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Bio-inspired magnetite/lignin/polydopamine-glucose oxidase biosensing nanoplatform. From synthesis, via sensing assays to comparison with others glucose testing techniques

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ABSTRACT

Glucose monitoring has become a crucial part of diabetes care, and is also of importance in the food industry. However, the measurements are subject to certain limitations and errors. These may result from many factors, including the strip manufacturing process, inappropriate storage, temperature, coding, aging, etc. Here, we discuss the measurement of glucose in real samples using techniques such as photometric assay, glucometers, and using a proposed biosensor. Biosensor platforms based on the multicomponent material magnetite/lignin/polydopamine-glucose oxidase with the addition of ferrocene and a dedicated carbon paste electrode (CPE/Fe_3O_4/Lig/PDA/GOx/Fc) were fabricated for glucose detection in real, commercially available glucose-based samples.
To determine the morphological features of the materials, Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), atomic force microscopy (AFM) and zeta potential measurements were carried out. Moreover, to determine the effectiveness of glucose oxidase immobilization the Bradford assays was applied. Analysis of glucose-based products was carried out based on photometric measurements using an AU480 Chemical Analyzer from Beckam Coulter, with the use of three glucometers (Wellion Calla light® WELL 900LB, CERA-CHEK 1Code®Model G400, iXell®Rev.04/10-PL), and with the use of our proposed CPE/Fe_3O_4/Lig/PDA/GOx/Fc biosensor. Tests on real samples demonstrated the repeatability of the results. The results showed that this biosensor has excellent potential for application in the determination of glucose in various commercial products.

1. Introduction

The effects of rapid technological progress are currently being felt in many fields of science. In recent years, in particular, there has been a clear trend towards the miniaturization of devices, resulting from the rapidly developing smart technology. Biosensors are a type of measuring devices that are increasingly commonly used due to their high sensitivity and selectivity [1–6]. Biosensors are characterized by a sensitive element in the form of biological material. They are used to detect, transmit and record information that is processed into an analytical signal, enabling their use in many areas [7–11]. The number of scientific publications on biosensors, including those using polydopamine or magnetite, is also increasing. For example, Ang et al. showed that a polydopamine coating can avoid the aggregation and degradation problems caused by the use of magnetite nanoparticles in biosensor applications [12]. Another proposed biosensor system was reported by H. Peng et al. [13], who proposed the synthesis of multifunctional core–shell glucose oxidase/Au/PDA/Fe_3O_4 magnetic nanoparticles and confirmed the electroactivity of the resulting system. Yari et al. presented a biosensor for the detection of DNA, consisting of Fe_3O_4/PDA nanoparticles [14]. They designed an enzyme-free, sensitive and selective fluorescent biosensor. Similar research was conducted by Salazar et al., who presented PDA-modified magnetic nanoparticles and an application of that material in an electrochemical enzyme biosensor [15]. Their biosensor system was successfully used to detect phenolic compounds. These are not the only scientific publications dealing with this subject. In view of the growing popularity of polydopamine, it is expected that the number of works published in this area will continue to increase.

Lignin is an the second most abundant natural polymer, after cellulose, in biomass. It is inexpensive aromatic biopolymer obtainable by-product of the wood pulping process. At present, lignins have been evaluated for their versatile applications in many fields like electrochemisty, pharmacy, biomedicine and also in sensors. Pishnamazi et al. presented bleds consist of microcrystalline cellulose, lactose and lignin for improvement the understanding of dry granulation of pharmaceutical excipients by roll compaction process, and to implement the quality by-design (QbD) approach [16]. Komura et al. showed water-soluble polysaccharides from *Pleurotus ostreatus* var. *florida mycelial* biomass indeed [17]. In our previous work we have proposed the use of

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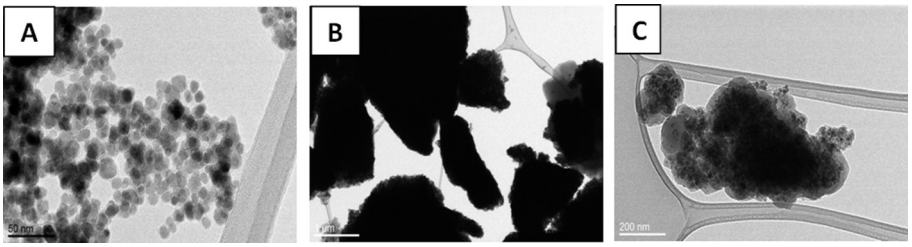

Fig. 1. TEM micrographs: (A) Fe_3O_4, (B) Fe_3O_4/Lig, (C) Fe_3O_4/Lig/PDA.

a silica–lignin hybrid material, SiO_2-Lig, for the effective immobilization of glucose oxidase [18,19], also as precursor of advanced materials and electroactive blends [20,21]. It has also been shown that a carbon paste electrode modified with SiO_2-Lig/GOx can be used as a biosensor for the determination of glucose [22].

