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

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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,

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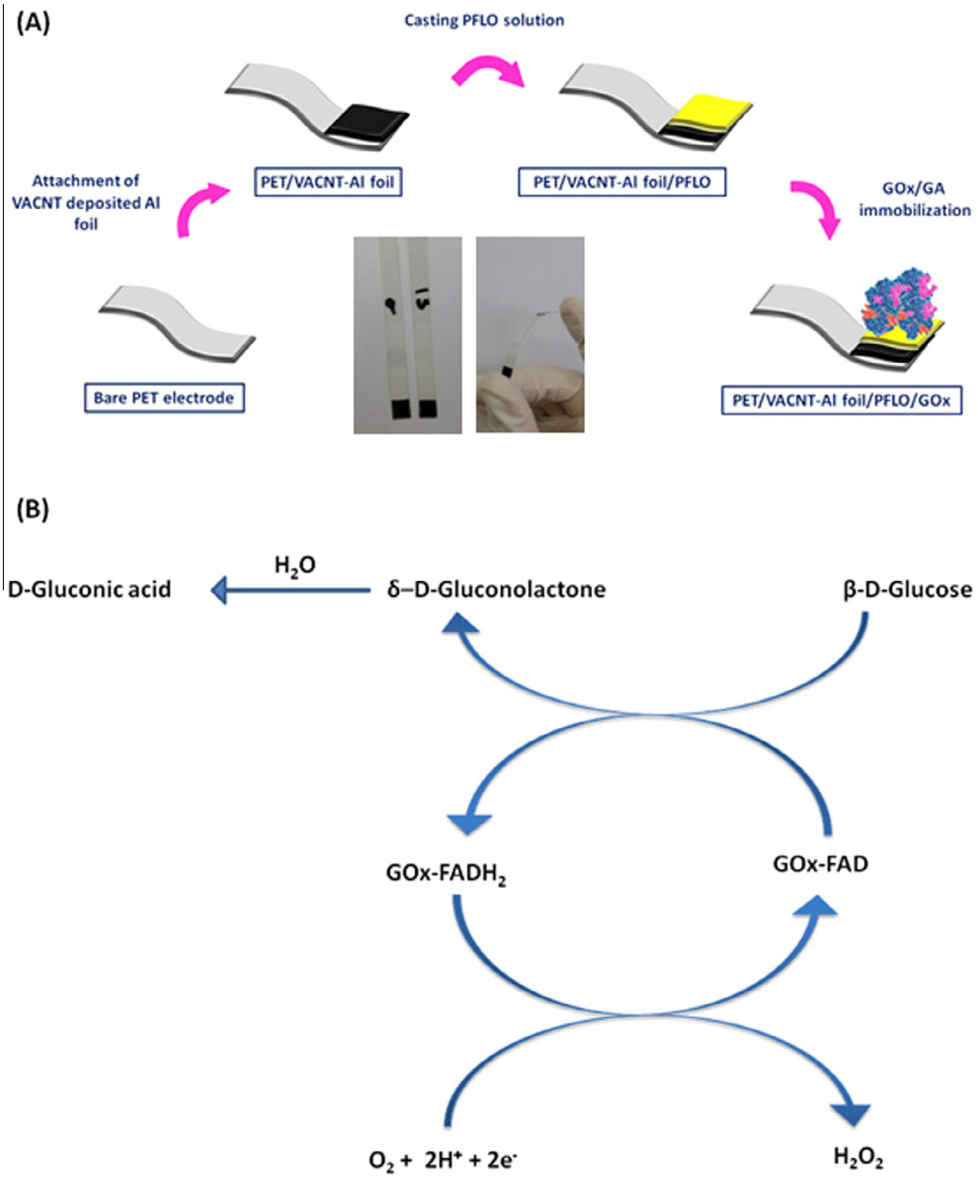
reliable and low-cost determination of various analytes and acts as a very effective analytical tool (Gokoglan, Soylemez, Kesik, Toksabay, & Toppare, 2015; Gvozdenovic et al., 2011). Moreover, their biocompatibility and sufficient stability make them excellent matrices for enzyme immobilization and lead 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.

serves as a proper immobilizing platform for biomolecules and preserves enzyme activity for a long period (Soylemez, Kanik, Uzun, Hacioglu, & Toppare, 2014).

