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Chemical modification of a nanocrystalline TiO_2 film for efficient electric connection of glucose oxidase

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ABSTRACT

A novel biosensor for glucose was prepared by adsorption of 1,1′-bis(4-carboxybenzyl)-4,4′-bipyridinium di-bromide compound ($H_2BpybcBr_2$) onto the surface of a nanocrystalline TiO_2 film deposited onto FTO glasses, which was used as a platform to assemble the enzyme glucose oxidase to the electrode surface. The $H_2BpybcBr_2/TiO_2$/FTO modified electrode was characterized by scanning electron microscopy, X-ray fluorescence image, cyclic voltammograms and spectroelectrochemical measurements. The immobilization of GOD on functionalized TiO_2 film led to stable amperometric biosensing for glucose with a linear range from 153 μmol L^{-1} to 1.30 mmol L^{-1} and a detection limit of 51 μmol L^{-1}. The apparent Michaelis–Menten constant (K_m) was estimated to be 3.76 mmol L^{-1}, which suggested a high enzyme-substrate affinity. The maximum electrode sensitivity was 1.25 μA mmol L^{-1}. The study proved that the combination of viologen mediators with TiO_2 film retains the electrocatalytic activity of the enzyme, and also enhances the electron transfer process, and hence regenerating the enzyme in the reaction with glucose.

1. Introduction

The design and structural characterization of interfacial supramolecular assemblies in which biomolecules retain their natural function, e.g. proteins or enzymes that remain redox-active, is an area of intense research effort [1–4]. A major drive in this area is to create assemblies in which proteins are strongly adsorbed but retain their native properties, so that the assembly provides a well-defined environment in which electron transfer can be probed [5,6]. The intimate contact of the enzyme and the mediator is a pre-requisite for efficient electron transfer between the enzyme and the electrode [7]. Numerous ways for anchoring electrochemically active compounds onto electrode surfaces have been investigated aiming the shortening of the distance between the redox sites involved in the electron transfer reaction [8].

From this point of view, the self-assembly method of integration has been widely used in designing electronic devices and biosensors. In general, the microstructured semiconductor oxides have often been used as a supporting matrix for bioactive modification to form functionalized electrode materials [9]. Several metal multiporous film oxides, such as titanium oxide (TiO_2), zinc oxide (ZnO) and niobium oxide (Nb_2O_5), have been investigated in the respect of protein electrode interactions [10–12]. In this case, the covalent linkage of proteins to metal-oxide materials occurs by hydroxyl groups that are synthetically used for the coupling of organic materials. Furthermore, these porous membranes are obtained from semiconductor nanoparticles, providing a protected nanoreactive environment for biological processes. In fact, the immobilization of enzyme molecules onto TiO_2 electrodes was carried out by cross-linking and physical entrapment within inorganic laponite gel or organic polymer film [13,14]. However, these different procedures require a chemical step which would probably induce a chemical denaturation of biomolecules.

In our previous work, we described the immobilization of redox mediators and proteins onto protected porous silicon surfaces to obtain their direct electrochemical reactions and to retain their bioactivities as well [15]. That paper showed that microperoxidase-11 and viologens are able to establish chemical bonds with the 3-aminopropyltriethoxylsilane-modified porous silicon surface. The functionalization of the surfaces has been fully characterized by energy-dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS) to examine the immobilization of these mediators onto the solid surface. Amperometric and open-circuit potential measurements have shown the direct electron transfer between glucose oxidase and the electrode in the presence of the viologen mediator covalently linked to the 3-aminopropyltriethoxylsilane (APTES)-modified porous silicon surface. However, it showed some limitations such as low stability and reproducibility after some amperometric studies in phosphate buffer solution, even after surface chemical treatment, like

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lkylation or silanization. Reproducibility can be related to instability in aqueous media due to oxidation of the non-reactive Si–H bonds on the electrode surface.