In the present study, we aimed to optimize the synthesis of the Fe_3O_4/Lig/PDA/GOx system and to test it using real, commercially available glucose samples. The advanced electrochemical performance of the glucose biosensor was investigated by cyclic voltammetry and chronoamperometry.

2. Experimental

2.1. Materials and chemicals

The reagents used in the experiments were iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4\ H_2O$), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6\ H_2O$), ammonia solution (25%), kraft lignin, dopamine hydrochloride, phosphate (PBS) buffer (pH 7.4; 10 mM), citric buffer (pH = 5.0; 10 mM), glucose oxidase from *Aspergillus niger*, and commercial products containing glucose (1WW I and II produced by Medmess, Oshee isotonic drink I and II by Oshee, 5% glucose infusion liquid by Braun, glucose syrup I and II by Food Colours, glucose standard I by STAMAR and glucose standard II by PUT). A carbon paste electrode (CPE), ferrocene and carbon paste were used to build a basic biosensor. The chemical reagents were purchased from Sigma-Aldrich, except for the CPE, carbon paste (BASi, USA), glucose-based products (obtained from a supermarket and pharmacy) and three glucometers (Wellion Calla light® WELL 900LB, CERA-CHEK 1Code®Model G400, iXell®Rev.04/10-PL). All chemicals and solvents except the last listed were of reagent grade.

2.2. Synthesis and modification of bare Fe_3O_4 and Fe_3O_4/Lig/PDA

For the synthesis of magnetite nanoparticles a method of chemical co-precipitation was used. In the synthesis, 1.5 g of $FeCl_2 \cdot H_2O$ and 3 g of $FeCl_3 \cdot H_2O$ were used, dissolved in 100 mL of demineralized water. The system was heated to 90 °C, and then 20 mL of ammonia water (25%) was added. The solution was stirred while maintaining constant temperature conditions, and the entire process was carried out under a nitrogen atmosphere. After a certain time, the mixture was cooled to 25 °C. The resulting product was dried at 45 °C in an oven.

Co-precipitated magnetite nanoparticles were modified with (3-aminopropyl)triethoxysilane (APTES) in water and methanol (1:4:16 by volume). The final paste product was subjected to distillation in order to evaporate the solvent.

A 135 mL mixture of dioxane and distilled water (8:1) was added to a reactor, followed by the addition of 4 g of lignin. A water solution of iodine(VII) sodium was then dispensed at a speed of 12 mL/min. The synthesis process of the hybrid system was run without access to light for 1.5 h. After the set time, 4 g of modified magnetite was added, and stirred for 1 h. Water and dioxane were evaporated using a vacuum evaporator. The obtained hybrid material was washed several times with water and left to dry in an oven for 24 h at 45 °C.

To obtain the Fe_3O_4/Lig/PDA system, 100 mg of the Fe_3O_4/Lig material was added to 200 mL of TRIS buffer, and next 100 mg of dopamine hydrochloride was added, with stirring on a magnetic stirrer for 5 h at 25 °C. After that time the material was collected by means of an external magnetic force. The precipitate was washed several times with water and then allowed to dry at 25 °C. After drying, the material was ground with a mortar to facilitate subsequent dosing.

2.3. Glucose oxidase immobilization on the Fe_3O_4/Lig/PDA platform

To determine the effectiveness of glucose oxidase immobilization the Bradford assays was applied. The analysis is a spectrophotometric measurement (at wavelength $\lambda = 595$ nm) of a Coomassie Brillant Blue G-250 combination with amino acid residues containing a positive charge. These include mainly arginine, and to a slightly lesser extent: histidine, lysine, proline, tryptophan and tyrosine. The Brillant Blue G-250 links with the mentioned amino acids causing the colour changes from brown to blue. The intensity of the colour depends on the concentration of amino acids contained in the analyzed solution. The Bradford method belongs to relatively universal and precision analyzes [23].