Furthermore, the vertical structure of CNTs is expected to provide high surface matrix for the biomolecules. They are special due to their array of conducting networks, which provide a high-surface matrix for the biomolecules and the mediation of communication between the biomolecule and the electrochemical transducer (Zhu et al., 2012). Wang et al. showed that vertically adhered MWCNTs platform offered a fast response to glucose (Wang, Zhang, Wang, & Yoon, 2003). In another study, Gao et al. developed a new electrode platform consisting of aligned and highly oriented CNT coated CPs for the detection of glucose (Gao, Dai, & Wallace, 2003). This platform allowed the fabrication of sensitive and selective glucose sensor with roughly linear response to glucose in the range of 0–20 mM. In addition, combination of CNTs with a CP enhances the biosensor performance (Wan, Yuan, Li, Neoh, & Kang, 2010). Wan et al. described a Au-g-PANI-c-(CS-CNTs)-GOx biosensor (Wan et al., 2010). This combination improved biosensor sensitivity and glucose affinity. Although PANI has been used for biosensor applications for the detection of glucose, the use of PFLO for the same purpose remained elusive. Hence, we designed a novel platform containing VACNTs and PFLO as the CP. In the absence of the polymer, an appropriate platform was not provided for biomolecule stabilization. VACNTs have hydrophobic nature. By this way, it was difficult to hold GOx molecules uniformly together on CNT surfaces. Since this situation limits their practical use in biosensor applications, their combination with a CP is essential. Use of a CP improves communication between the modified surfaces and the biomolecule. The synergistic effect of the use of VACNTs and CP together allowed the stabilization of the biolayer on the electrode surface and formed a good scaffold for glucose detection.

Herein, a novel biosensor platform with the incorporation of VACNTs and a CP was developed for the first time to detect glucose. Fabricated biosensors were assembled onto PET substrates. In addition to providing flexibility, such plastic substrate based biosensing devices are promising with their low weight and low cost, which is ideal for disposable biosensors. Following decoration of PFLO onto VACNTs, the electrodes were used as the immobilization matrix for GOx using glutaraldehyde as the crosslinking agent for the construction of flexible glucose biosensors (Scheme 1). Optimization studies were carried out for achieving the most enhanced results in the fabrication of the biosensors. The proposed biosensor exhibited good performance and utilized for the determination of the quantity of glucose in commercial beverage samples.

2. Material and methods

2.1. Materials and apparatus

Poly(9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl)–end capped with 2,5-diphenyl-1,2,4-oxadiazole (PFLO) was purchased from American Dye Source, Inc. 0.025 M Na_2HPO_4 and 0.025 M NaH_2PO_4 which were used for the preparation of buffer solutions were supplied from Fisher Scientific Company. Chloroform and glucose were purchased from Sigma-Aldrich. Glucose oxidase (GOx) was purchased from Aspergillus Niger (17300 units/g solid), and glutaraldehyde (GA) as the crosslinking agent was purchased from Fluka Buchs, Switzerland. All chemicals were used without any further purification.

Pure aluminum foils (Alfa Aesar, 0.025 mm thick, 99.45% metal basis) were used as the substrate for the growth of CNTs. Foils were cleaned by sequential rinsing with acetone (99.8%), isopropanol (99.8%) and distilled water (18.3 MΩ), followed by furnace drying at 80 °C. Catalyst was deposited onto the cleaned foils via ultrasonic spray pyrolysis (USP) method. A 5×10^{-3} M ethanolic solution (5 mL) of iron chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 97%) was used for USP.

For amperometric experiments, a Palmsens was used (Palm Instruments, Houten, The Netherlands). Amperometric measurements were performed using ITO-PET electrode (Vision Tech, 40 O/sq cm) (as the working electrode), Ag wire (as the reference electrode) and a platinum wire (as the counter electrode). To investigate surface morphology for biosensor construction, JEOL JSM-6400 model scanning electron microscope (SEM) device was used. CNTs were also characterized by transmission (TEM) electron microscopes and Raman spectroscopy. For TEM analysis, a JEOL TEM 2100F microscope (operated at 200 kV) was used. For the preparation of TEM samples, CNTs scraped off the foils were dispersed in ethanol and this solution was drop casted onto lacey carbon coated copper grids. A Horiba Jobin Yvon Raman System with a laser wavelength of 532 nm was used for the characterization of as-grown samples.

