio, good dispersibility in water, good biocompatibility, and low manufacturing costs for large scale production [19,20]. These particular features have attracted many researchers to perform interdisciplinary research on GO-based nanomaterials. It has been demonstrated that due to its sheet-like structure, containing oxygen functional groups, GO nanosheets can be a potentially suitable matrix for the construction of electrochemical sensors and biosensor substrates with high sensitivity and stability. Earlier studies have demonstrated a direct electrochemistry of glucose oxidase enzyme on graphene and graphene-based hybrid materials for glucose biosensing [6,7,9,13,21–23]. However, these graphene and/or GO-based hybrid materials utilized for the development of electrochemical glucose biosensors are mostly fabricated by physical modification, and are not chemically bonded or functionalized. This might result in a lack of long-term binding affinity, and stability issues, between nanostructures and graphene-based materials during electrochemical analysis.

Metalloid polymer hybrid (MPH) is a class of nanomaterial composed of both metal and non-metal in the form of composite structures coated by an inert polymer molecule. MPHs have received considerable attention in recent years due to their optoelectronic, thermal and thin solid film properties [24,25]. Easy preparation, self-redox wave generation and nanoporous structures are significant advantages of MPHs for the entrapment of electron transfer mediators. For instance, silver-doped composites with a silane-modified electrodes [26], and a poly(ethylene glycol) (PEG) layer on the silver-silica composite surface [27], have demonstrated prominent electron transfer kinetics, and promotion of active immobilization of glucose oxidase on the electrode interface, respectively.

In this study, we propose a new hybrid combination composed of multiple nanoscale materials into single nanoplatform. At first, we synthesize a MPH nanoparticle structure consisting of silver-silica ($Ag@SiO_2$) and polyethylene glycol (PEG) with an average size distribution of 12.5 ± 2 nm. The synthesized MPHs were then silanized using 3-aminopropyl-triethoxysilane and were functionalized on the surface of a GO nanosheet by a covalent reaction between the amine group of silanized-MPHs and the carboxylic acid groups of GO nanosheet. Fundamental spectroscopy characterization, such as ultraviolet–visible absorbance, Raman spectrum and Fourier-transform infrared spectrum revealed that the MPHs were firmly functionalized on the surface of the GO nanosheet. The electrochemical characterization (cyclic voltammogram) of the gold-printed circuit board (Au-PCB) electrode modified with GO functionalized MPHs (FGO) exhibited a significantly improved redox response compared to the bare Au-PCB electrode. Synergistic features obtained from the multifunctional nanohybrid (containing $Ag@SiO_2$-PEG; MPH) functionalization on the surface of GO nanosheet are expected to be the vital factors involved in its enhanced DET properties, by exhibiting the smallest difference of redox potential near zero volts. The fabricated Au-PCB-FGO working electrode was developed for amperometric glucose biosensing under different sample conditions (such as known glucose concentrations in buffer and urine samples from diabetic patients).

2. Experimental

2.1. Materials

Reagents required for the synthesis and silanization of MPHs such as silver nitrate ($AgNO_3$), tetraethoxysilane (TEOS) ($Si(OC_2H_5)_4$), sodium borohydride ($NaBH_4$), ammonium hydroxide (NH_4OH), poly(ethylene glycol) (PEG) (Mn = 10,000 g/mol) and 3-aminopropyltriethoxysilane (3-APTES) were purchased from Sigma–Aldrich. Expandable graphite powder, D(+)glucose, glucose oxidase (GOx) from *Aspergillus niger*, phosphate buffered saline (PBS) and N-[Tris(hydroxymethyl)methyl]-2-aminoethanesulfonic acid sodium salt (TES) buffer were also obtained from Sigma–Aldrich. Sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl) and anhydrous ethanol (C_2H_5OH) were obtained from Daejung Chemicals and Metal Ltd., Republic of Korea. Milli-Q water with resistance greater than 18 MΩ was used throughout in our experiments. All reagents were used as received, and without further purification.

The clinical diabetic patients hyperglycemic urine and serum samples utilized in the analysis were kindly provided by Seoul National University Bundang Hospital, Seoul, Republic of Korea. All sample collection and experiments were performed according to a protocol approved by the institutional review committee at Seoul National University Bundang Hospital. Before contribution in any study-related procedures, all patients gave their written informed consent.

2.2. Instrumentation

Ultraviolet–visible (UV–vis) absorbance spectra for aqueous solutions of GO nanosheets, MPHs and FGO nanosheets were measured using a Varian Cary 50 spectrophotometer. Raman spectral study of pristine GO nanosheets and FGO nanosheets were measured using a LabRam HR800 micro-Raman spectroscope (Horiba Jobin-Yvon, France) using 100× objective lens at room tempearature, with a 532 nm Nd:YAG laser beam and 1800 lines per mm grating. Aqueous dispersion of GO and FGO nanosheets were drop cast onto a cleaned glass substrate (2 cm × 2 cm) and solvent was allowed to evaporate at ambient temperature before measurements were carried out. High-resolution transmission electron microscopy (HR-TEM) image of GO, MPHs and FGO nanosheets was performed using a Cs-corrector-equipped Titan 80-300 device (FEI, Hillsboro, OR) operated at 300 kV. The samples used for imaging were prepared by drop-casting ~10 μL onto the surface of copper grid, and allowing the solvent to evaporate before measurement. Fourier-transform infrared spectrophotometer (FT-IR, NICOLET 6700) using a KBr disk at a resolution of 4 cm^{-1} was used to determine the chemical structure and functional group modifications.

Cyclic voltammogram (CV) measurements of the Au-PCB electrode (home-made design by Korea Electronics Technology Institute (KETI)) and Au-PCB modified with FGO nanosheet electrode, was carried out using a VersaSTAT 3 in a three-electrode configuration. Customized Au substrate on PCB chip was fabricated by an electroplating method. The central circle-shaped Au substrate with an area of 2 mm in diameter was used as working electrode. The two crescent-shaped Au substrates with a length of 4.3 mm and a breadth of 0.8 mm were used as counter and reference electrodes. Amperometric response of Au-PCB-FGO/GOx electrodes against commercial glucose and clinical samples which were measured at room temperature with a Keithley 2635 A sourcemeter (Keithley Instruments Inc., Cleveland, OH, USA) connected to a computer supported with Lab view software.

2.3. Synthesis of MPHs

MPHs comprised of $Ag@SiO_2$-PEG with a particle size distribution of 12.5 ± 2 nm were synthesized following an ultrasonochemical strategy [25]. Briefly, an aqueous solution of a precursor 150 μL (30 mM) $AgNO_3$ was added to a reaction vessel containing 12 mL of PEG (M_n = 10,000 g/mol) as a stabilizing agent and 300 μL (30 mM) of $NaBH_4$ as a reducing agent. Under optimized conditions, including amplitude (35%), probe temperature (65 °C), and pulse on-off cycle

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