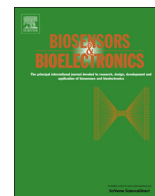




ELSEVIER

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

A novel multicomponent redox polymer nanobead based high performance non-enzymatic glucose sensor

A.I. Gopalan^{a,b,c,1}, N. Muthuchamy^{a,1}, S. Komathi^a, K-P Lee^{a,b,c,*}

^a Department of Chemistry Education, Kyungpook National University, Republic of Korea

^b Research Institute of Advanced Energy Technology, Kyungpook National University, Republic of Korea

^c Department of Nanoscience and Nanotechnology, Kyungpook National University, Republic of Korea

ARTICLE INFO

Article history:

Received 25 August 2015

Received in revised form

26 October 2015

Accepted 27 October 2015

Keywords:

Multicomponent

Nanobead

Glucose

Non-enzymatic

ABSTRACT

The fabrication of a highly sensitive electrochemical non-enzymatic glucose sensor based on copper nanoparticles (Cu NPs) dispersed in a graphene (G)-ferrocene (Fc) redox polymer multicomponent nanobead (MCNB) is reported. The preparation of MCNB involves three major steps, namely: i) the preparation of a poly(aniline-co-anthranilic acid)-grafted graphene (G-PANI(COOH)), ii) the covalent linking of ferrocene to G-PANI(COOH) via a polyethylene imine (PEI), and iii) the electrodeposition of Cu NPs. The prepared MCNB (designated as G-PANI(COOH)-PEI-Fc/Cu-MCNB), contains a conductive G-PANI(COOH), electron mediating Fc, and electrocatalytic Cu NPs that make it suitable for ultrasensitive non-enzymatic electrochemical sensing. The morphology, structure, and electro activities of MCNB were characterized. Electrochemical measurements showed that the G-PANI(COOH)-PEI-Fc/Cu-MCNB/GCE modified electrode exhibited good electrocatalytic behavior towards the detection of glucose in a wide linear range (0.50 to 15 mM), with a low detection limit (0.16 mM) and high sensitivity ($14.3 \mu\text{A mM}^{-1} \text{cm}^{-2}$). Besides, the G-PANI(COOH)-PEI-Fc/Cu-MCNB/GCE sensor electrode did not respond to the presence of electroactive interferences (such as uric acid, ascorbic acid, and dopamine) and saccharides or carbohydrates (fructose, lactose, D-isoascorbic acid, and dextrin), demonstrating its selectivity towards glucose. The fabricated NEG sensor exhibited high precision for measuring glucose in serum samples, with an average RSD of 4.3% and results comparable to those of commercial glucose test strips. This reliability and stability of glucose sensing indicates that G-PANI(COOH)-PEI-Fc/Cu-MCNB/GCE would be a promising material for the non-enzymatic detection of glucose in physiological fluids.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The development of a sensitive glucose detection method is of overriding importance in clinical diagnostics, especially for the diagnosis of diabetes mellitus (Tang et al., 2010). According to the World Health Organization, approximately 350 million people worldwide have diabetes (Alwan 2011) and it is projected that diabetes will be the 7th leading cause of death by 2030. Enzyme-based electrochemical glucose sensors, utilizing the immobilized enzymes glucose oxidase (GOx) or glucose dehydrogenase (GDH) on various substrates, are topics investigated in most of the previous studies related to this field (Chen and Chatterjee, 2013; Nichols et al., 2013; Santhosh et al., 2009). Although, enzyme-based electrochemical sensors exhibit good selectivity and high stability, the activity of the enzyme is liable to be affected by temperature,

pH, humidity and toxic chemical. And, the electron transfer process of enzyme is restricted at the electrode surface (Zhu et al., 2012). These drawbacks in enzyme-based glucose sensors necessitate the development of non-enzymatic glucose (NEG) sensors that can have advantages over the enzyme-based sensors (Wang et al., 2008; Zhong et al., 2012). Amongst NEG sensors, electrochemical sensors based, on the direct electrocatalysis of glucose on the electrode surface are popular due to their advantages in terms of good sensitivity, simplicity, high selectivity, and short response time (Zhu et al., 2011). Generally, a high performance NEG sensor should exhibit a combination of performance parameters such as high sensitivity, fast response, good selectivity, and stability, according to the need. Such a high performance NEG sensor is expected to be designed and fabricated from a sensing material having the adequate composition of chemical components, surface properties, and micro/nano structures. However, the development of such efficient NEG sensing materials remains a challenge.