2.2. Electrode preparations and measurement procedure

Aluminum foils attached to a heater set at 150 °C, placed on an automated x–y stage positioned 5 cm below the nozzle. Following deposition, substrates were annealed in air at 500 °C for an hour. VACNTs on prepared aluminum foils were grown using the AIXTRON Black Magic 2-inch PECVD system. For VACNT growth, first the chamber was vacuumed down to 0.1 mbar and then the pressure was set to 8 mbar and kept constant till the end of the growth. A 300 cm^3/min hydrogen (H_2) gas was introduced into the system and temperature was increased to 600 °C at a rate of 200 °C/min. At this temperature, samples were annealed for 2 min. At the end of the annealing process, the precursor gas, acetylene (C_2H_2) was introduced into the system at a flow rate of 20 sccm, which initiated the CNT growth. At this point, temperature was raised to 615 °C at a heating rate of 200 °C/min. The growth lasted for 5 min and right at the end of growth H_2 and C_2H_2 flows were stopped and the chamber was cooled to room temperature by nitrogen (N_2) flow (1000 sccm). Following venting, samples were collected.

PET/VACNT-Al foil/PFLO/GOx flexible electrodes were prepared according to the following procedure: After cutting PET electrode in particular dimensions (0.5 cm × 5 cm), the VACNT-Al foil (0.5 cm × 0.5 cm) was fixated using a silver conductive paint, which is a kind of glue, onto the PET electrode. The 10 μL polymer solution (1.0 mg/mL) was dropped onto the VACNT-Al foil modified surface allowed to dry for 1.5 h. Then, to prepare desired flexible biosensor, 10 μL of GOx (50 mM pH 7.0 phosphate buffer solution (PBS) containing 28.68 U GOx) were spread over the modified electrode surface. 5 min later, 5 μL GA (1%) were added on the electrode surface as a crosslinking agent. Then the electrodes were left to dry for 2.5 h at room temperature. Finally, it was rinsed with distilled water to get rid of unbounded GOx molecules. Hence, flexible PET/VACNT-Al foil/PFLO/GOx biosensor was fabricated successfully. The proposed architecture for the biosensors is illustrated in Scheme 1. When not in use, the electrodes were kept in a refrigerator at 4 °C. The electrode surface was rinsed carefully with distilled water prior to each measurement. For the measurement procedure, glucose solution was prepared. 0.18 g glucose (1 mmol) was dissolved in 10 mL PBS (50 mM, pH 7.0).

Measurements were carried out in PBS (50 mM, pH 7.0) at −0.7 V versus Ag wire. Amperometric determination of the biosensor response was achieved following the decrease in oxygen level as a result of enzymatic reaction. Following the application of desired working potential, currents were allowed to reach steady-state condition. Then, glucose was injected in the working buffer solution and current change was recorded upon applied potential (Fig. 2(D)).

3. Results and discussion

3.1. Characterization of vertically aligned carbon nanotubes (VACNT)

The VACNTs were grown on aluminum foil. There are two different methods for the fabrication of flexible electrodes decorated with vertically aligned CNTs. In the first and mostly investigated method, aligned CNT electrodes were fabricated in a complex way, which includes peeling off the CNTs from the growth substrate (usually silicon or quartz substrates are used) followed by the deposition (evaporation/sputtering) of charge collecting metal layers (Chen et al., 2007; Pushparaj et al., 2007). In the second method, aligned CNTs can be directly grown on flexible charge collectors by means of a low temperature chemical vapor deposition (CVD) (Wei et al., 2013). Flexible charge collectors can readily be available as metal foils like aluminum and copper. The method investigated herein, including the solution based deposition of catalyst as well as the CNT growth, not only simplifies the fabrication procedure; but also makes the fabrication cost effective. In addition, this work points out the potential of investigated methods in a roll-to-roll process for industrialized mass production.

Photograph of aluminum foils with VACNTs are shown in Fig. 1 (A). These foils were then cut to desired sizes for the fabrication of sensors. Cross-sectional SEM image of the CNTs grown on aluminum foils is provided in Fig. 1(B). From the SEM image, lengths of the CNTs were measured as 2–3 μm. Raman spectra of the CNTs are provided in Fig. 1(C). As-grown CNTs were found to be highly defective with an I_D/I_G ratio that is greater than 1. TEM image of the CNTs are shown in Fig. 1(D). TEM analysis revealed that the obtained CNTs were few walled (2–8 sidewalls) and defective in nature, which is in agreement with the Raman results.