For the adsorption immobilization process, 50 mg Fe_3O_4/Lig/PDA matrix, 5 mg glucose oxidase and 1 mL citrate buffer pH 5.5 were combined. A magnetic stirrer was applied to the test tube to ensure thorough mixing. Immobilization was carried out on laboratory magnetic plates for 24 h at 25 °C. After immobilization, the system was centrifuged at 15,000 rpm for 5 min. The material was then separated from the filtrate and the precipitate was allowed to dry for 24 h, at ambient temperature.

2.4. Construction of a biosensor based on the Fe_3O_4/Lig/PDA/GOx platform (CPE/Fe_3O_4/Lig/PDA/GOx/Fc electrode)

To construct the glucose biosensor system, 30 mg Fe_3O_4/Lig/PDA/GOx and 30 mg of carbon paste were weighed out, and were mixed thoroughly in a mortar. Before mixing, the mediator ferrocene (2 mg) and one drop of paraffin oil were added. The obtained paste was applied to the carbon paste electrode (CPE). The modified electrode was denoted as CPE/Fe_3O_4/Lig/PDA/GOx/Fc. It served as the working electrode and was used as a glucose biosensor. When not in use, the biosensor system was stored in a refrigerator.

2.5. Physicochemical analysis

The composition of the obtained multicomponent system was determined by Fourier transform infrared spectroscopy (FTIR). FTIR spectra

Table 1
Zeta potential measurements for Fe_3O_4, Fe_3O_4/Lig, and Fe_3O_4/Lig/PDA.

Sample	Zeta potential (mV)
Fe_3O_4	−32.0
Fe_3O_4/Lig	−18.5
Fe_3O_4/Lig/PDA	−27.5

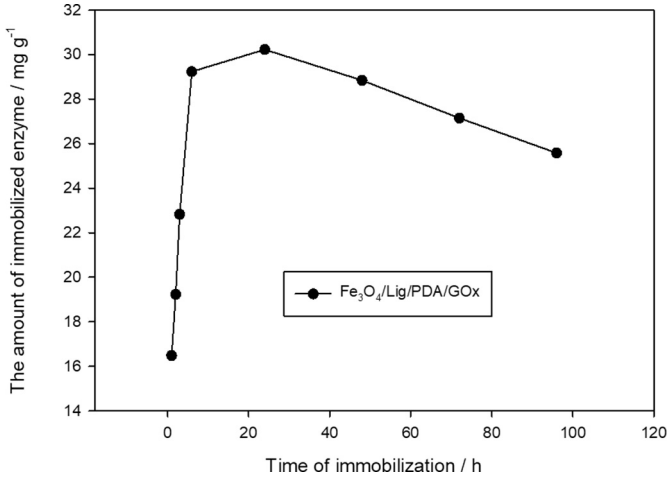

Fig. 2. The amount of immobilized glucose oxidase onto the material Fe_3O_4/Lig/PDA from GOx solution 5 mg mL^{-1}, in different times, based on Bradford method.

were prepared using a Vertex 70 spectrometer (Bruker, Germany). Materials were analyzed in the form of tablets, made by mixing 250 mg of anhydrous KBr and 2 mg of the analyzed substance under a pressure of 10 MPa. The FTIR analysis was performed at a resolution of 0.5 cm^{-1} in the wavenumber range 4000–500 cm^{-1}. To determine the surface morphology of the products, they were analyzed with a scanning electron microscope (SEM), a transmission electron microscope (TEM) and an atomic force microscope (AFM). In TEM analysis, electrons passing through the sample were recorded using a JEOL JEM-1400 analyzer with maximum 120 kV acceleration and with 2 nm resolution. The AFM measurements were made using an Agilent 5500 atomic force microscope in intermittent contact mode in ambient conditions. To evaluate the stability of the material in liquid solvent, the zeta potential (ZP) was analyzed by the ELS technique. ZP values were determined using a Zetasizer Nano ZS (0.6–6000 nm) from Malvern Instruments Ltd. (UK).

2.6. Electrochemical tests

Electrochemical measurements were performed using a μ-Autolab III (ECO Chemie, Netherlands) potentiostat/galvanostat. A conventional three-electrode configuration was applied with Ag/AgCl/(3 M KCl) as the reference electrode, a Pt wire as the counter electrode and a modified carbon paste electrode (CPE/Fe_3O_4/Lig/PDA/GOx/Fc) as the working electrode. High-purity nitrogen was used for deoxygenation of the supporting electrolytes before all experiments.

