Food Chemistry 220 (2017) 299–305

Contents lists available at ScienceDirect

Food Chemistry

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

A novel approach for the fabrication of a flexible glucose biosensor: The combination of vertically aligned CNTs and a conjugated polymer

Tugba Ceren Gokoglan [a], Saniye Soylemez [a,1], Melis Kesik [a], Itir Bakis Dogru [b], Onur Turel [c], Recep Yuksel [b], Husnu Emrah Unalan [b,c], Levent Toppare [a,d,e,f,*]

[a] Department of Chemistry, Middle East Technical University, Ankara 06800, Turkey
[b] Micro and Nanotechnology, Middle East Technical University, Ankara 06800, Turkey
[c] Department of Metallurgical and Material Engineering, Middle East Technical University, Ankara 06800, Turkey
[d] Department of Biotechnology, Middle East Technical University, Ankara 06800, Turkey
[e] Department of Polymer Science and Technology, Middle East Technical University, Ankara 06800, Turkey
[f] The Center for Solar Energy Research and Application (GUNAM), Middle East Technical University, Ankara 06800, Turkey

ARTICLE INFO

Article history:
Received 6 July 2016
Received in revised form 4 October 2016
Accepted 4 October 2016
Available online 5 October 2016

Keywords:
Conjugated polymer
Glucose oxidase
Enzyme electrode
Amperometric biosensor
Vertically aligned carbon nanotubes
Glucose biosensor

ABSTRACT

A novel flexible glucose biosensor using vertically aligned carbon nanotubes (VACNT) and a conjugated polymer (CP) was fabricated. A scaffold based on VACNT grown on aluminum foil (VACNT-Al foil) with poly (9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl)–end capped with 2,5-diphenyl-1,2,4-oxadiazole (PFLO) was used as the immobilization matrix for the glucose biosensor. Glucose oxidase (GOx) was immobilized on a modified indium tin oxide (ITO) coated polyethylene terephthalate (PET) electrode surface. The biosensor response at a potential of −0.7 V versus Ag wire was followed by the decrease in oxygen level as a result of enzymatic reaction. The biosensor exhibited a linear range between 0.02 mM and 0.5 mM glucose and kinetic parameters (K_M^{app}, I_{max}, limit of detection (LOD) and sensitivity) were estimated as 0.193 mM, 8.170 µA, 7.035×10^{-3} mM and 65.816 µA/mM cm^2, respectively. Scanning electron microscopy (SEM) was used for surface characterization. The constructed biosensor was applied to determine the glucose content in several beverages.

1. Introduction

Glucose detection is a crucial issue since diabetes mellitus is one of the leading causes of death and disability in the world (Yang, Chen, Ren, Zhang, & Yang, 2015). Abnormality of the glucose level in human blood causes several disorders such as blindness, nerve degeneration and kidney failure (Zhu et al., 2012). The diagnosis and management of diabetic patients require exact monitoring and control of the glucose level in the body. Therefore, continuous testing of glucose level is crucial to prevent long-term complications. Various methods have been proposed for the glucose analysis such as spectrophotometric, chromatographic and electrochemical approaches. Nevertheless, these methods have definite disadvantages like high cost, requirement of pre-treatment of the samples, lack of selectivity and long analysis time. On the other hand, enzymatic methods have been employed to detect glucose in samples since they have non-interfering effect and an excellent specificity to the analyte. Nowadays, the glucose biosensors have an important role for diagnostic, control and treatment of diabetes mellitus. Moreover, they are valuable devices for food technology since they bring simple, low cost, accurate and reliable determination of glucose and act as a very effective analytical tool in the food quality control. The development of GOx based biosensors has rapidly increasing in the field of food processing industries for the detection of glucose. GOx is a homodimer enzyme, which contains two molecules of the cofactor flavin adenine dinucleotide (FAD). This redox enzyme converts glucose into glucono-lactone under reduction of the FAD prosthetic group.

To detect analytes properly in any test solution, surface design is a crucial step for biosensor construction (Chen, Xie, et al., 2013). Conjugated polymers have been widely investigated in biomedical applications and bio-sensing systems due to their unique properties (Cesarino, Moraes, Lanza, & Machado, 2012). CP-modified electrodes create a new perspective in the design of biochemical sensors. Such biosensor architecture brings simple, accurate,

* Corresponding author at: Middle East Technical University, Department of Chemistry, 06800 Ankara, Turkey.