In recent years, nanomaterials were extensively utilized in electrochemical sensors due to their high surface area, good mass

* Corresponding author at: Department of Chemistry Education, Kyungpook National University, Republic of Korea.

E-mail address: kplee@knu.ac.kr (K.P. Lee).

¹ Authors contributed equally.

transport and catalysis (Gopalan et al., 2009; Katz et al., 2004). High performances on glucose detection have been achieved using various nanomaterials that include metal nanoparticles (MNPs) (Bai et al., 2008; Li et al., 2014b; Manesh et al., 2010a) and carbon-based nanomaterials (graphene (G), nanodiamonds, and carbon nanotubes) (Gao et al., 2014; Komathi et al., 2009; Kwak et al., 2012; Wang et al., 2013). Furthermore, vast feasibilities for the preparation of nanomaterials, open-up a plethora of highly selective and sensitive glucose sensors (Toghiani and Compton, 2010). It must be noted that a combination of sensing performances, such as sensitivity, selectivity, and stability, could not be deduced for a sensor utilizing a single nanocomponent-based sensing material. On the other hand, multiple components, with each individual component having unique advantages for improving sensing performances, can be put together in the form of a composite or hybrid to meet the multiple performance requirements of a biosensor. However, significant challenges exist in assembling or inter-connecting the multiple components.

Polymeric nanospheres or nanobeads (NBs) have received much attention in drug delivery systems (Davis and Illum, 1988), biomolecule support structures (Lok and Ober, 1985), and catalysis (Zhang et al., 2008). Keeping in view of the targeted applications (Saquing et al., 2009; Sathe et al., 2006), considerable efforts have been made towards the synthesis of polymer NBs. Conducting polymers (CPs), with fine tunable electronic properties, are attractive materials for sensing applications (Lange et al., 2008; Manesh et al., 2007, 2008, 2010b). The molecule-analyte interactions and electrochemical signal generation in a sensor can be fine-tuned through CPs. As well, CPs are adaptable for functionalization group, nanostructuring to have defined morphologies and co-deposition with MNPs (Forzani et al., 2004; Janata and Josowicz, 2003; Ragupathy et al., 2009; Dhand et al., 2011; Huang and Kaner, 2004; Lee et al., 2010, 2013, 2014). Compared with their bulk form, nanostructured CPs exhibit several advantageous properties that include a large surface area, a shortened pathway for charge/mass/ion transport, and electron mediation that can lower the internal impedance between the electrode and analyte. These are all beneficial characteristics for electrochemical sensors (Zhang et al., 2013). A variety of 1D and 2D CP nanostructures, such as nanowires and nanotubes, have been developed and applied to sensing applications (Oh et al., 2013; Yoon et al., 2009). Various 3D CP nanostructures have been developed and reviewed (Li et al., 2009). Particularly, CP gels or NBs with 3D frameworks were of significant importances because of their intrinsic properties (Lu et al., 2014).

Recently, a new trend in material science that exploits the synergistic advantageous properties of individual nanomaterials, such as G and MNP, has emerged. Also, there is a need for the development of multicomponent CP nanostructures in the form of polymeric NBs (Fang et al., 2010; Howes et al., 2010; Mi et al., 2010). One of the challenges in developing multicomponent NBs based electrochemical sensors, is the difficulty in the integration of multiple components while preserving the large surface area, electronic transport, and specific functional groups to achieve high sensitivity and selectivity to the designed sensors (Sathe et al., 2006). Various components in a multicomponent CP-based NB can be included through physical entrapments or the formation of co-networks in the design of electrochemical biosensors (Brahim et al., 2002; Mano et al., 2007). The physically entrapped components based NBs or gels have restricted sensing applications. However, the leaching probabilities of the component(s) from the NBs during the sensing process caused limited functions. Thus, the development of covalently inter-linked multicomponent-based NBs, through co-network formation between the components, is highly warranted for sensor applications. However, to the best of our knowledge, reports on the preparation of multicomponent CP-

based NBs (MCNBs) and their utilization for sensor applications are scarce. Motivated by the challenges in the preparation of multicomponent CP-based NBs, in this work, we have designed the synthesis of a novel multicomponent NB, comprising a functionalized CP, G, ferrocene (Fc), and copper nanoparticles (Cu NPs). We also evaluated the MCNB as a high sensitive NEG sensor.