The glucose level was tested photometrically using an AU480 Chemical Analyzer (Beckam Coulter). The basic principle of photometry is to measure the amount of light absorbed by the sample in the solution. In the test, a prepared sample was placed in a suitable rack, and this was then placed in the analyzer.

In the procedure of measurement via glucometers, each of them was used with a drop of a glucose-based product placed in a new lancet; after an appropriate time (5–7 s) a reading was taken from the device display. Each glucose-based solution was tested three times.

3. Results and discussion

3.1. TEM and zeta potential assays

The TEM image for magnetite (Fig. 1A) shows single well-formed nanoparticles with a uniform structure. The particles obtained by the co-precipitation method have diameters of 8 to 12 nm. In addition, partial particle agglomeration is observed. In the TEM image for the Fe_3O_4/Lig hybrid material (Fig. 1B) stable, irregularly shaped structures are shown. The increased scale relative to magnetite is caused by the lignin molecules. Modified magnetite and lignin molecules joined together to form clusters with no clearly outlined boundaries. Fig. 1C shows Fe_3O_4/Lig coated with polydopamine. The hybrid material is surrounded by the polydopamine unevenly, creating a matrix of irregular shape. On the basis of this, it can be concluded that the process of formation of the Fe_3O_4/Lig/PDA multicomponent system was successful.

To evaluate the effectiveness of the formation of the Fe_3O_4/Lig/PDA system and its components, zeta potential was determined at a constant pH of 8.5 (Table 1). This method also served to determine the stability of individual systems. The results showed magnetite to be a stable compound with a potential of −32 mV. The Fe_3O_4/Lig/PDA system had a higher zeta potential than the hybrid material (−27.5 mV). This result indicates that the polydopamine coating was successful. In addition, the system containing polydopamine exhibited better stability than the unmodified Fe_3O_4/Lig material (−18.5 mV).

3.2. Immobilization of glucose oxidase (GOx) on the Fe_3O_4/Lig/PDA platform

The Bradford method was used to determine the quantity of enzyme immobilized on the Fe_3O_4/Lig/PDA matrix. Following determination of the quantity of enzyme that remained in the solution after adsorption immobilization, the quantity of immobilized biocatalyst per gram of Fe_3O_4/Lig/PDA support was calculated. The results are summarized in Fig. 2.

The tests were carried out for five samples. The enzyme immobilization process was carried out for 24 h. Based on previous studies dealing with optimization of the conditions of immobilization of GOx on the surface of the Fe_3O_4/Lig/PDA system, this time was determined as optimal. The amount of absorbed enzyme in each of the samples is comparable, and on averaging the results it can be concluded that this method enables the immobilization of 29.44 ± 2.39 mg of enzyme per g of support. The obtained results of the immobilization efficiency compared to other published data are quiet good indeed. In our previous studies, the amount of the immobilized glucose oxidase was obtained for SiO_2/Lig hybrid material (25.89 mg g^{-1}), silica (12.88 mg g^{-1}) and graphite (7.58 mg g^{-1}) [22]. Ramon-Marquez T. et al. showed the effectiveness of glucose oxidase immobilization on

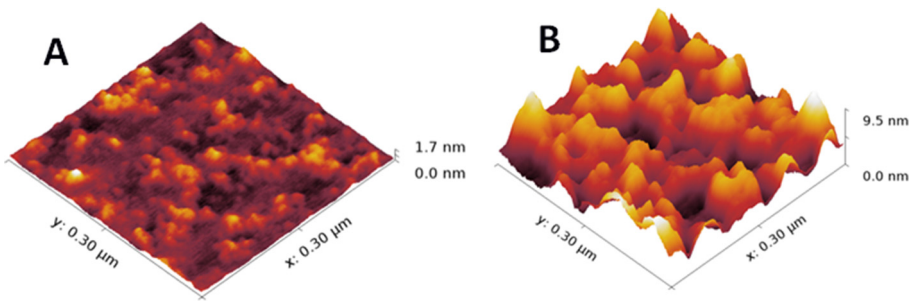

Fig. 3. AFM images of Fe_3O_4/Lig/PDA before (A) and after (B) GOx immobilization.