3.2. Optimization studies

To obtain the best biosensor performance, the effect of GOx amount, polymer concentration and pH of the buffer solution on the sensor performance were investigated. First, GOx molecules were immobilized on the modified electrode surfaces with different amounts (0.8, 1.2, 1.6, 2.0 and 2.4 mg) to investigate the effect of the GOx amount. The biosensor responses were monitored while the other parameters were kept constant (Fig. 2(A)). The highest signal was recorded for the biosensor constructed using 1.6 mg GOx, which was chosen as the optimum enzyme amount and used for the subsequent experiments.

Afterwards, the effect of polymer concentration on the amperometric response was investigated. Different concentrations of the polymer solution (0.5, 1.0, 1.5 and 2.0 mg/mL) were prepared and drop casted onto the modified electrode surface. Optimum concentration of the polymer solution was found to be 1.0 mg/mL. As illustrated in Fig. 2(B), optimum biosensor response was recorded with the optimum concentration of polymer. A control experiment was performed without polymer. In this case, no remarkable response was obtained under the same experimental condition described above. During the amperometric measurements, unstable amperometric signals were recorded in the absence of the polymer. As a result, it was difficult to obtain consecutive measurements. Therefore, we are not reporting these abnormal amperometric responses for pristine VACNT biosensors. Hence, the best biosensor performance was obtained when using VACNTs with PFLO.

The activity of GOx is directly affected by the pH and thus we investigated the effect of pH using different buffer solutions within a pH range of 6–8 (sodium phosphate buffer at pH 6.0, 6.5, 7.0, 7.5 and 8.0). Throughout the experiments, newly prepared GOx electrodes were utilized. As shown in Fig. 2(C), the largest biosensor response was obtained at a pH of 7.0. Hence, for subsequent experiments, pH 7.0 PBS was chosen as the optimal condition for the detection of glucose.

Many other electroactive species commonly coexist in the biological fluids, such as ascorbic acid and urea, can also be oxidized and the corresponding electrochemical signals can severely affect the selectivity of the electrochemical biosensors. For this purpose, possible interferents were analyzed for the proposed biosensor (Fig. 2(D)). Separately, such interferents (0.5 mM) were tested by

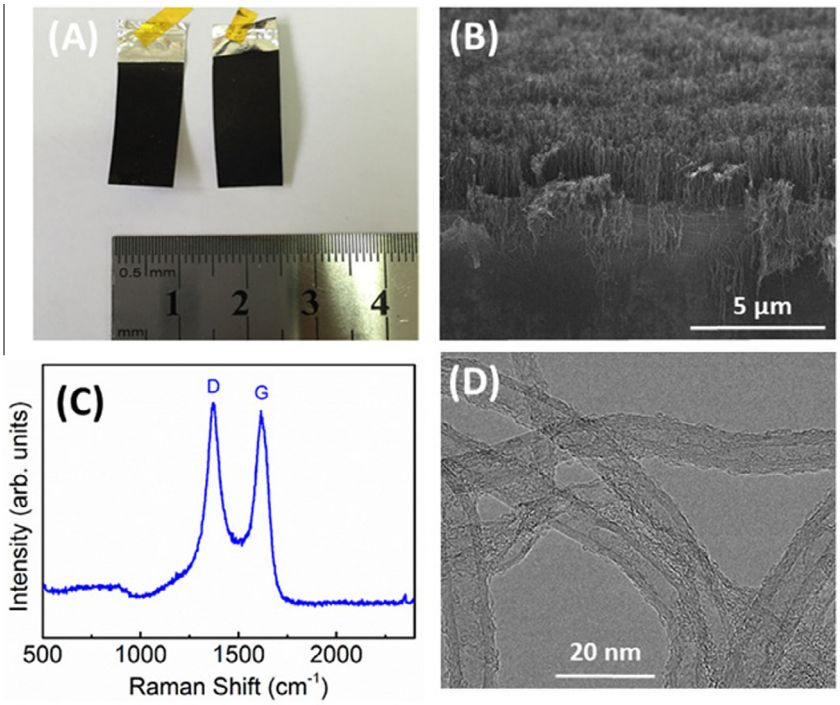


Fig. 1. (A) Photograph of CNTs grown on (1 cm × 3 cm) aluminum foils. Cross-sectional SEM image (B), Raman spectra (C) and TEM image (D) of VACNTs grown on aluminum foils.