Transparent nanocrystalline TiO_2 films have been widely employed in the development of several devices such as dye-sensitized solar cells or electrochromic windows due to their characteristics, such as wide band-gap and inertness, among others [16,17]. They consist of interconnected nanocrystallites forming a sponge-like film with a large internal surface area. In this work, a thin nanocrystalline TiO_2 film was employed as nanostructured support to enhance the bioelectrocatalytic behavior of glucose oxidase and the electrochemical reproducibility of the system when compared to porous silicon surfaces previously described. In order to immobilize the enzyme on the surface of TiO_2, 1,1′-bis(4-carboxybenzyl)-4,4′-bipyridinium di-bromide was adsorbed onto the titanium dioxide surface. The condensation of the carboxylic group of this compound with the lysine residues of the glucose oxidase allows the chemical bonding of the organic compound with the enzyme. In this approach, the organic compound acts as a molecular wire to link the enzyme and the oxide surface, making this material a good candidate for the manufacturing of bioelectronic devices based on molecular recognition and self-organization. The proposed adsorption is depicted in Scheme 1.

2. Materials and methods

2.1. Materials

The bipyridinium salt $H_2BpybcBr_2$ was synthesized by the reaction of 4-(bromomethyl)benzoic acid with 4,4′-bipyridine according to the literature [15]. Glucose oxidase (E.C. 1.1.3.4), type VII, from *Aspergillium niger* was purchased from Sigma Chemical Co., and titanium isopropoxide was purchased from Fluka, and were used without further purification.

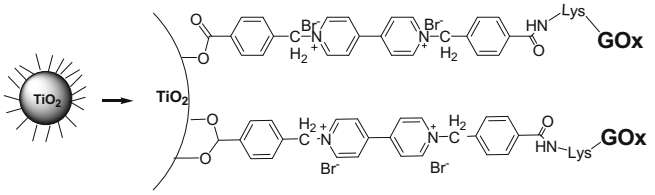
2.2. Preparation of nanocrystalline TiO_2 film and anchorage of $H_2BpybcBr_2$ onto electrode surface

Colloidal TiO_2 employed in preparation of films for electrochemical measurements was obtained by hydrolysis of titanium isopropoxide followed by hydrothermal growth of the particles [18]. The colloidal TiO_2 was deposited onto FTO glasses (fluorine-doped tin oxide – Pilkington TEC15, thickness 2.5 mm, sheet resistance 15Ω/sq) by painting technique and sintered at 450 °C for 30 min.

The TiO_2 electrodes were immersed in an ethanolic saturated solution of the viologen compound $H_2BpybcBr_2$ for 24 h. After the substrate was removed from the solution, it was rinsed with ethanol and dried under a nitrogen stream. From now onwards in the text, this electrode will be referred to as $H_2BpybcBr_2/TiO_2/FTO$ (Scheme 1).

2.3. Immobilization of glucose oxidase at $H_2BpybcBr_2/TiO_2/FTO$ film

For linking the enzyme by peptide bonding, the $H_2BpybcBr_2/TiO_2/FTO$ modified electrode was immersed in an aqueous solution containing 20 mg of GOD dissolved in 1 mL of 10 mmol L^{-1} phosphate buffer solution pH 7.0 + 50 mmol L^{-1} of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide for 5 h at room temperature under continuous stirring. After being rinsed with distilled water, the electrode was stored in 10 mmol L^{-1}, pH 7 phosphate buffer at 4 °C.



Scheme 1. Schematic representation of the functionalized nanocrystalline TiO_2 film.

2.4. Film characterization

The morphology of TiO_2 films and the size of the oxide particles were characterized by scanning electronic microscopy, SEM, by using a JEOL FEG-SEM (JSM 6330F) or a JEOL LV-SEM (JSM 5900LV) microscope. Optical absorbance spectra were recorded in a Varian Cary-50 Bio spectrophotometer. A chemical mapping analysis was carried out using an energy-dispersive micro-X-ray fluorescence spectrometer (Shimadzu, mEDX-1300) with an accelerating voltage of 50 kV and a lateral step of 5 mm.

2.5. Electrochemical measurements

Cyclic voltammetry (CV) and chronoamperometry (CA) experiments were performed with an AutolabPGSTAT30 (Eco Chemie) electrochemical system. All potentials are referred to SCE electrode while a platinum foil was employed as the auxiliary electrode. The FTO glasses containing TiO_2 film (1 cm^2) on the surface were used as working electrode. All solutions were purged with nitrogen for at least 20 min prior to experiments and a nitrogen environment was then kept over the solution in the cell.