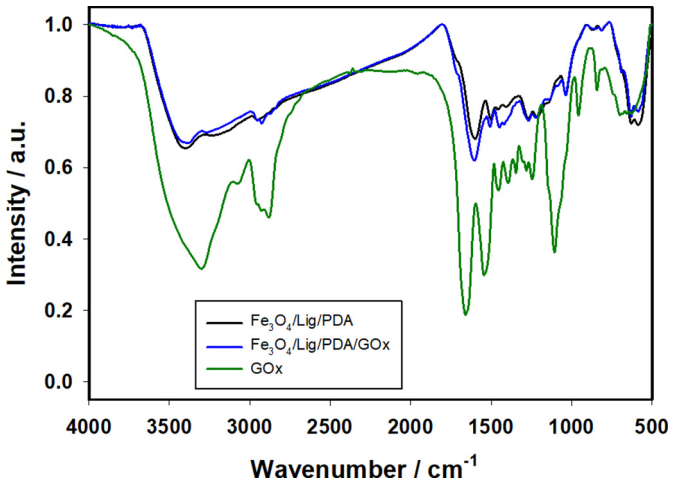

Fig. 4. FTIR spectra of components and materials: Fe_3O_4/Lig/PDA with and without GOx and mere GOx.

PolymP®-Link (12 mg g^{-1}), PolymP®-Cl (35 mg g^{-1}) and PolymP®-Epoxy (45 mg g^{-1}) [24]. Ahmadi M. et al. obtained the immobilization efficiency of GOx carried out on Meso-Porous Glass-Ceramic with the Skeleton of $CaTi_4(PO_4)_6$ (27 mg g^{-1}) [25].

To determine the geometrical structure and surface of the matrix before and after immobilization of GOx, atomic force microscopy was used. The images obtained are presented in Fig. 3. Comparing the upper images depicting the matrix surface, there is observed a several-fold increase in the Z-axis parameter. Additionally, the surface of the matrix in the second image is significantly smoothed. This demonstrates the effectiveness of the coating of the hybrid with PDA.

The AFM images reveal significant changes in the samples containing GOx. Surface roughness increases on average approximately 10-fold for the GOx-coated samples.

3.3. FTIR analysis

FTIR spectra were used to identify the characteristic functional groups of the test substances and to determine the effectiveness of immobilization of glucose oxidase on the Fe_3O_4/Lig/PDA matrix surface. Analyses were performed for the native enzyme glucose oxidase and for the Fe_3O_4/Lig/PDA matrix before and after the immobilization process. The spectra obtained are shown in Fig. 4.

The FTIR spectra contain a band corresponding to stretching of —OH groups in the wavenumber range 3600–3400 cm^{-1}, which is more intense for the matrix after the immobilization process, and masked the signals from —NH_2 groups. At wavenumber 2900 cm^{-1}, bands corresponding to deformation vibrations of the groups —CH_2 and —CH_3 are visible. Signals in the range 1600–1575 cm^{-1} are attributed to stretching vibrations of C═C groups in aromatic rings.

In the range 1650–1580 cm^{-1} there is a band originating from the amide I bond, confirming the presence of lignin in the tested material. This signal is formed by overlapping tensile vibrations of the carbonyl group C═O in the —$NHCOCH_3$ moiety. The second amide bond present in the lignin structure generates a signal at the wavenumbers 1540 cm^{-1} and 1460 cm^{-1}. This signal confirms the presence of bending vibrations of the —NH group and stretching vibrations of the —CN group. A signal corresponding to the amide III bond, originating from —NH bending vibrations and stretching vibrations of —CN groups, appears at a wavenumber of 1310 cm^{-1} [26].

The effectiveness of the enzyme curing process on the surface of the support is confirmed by signals around 3000 cm^{-1} and in the range 1500–1000 cm^{-1}. FTIR spectroscopic analysis thus confirmed the effectiveness of the immobilization process [26,27].