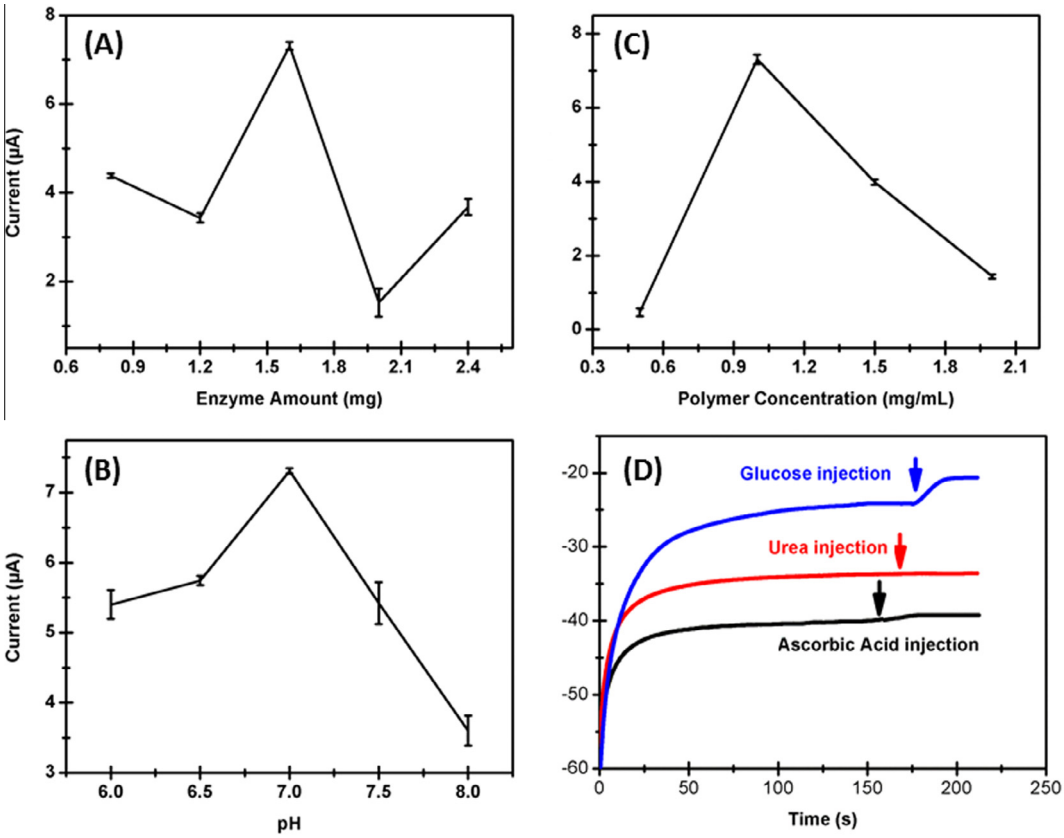


Fig. 2. Effect of (A) GOx amount, (B) pH, (C) PFLO concentration on the biosensor response and (D) Amperometric responses of the PET/VACNT-Al foil/PFLO/GOx to glucose and interference studies with ascorbic acid and urea (0.5 mM) in 50 mM phosphate buffer, pH 7.0, 25 °C, −0.7 V. Error bars show standard deviations (SD) of three measurements.