Graphene (G) and its derivatives have attracted noteworthy attention for their potential applications in electrochemical sensors due to their desirable properties, such as a large surface area, fast electron transfer rate, and low charge-transfer resistance (Kang et al., 2009; Zheng et al., 2015a,b). Functionalized G can have a high degree of edge-plane defect sites that can provide active sites for electron transfer reactions (Wu et al., 2013; Zhu et al., 2012). The other important aspects of functionalized G are i) ease of structural modification through covalent or noncovalent pathways, and ii) its function as 2D support for loading various polymers or MNPs. These special features can give rise to the design and preparation of various G-nanohybrids. Such prepared G-nanohybrids exhibited improved sensor performances due to synergistic interactions between G and the other components (Shan et al., 2010; Su et al., 2011; Tung et al., 2015; Zhong et al., 2010). To date, ferrocene (Fc) has been regarded as one of the successful redox mediators in electrochemical sensors because of its well-behaved electrochemical properties. Fc has a lower oxidation potential to lose an electron and can exist in two stable redox states (ferrocene and ferrocenium). When Fc or its derivatives are properly integrated with polymers (Rapakousiou et al., 2015), the integrated structures exhibit a fast electron transfer rate and excellent charge/discharge characteristics. Both properties are beneficial for electrochemical sensors (Sun et al., 2014). Keeping these aspects in view, a variety of Fc inclusion procedures have been developed to fabricate reagentless amperometric sensors (Şenel et al., 2013; Zheng et al., 2012). Single-walled carbon nanotubes were integrated with Fc in order to increase the sensitivity of glucose sensing (Tran et al., 2011). It has been demonstrated that a combination of Fc and G can generate redox mediator-functionalized G having good conductivity and dispersibility. These beneficial properties were exploited for electrochemical sensing (Huang et al., 2015; Liu et al., 2013). Copper nanoparticle (Cu NP)-based electrode materials exhibited excellent electrocatalytic oxidation of glucose and were used in NEG sensors (Li et al., 2014a; Zhang et al., 2012a; Zhuang et al., 2008). In the last few years, studies on the preparation and use of Cu nanostructures/graphene composites were of great relevance to the development of NEG sensors (Chen et al., 2011; Jiang et al., 2014; Luo et al., 2012a, 2012b; Xi et al., 2014).

In this paper, we demonstrate the use of a novel CP-based MCNB, comprising a functionalized CP, Fc, and Cu NP for efficient NEG sensing (Scheme 1). We have chosen poly-(aniline-co-anthranilic acid)-grafted G sheets [designated as G-PANI(COOH)] as the parent CP, and branched polyethyleneimine (b-PEI) as the cross-linking polymer, ferrocene carboxyaldehyde (Fc-CHO) as the cross-linker, and Cu NPs for the preparation of the new MCNB. The components G-PANI(COOH), b-PEI, and Fc-CHO were integrated to form a cross-linked network structure, and further dispersed with the Cu NPs to obtain G-PANI(COOH)-PEI-Fc/Cu-MCNB. The preparation of the new G-PANI(COOH)-PEI-Fc/Cu-MCNB involved the following stages. Firstly, G-PANI(COOH) was synthesized (Stage I, Scheme 1) through polymerization of a mixture of aniline and anthranilic acid in the presence of an amine-functionalized G (G-NH₂). Then, the -COOH groups in G-PANI(COOH) were covalently linked to b-PEI via 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC)/N-hydroxysuccinimide (NHS) chemistry to obtain G-PANI(COOH)-PEI (Stage II, Scheme 1). Next, the larger number of -NH₂ groups existing in the G-PANI(COOH)-PEI were cross-linked with Fc-CHO to generate a composite network via Fc bridges,

Download English Version:

<https://daneshyari.com/en/article/7230399>

Download Persian Version:

<https://daneshyari.com/article/7230399>

[Daneshyari.com](https://daneshyari.com)