3.4. Electrochemical properties of CPE/Fe_3O_4/Lig/PDA/GOx/Fc modified electrode

The cyclic voltammetric responses of CPE/Fe_3O_4/Lig/PDA/GOx/Fc in phosphate buffer (pH 7.4), in the absence and presence of a series of glucose solutions in concentrations from 5 to 20 mM, are shown in Fig. 5A. An increase in the anodic peak with a simultaneous decrease in the cathodic peak is recorded when glucose concentration increases. This behavior suggests that glucose is oxidized by the GOx immobilized on Fe_3O_4/Lig/PDA, and the process is further mediated by the Fc^+/Fc redox couple [5,22]. As Fig. 5B shows, when glucose concentration is higher than 20 mM, the voltammetric response begins to level off, suggesting the Michaelis–Menten kinetics typically observed for enzymatic biosensors [2]. From the curve shown in Fig. 5B, the Michaelis–Menten constant (Km_{app}) was found to be 6.8 mM. This indicates that the immobilized GOx exhibits high enzymatic activity and affinity to glucose.

To investigate the electrocatalytic feasibility and analytical performance of the CPE/Fe_3O_4/Lig/PDA/GOx/Fc electrode in glucose determination, chronoamperometry at a constant potential of 0.6 V was performed in phosphate buffer (pH = 7.4). As can be seen in Fig. 6A, the CPE/Fe_3O_4/Lig/PDA/GOx/Fc biosensor exhibits well-defined amperometric currents on successive addition of glucose, confirming the good catalytic performance of GOx after its immobilization on the Fe_3O_4/Lig/PDA matrix. The response current was linear with respect to glucose concentration in the range 10–90 mM, as shown in Fig. 6B.

3.5. Real sample analysis with the CPE/Fe_3O_4/Lig/PDA/GOx/Fc biosensor vs. other methods

To evaluate the performance of the CPE/Fe_3O_4/Lig/PDA/GOx/Fc biosensor in practical analysis, the electrode was used to determine glucose

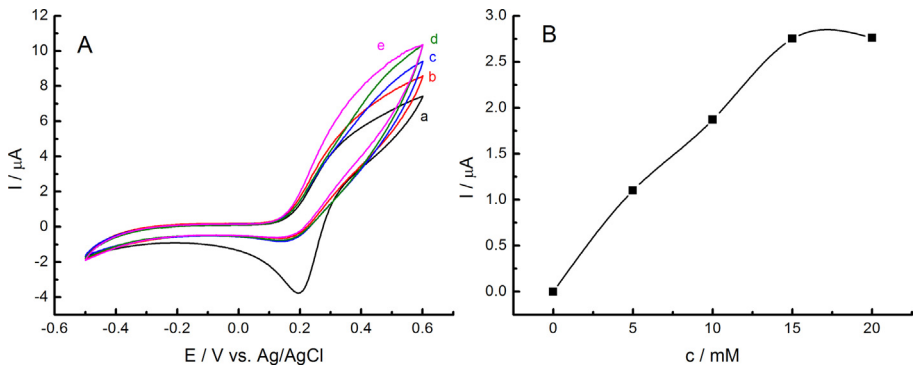

Fig. 5. (A) CV spectra of CPE/Fe_3O_4/Lig/PDA/GOx/Fc in blank PB (a) and with 5 (b), 10 (c), 15 (d) and 20 mM of glucose. Scan rate 10 mVs^{-1}. (B) The plot of catalytic current vs. glucose concentration.

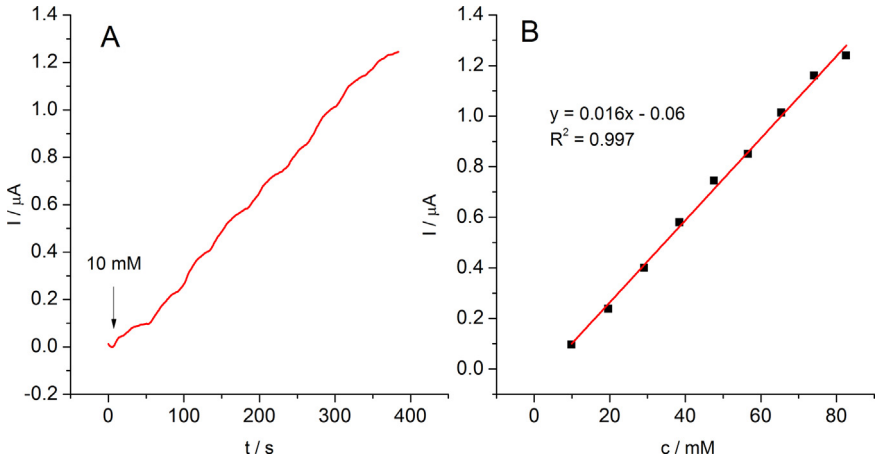

Fig. 6. (A) Chronoamperometric curve recorded at 0.6 V in PBS (pH = 7.4) in stirring conditions after successive additions of glucose. (B) The related calibration graph.