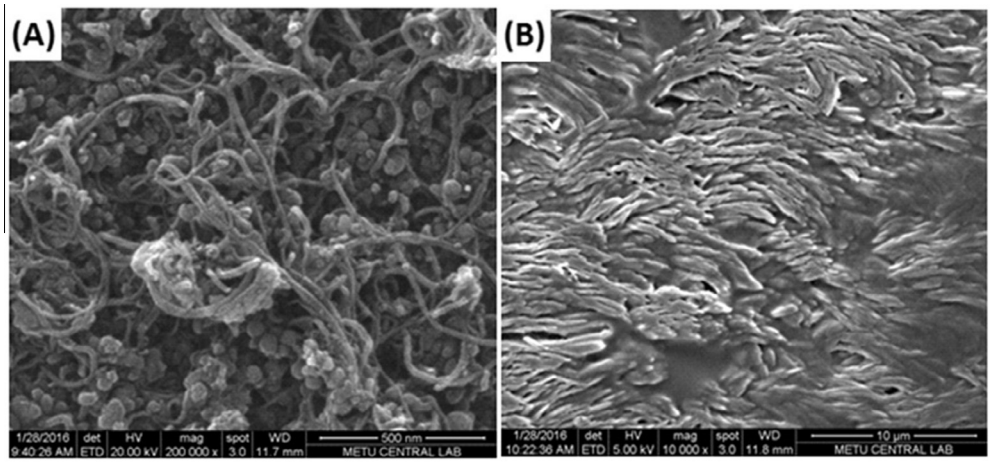


Fig. 3. SEM images of (A) VACNT-Al foil/PFLO and (B) VACNT-Al foil/PFLO/GOx.

injecting into the reaction cell instead of glucose during amperometric measurements; following the injection of such interferents into the reaction cell, no considerable signal was observed. These results show that no interference effect was recorded at −0.7 V versus Ag wire under optimized working conditions. Therefore, the proposed biosensor was very suitable for the glucose detection in the real samples.

3.3. Surface characterization of the proposed biosensor

Fig. 3 compared the SEM images for VACNT-Al foil/PFLO (A) and VACNT-Al foil/PFLO/GOx (B) electrode surfaces. Both cauliflower-like structure of polymer and VACNT was seen clearly which proved well incorporation of the structures on the electrode surface. As seen in Fig. 3(B), following the GOx immobilization, the surface was greatly changed and biomolecule was homogenously formed on the polymer and VACNT modified surface. These figures prove successful surface modification for each step.

3.4. Characteristics of the biosensor for the detection of glucose

After all optimization studies, a calibration curve for glucose was plotted (Fig. 4). The current change was observed for the substrate over a concentration range of 0.02–0.5 mM. This is shown by an equation (R^2 = 0.9955) provided within Fig. 4. The constructed

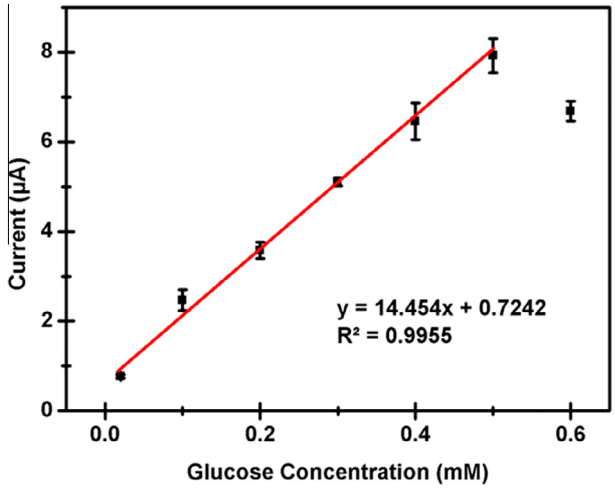


Fig. 4. Calibration curve for glucose (in 50 mM phosphate buffer, pH 7.0, 25 °C, −0.7 V). Error bars show standard deviation of three measurements.

biosensor showed a wide linear range. Limit of detection (LOD) was determined as 7.035×10^{-3} mM for glucose with S/N = 3 criteria. This value is lower compared to the other reported glucose biosensors in literature (Ayranci et al., 2015; Kwak et al., 2012; Sekar, Shaegh, Ng, Ge, & Tan, 2014; Zhang et al., 2014). K_M^{app} and I_{max} and sensitivity values were calculated as 0.193 mM, 8.170 μA and 65.816 μA/mM cm^2, respectively. The proposed biosensor (PET/VACNT-Al foil-GOx) has smaller K_M^{app} value than previously reported studies (Emre et al., 2015; Gao et al., 2014; Krikstolaityte et al., 2014; Sağlam, Kızılkaya, Uysal, & Dilgin, 2016) since combination of CP and VACNT provides high affinity of GOx towards glucose. Also, PET/VACNT-Al foil/PFLO/GOx electrode exhibits very high sensitivity compared to some other studies reported in the literature (Sağlam et al., 2016; Xia et al., 2014). Comparison of analytical parameters of the present biosensor with the previously reported studies is summarized in Table 1.