3. Results and discussion

3.1. Morphology and electrochemical characterization of $H_2BpybcBr_2$ adsorbed onto nanocrystalline TiO_2 film

TiO_2 was prepared by the sol–gel procedure and the films were obtained by painting the FTO (fluorine-doped tin oxide) conducting glass electrode, as described in the literature [18]. After drying, the layer underwent sintering at a temperature of 450 °C so that organic components would burn off while the TiO_2 particles formed a continuous electrically percolating network. Fig. 1 shows the surface morphologies of the nanocrystalline TiO_2 film by scanning electron microscopy (SCE). The films are rough and porous, similar to a sponge-like material and its nanocrystals are around 17 ± 3 nm. This film can be a promising material for enzyme immobilization, owing to its high biocompatibility and large specific surface area of nanosized particles. In fact, recent work has demonstrated that the porous nanocrystalline TiO_2 film can retain the biological activity of proteins [19–21], so it suggested that this film would be useful to investigate the physical and chemical properties of protein molecules.

In order to improve the electron transfer between enzyme and electrode, we have studied the functionalization of the surface of nanocrystalline TiO_2 film with 1,1′-bis(4-carboxybenzyl)-4,4′-bipyridinium di-bromide compound by immersing the processed electrode in a saturated viologen solution for some hours. The TiO_2 surface contains –OH groups that can be used to interact with –COOH groups from the viologen compound $H_2BpybcBr_2$ by formation of an ester bond [15,22,23], which will be later used to covalently attach the enzyme to the electrode surface. Fig. 1B shows the X-ray fluorescence image of bromide ions, which clearly indicates a homogeneous distribution of the mediator in the film, once the bromide anion is the counter-ion of $H_2BpybcBr_2$. This result confirms the modification of the surface of the nanocrystalline TiO_2 film with viologen compounds as well as the applicability of this microscopy technique for the simple screening of such supported mediator onto electrode surfaces.

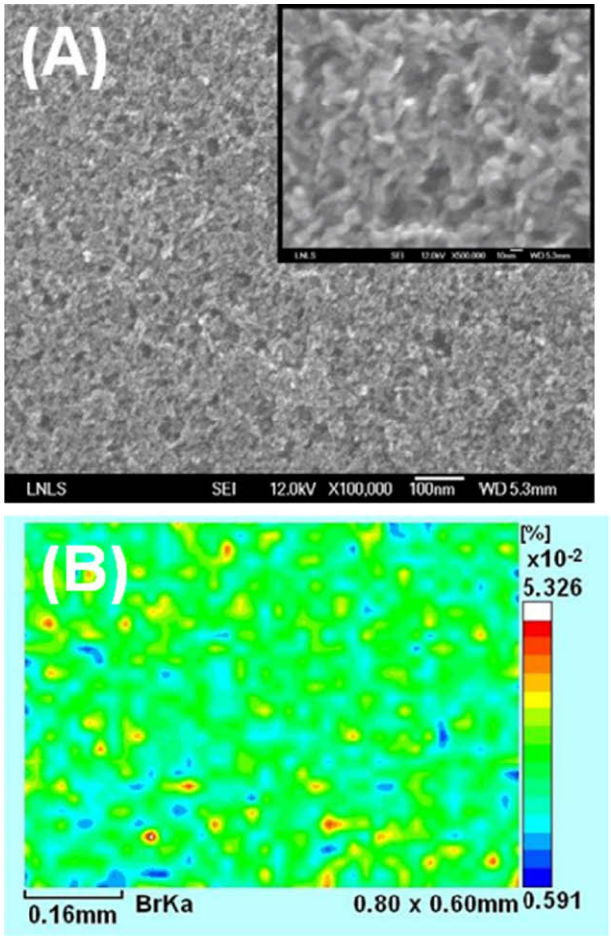


Fig. 1. (A) SEM image of the TiO_2 surface prior to functionalization (inset: higher magnification of the same image) and (B) X-ray fluorescence analysis.

To characterize the immobilization of $H_2BpybcBr_2$ onto the electrode surface, cyclic voltammograms of the TiO_2/FTO and $H_2BpybcBr_2/TiO_2$/FTO electrodes were recorded in 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) at a sweep rate of 50 mV s^{-1}. The peak potentials of the first and second reduction waves were found at −0.34 and −0.62 V *versus* SCE, respectively, which are assigned to the $H_2BpybcBr_2$ modified electrode. Many viologen derivatives show two reduction waves whose potentials present almost the same values obtained here [23–25]. Besides, the peak potentials are similar to that obtained in homogeneous DMSO solution containing $H_2BpybcBr_2$ (0.01 mol L^{-1}) and $LiClO_4$ (0.10 mol L^{-1}) under a nitrogen atmosphere, as shown in inset Fig. 2.