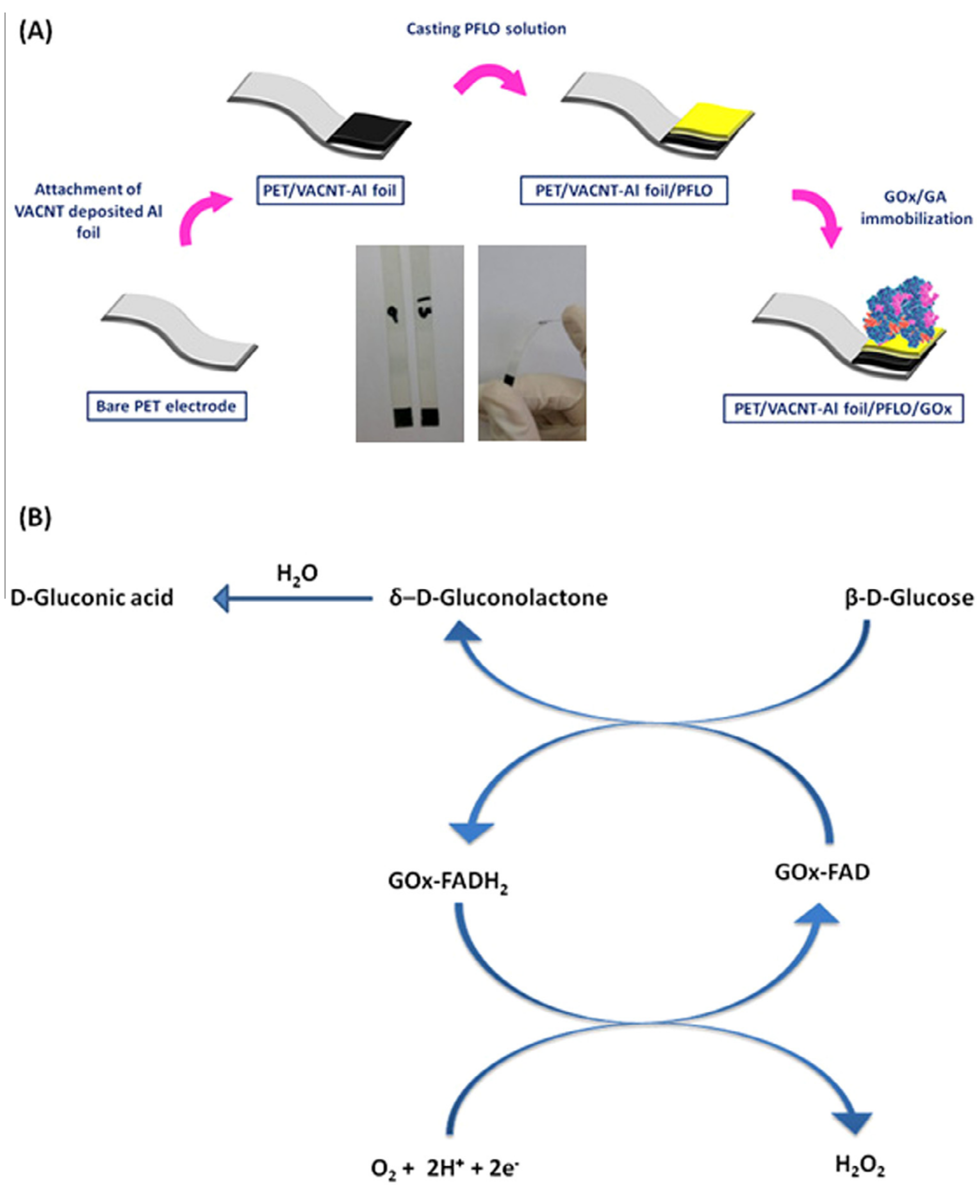
E-mail addresses: tugba.ceren@windowslive.com (T.C. Gokoglan), saniyesoylemez@gmail.com (S. Soylemez), kesik.melis@gmail.com (M. Kesik), e165033@metu.edu.tr (I.B. Dogru), e174543@metu.edu.tr (O. Turel), reyuksel@metu.edu.tr (R. Yuksel), unalan@metu.edu.tr (H.E. Unalan), toppare@metu.edu.tr (L. Toppare).

[1] On leave from Ordu University.

http://dx.doi.org/10.1016/j.foodchem.2016.10.023
0308-8146/

reliable and low-cost determination of various analytes and acts as a very effective analytical tool (Gokoglan, Soylemez, Kesik, Toksabay, & Toppare, 2015; Gvozdenovic et al., 2011). Moreover, their biocompatibility and sufficient stability make them excellent matrices for enzyme immobilization and lead to a more efficient charge transfer between the enzyme and the electrode. A number of studies in literature have demonstrated that the use of a CP as an immobilization support material improves the biosensor performance. Singhal et al. designed a conjugated polymer based glucose biosensor and the obtained biosensor showed high sensitivity with low LOD value in excellent stability (Singhal, Chaubey, Kaneto, Takashima, & Malhotra, 2004). In addition, Kros et al. noticed that the main advantage of conjugated polymer based biosensor is its superior electrochemical stability (Kros, van Hövell, Sommerdijk, & Nolte, 2001). This type of biosensors has potential applications for long-term glucose measurements. In another study, Sharma et al. have prepared an amperometric glucose biosensor and reported that operational stability of the sensor is remarkable (Sharma et al., 2004). Therefore, CPs have been widely used as one of the most promising materials for biomolecule deposition in the development of various types of biosensors.

Carbon nanotubes (CNTs) can be employed as a component for the construction of reliable and robust electrochemical biosensors. They are highly suitable materials as biocompatible platforms in biotechnological applications (Chen, Lee, & Chiu, 2013; Zhang, Grüner, & Zhao, 2013) since their usage in surface design offers several advantages such as good chemical and mechanical properties, good electrical conductivity and high surface area. These unique properties make them extremely attractive for the design of electrochemical sensing devices, especially in bio-sensing systems. In literature, various studies have shown that CNT based electrochemical transducers enhance biosensor performance via improving the enzyme stability. A novel glucose biosensor based on a chitosan-bovine serum albumin (Chi-BSA) cryogel, multi-walled carbon nanotubes (MWCNTs) and ferrocene (Fc) was successfully fabricated by Fatoni and co-workers (Fatoni et al., 2013). It was reported that the MWCNTs/Chi-BSA-Fc/GOx biosensor showed high operational stability with a wide linear range and low K_M value. Meanwhile, Palanisamy developed an amperometric glucose biosensor using a MWCNT/graphene oxide hybrid composite (Palanisamy, Cheemalapati, & Chen, 2014). In another study, it was concluded that the combination of CPs and CNTs



Scheme 1. The representation of (A) proposed flexible glucose biosensor and (B) reaction mechanism of glucose oxidase.