Biosensor repeatability was tested by ten successive measurements in the same day. According to these measurements, standard deviation (SD) and the relative standard deviation (RSD) were calculated as 0.376 and 6.82%, respectively. According to these results, use of a CP modified VACNT-Al foil contributed to the improvement of sensitivity. This biosensor represented a promising analytical tool due to its high stability.

3.5. Detection of glucose content in beverages

The proposed biosensor was used to analyze the glucose content in commercial milk, strawberry soda, and orange soda under optimized conditions. The chosen samples were injected without any pretreatment into the reaction cell instead of glucose. Then, their amperometric responses were recorded. The experiments were repeated three times for each sample. After that, the concentration of the samples was calculated using the equation obtained in the calibration graph (Fig. 4). The results were compared with glucose concentrations reported within the product label of the samples to test accuracy of the biosensor (Table 2). As shown in Table 2, the results are compatible with the product label. Hence, the prepared biosensor was successfully utilized for glucose analysis.

4. Conclusions

This is the first example on the combination of VACNTs with a CP as the immobilization matrix for the construction of a flexible glucose biosensor. The proposed novel matrix offers a perfect immobilization for biomolecule deposition. The fabricated biosensors exhibited superior kinetic parameters such as K_M^{app}, I_{max}, high sensitivity with a wide linear range and low limit of detection. Following optimization, the fabricated biosensors were successfully utilized for the determination of glucose in commercial beverages, where very promising results were obtained. The biosensor structure investigated herein taking advantages of nanostructured VACNTs and PFLO, holds strong promise for the development of novel biosensors and other bioelectrochemical devices.

Table 1
Comparison of analytical parameters obtains from PET/VACNT-Al foil/PFLO/GOx with different electrodes in the literature for electrochemical of glucose dependent on GOx.

Sensing matrix	K_m^{app} (mM)	LOD (mM)	Sensitivity (μA/mM cm^2)	References
Au/PPy/GOx	15.90	NR	1.90	Palod and Singh (2015)
ITO/ZnO/AuNPs/GOx	1.70	NR	3.12	Tian, Alex, Siegel, and Tiwari (2015)
PGA/GCE/GOx	NR	120×10^{-3}	2.13	Zhou, Tan, Zheng, Kong, and Li (2015)
AAO/Pt/PPy/GOx	NR	250×10^{-3}	18.60	Palod, Pandey, Hayase, and Singh (2014)
PPG/GOx	NR	30×10^{-3}	21.0	Homma, Ichimura, Kondo, Kuwahara, and Shimomura (2014)
P(TPFc-co-TPA)/GOx	20.23	30×10^{-3}	0.10	Soganci, Demirkol, Ak, and Timur (2014)
GC/PANI-OsCmplx/GOx	NR	80×10^{-3}	3.54	Antiochia, Mazzei, Gorton, Leech, and Favero (2014)
Ru-RP/GOx	11.10	290×10^{-3}	24.30	Deng, Teo, and Gao (2014)
$(PEI/MP\text{-}11)_2/PEI/(GOx+POPG+DPPG)_1$	NR	8.6×10^{-3}	0.91	Graça, de Oliveira, de Moraes, and Ferreira (2014)
p-Taurine/GOx/Nf	NR	60×10^{-3}	26.58	Madhu, Devadas, Chen, and Rajkumar (2014)
GOx–PLL/RGO–ZrO_2	NR	130×10^{-3}	11.65	Vilian, Chen, Ali, and Al-Hemaid (2014)
Poly(BEDOA-6)/Au NPs/MPA/GOx	0.81	25×10^{-3}	14.97	Kesik et al. (2013)
Au-g-PANI-*c*-(CS-CNTs)-GOD	5.35	100×10^{-3}	21.0	Wan et al. (2010)
PET/VACNT-Al foil/PFLO/GOx	0.193	7.035×10^{-3}	65.816	This work

Table 2
Results of glucose analyses in commercial beverages.

Glucose (mM)				
Sample	Product label	PET/VACNT-Al foil/PFLO/GOx	Relative error (%)	Standard deviations (SD)
S® milk	0.125	0.121	3.20	0.072
U® strawberry soda	0.243	0.247	−1.65	0.057
F® orange soda	0.325	0.325	0	0.059

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