in real samples. Samples of commercial drinks and infusion liquid were provided by a local supermarket and pharmacy. The amperometric assay was conducted at an applied potential of 0.6 V with the addition of 400 μL of the sample to 10 mL of PB (pH 7.4). The standard addition method was used and the glucose concentration in each sample was measured from the three standard additions. Table 2 shows the results of glucose determination for the selected real samples. Herein we carried out eight different types of commercially available products, that assays were repeated three times each of them. The performance of the CPE/Fe_3O_4/Lig/PDA/GOx/Fc biosensor was evaluated by comparison with reference photometric method. Moreover, in order to make a more qualitative and quantitative comparison of our biosensor accuracy, we performed the glucose determinations using commercial glucometers. As seen in Table 2, in comparison with a commercial glucometers excellent accuracy was observed. The glucose contents measured by our biosensor are very close to that was measured by photometric method. High accuracy and low standard deviation bring advantages for the use of the presented CPE/Fe_3O_4/Lig/PDA/GOx/Fc biosensor for real sample detection. The satisfactory recovery values indicate the reliability of the method. The results are in good agreement with the values given by the suppliers, indicating that the biosensor can be used for the determination of glucose in many types of samples. The high precision in measuring of glucose content in real samples with the novel CPE/Fe_3O_4/Lig/PDA/GOx/Fc biosensor indicates its promising applicability as a biosensor useful in the food industry.

4. Conclusion

The present work has been focused on the development of cost-effective and sensitive glucose biosensors under laboratory conditions. The prepared hybrid material based on magnetite, lignin and polydopamine is a good candidate for the biosensing and monitoring of glucose in real commercial samples. The results presented here show the potential of the proposed biosensing platform to achieve high sensing ability with good accuracy, mainly due to the high enzyme loading in the material: 29.44 ± 2.39 mg g^{-1} of support.

Although the magnetite/lignin/polydopamine-glucose oxidase hybrid material has been shown to have satisfactory properties for use in electrochemical glucose biosensors for selected commercial products, further effort should be focused on extending the application of the hybrid electrodes to the analysis of real samples of substances such as blood serum, human urine and pharmaceutical injections. Work is therefore continuing on the synthesis of various novel hybrid materials based on metal oxides and biopolymers.

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Table 2
Results of the determination of the amount of glucose in the samples defined by Fe_3O_4/Lig/PDA/GOx system vs. other glucose testing techniques on commercial samples.

Product	Manufacturer's data (mg/dL)	Photometric method (mg/dL)	Biosensor CPE/Fe_3O_4/Lig/PDA GOx/Fc (mg/dL)	Commercial biosensors (mg/dL)		
				Wellion WELL 900 LB	CERA-CMEK 1 Code model G400	iXell Rev. 04/10-PL
A	62	63 ± 0.02	**62 ± 1.9**	73 ± 0.7	18 ± 2.1	52 ± 2.3
B	102	101 ± 0.02	**101 ± 2.1**	158 ± 2.1	96 ± 4.2	159 ± 1.7
C	59	58 ± 0.02	**58 ± 1.4**	85 ± 1.3	28 ± 1.6	77 ± 1.2
D	123	115 ± 0.02	**112 ± 1.8**	181 ± 2.9	105 ± 3.3	184 ± 4.1
E	40–80	58 ± 0.02	**59 ± 2.4**	80 ± 1.4	24 ± 4.1	68 ± 1.6
F	120–240	172 ± 0.02	**174 ± 2.1**	231 ± 3.4	175 ± 3.3	273 ± 3.5
G	70	69 ± 0.02	**Too low**	24 ± 3.0	58 ± 1.8	46 ± 0.9
H	189	188 ± 0.02	**187 ± 2.7**	Too high	543 ± 4.2	Too high

A - Oshee for runners isotonic drink by Oshee.
B - Glucose 5% Intravenous Infusion by Braun Petzold.
C - 1WW I by Medmess.
D - 1WW II by Medmess.
E - Glucose syrup I by Food colours.
F - Glucose syrup II by Food colours.
G - Glucose Standard I by STAMAR.
H - Glucose Standard II by PUT.

Sc. for access to photometric assays at the Central Laboratory of the Orthopedic Rehabilitation Clinical Hospital in Poznan.

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