The surface coverage (Γ) of $H_2BpybcBr_2$ on the surface of nanocrystalline TiO_2 film was estimated from integration of the reduction peak in the CV according to $\Gamma = Q/nFA$, where Q is the charge involved in the reaction, n is the number of electrons transferred, F is Faraday constant, and A is the electrode area. The value of Γ = 8.29 nmol cm^{-2} of viologen was calculated (corrected for the TiO_2 background), which is in good agreement with the viologen compound that contains one phosphonic acid group ($-PO_3H_2$) linked to the viologen that was chemisorbed on nanostructured TiO_2 layer of thickness 2–10 μm (38 nmol cm^{-2}) [22].

Spectroelectrochemical measurements were performed for $H_2BpybcBr_2/TiO_2$/FTO electrode in the potential range from −0.40 to −0.70 V *versus* SCE in DMSO solution containing $LiClO_4$ (0.10 mol L^{-1}) under a nitrogen atmosphere (see Fig. 3). In negative potential at −0.4 V, a broad absorption band appeared over the 500–700 nm region while another intense absorption band appeared around 370 nm. Both absorption bands were assigned to a viologen cation radical. A point of convergence in the absorbance titration curves at 530 nm was observed when a potential −0.40 V was applied, close to the first reduction potential of −0.34 V obtained from the cyclic voltammogram (Fig. 2). In a more negative potential region, this broad band in the visible region faded, while the band around 370 nm increased. This behavior can be assigned to formation of neutral quinoid-like viologen as a two-electron reduced species [23]. These results demonstrate the physico-chemical adsorption of $H_2BpybcBr_2$ to the surface of nanocrystalline TiO_2 film. Moreover, it seems also quite suitable for the adsorption or immobilization of macromolecules, which hold great promise for the study of direct electron transfer of redox proteins and the construction of novel biosensors.

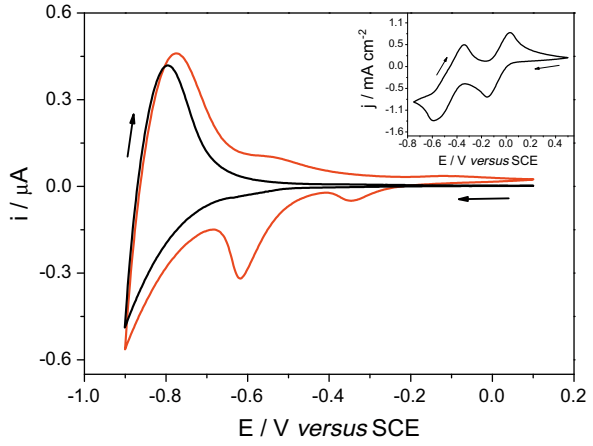


Fig. 2. Cyclic voltammograms of the TiO_2/FTO (black line) and $H_2BpybcBr_2/TiO_2$/FTO (red line) electrodes recorded in 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) at a sweep rate of 50 mV s^{-1} under nitrogen atmosphere. Inset: CV in homogeneous DMSO solution containing $H_2BpybcBr_2$ (0.01 mol L^{-1}) and $LiClO_4$ (0.10 mol L^{-1}) at 50 mV s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

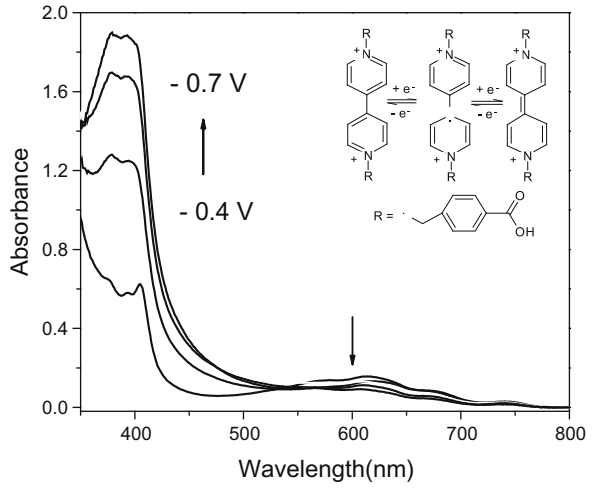


Fig. 3. UV–Vis spectra of the $H_2BpybcBr_2/TiO_2$/FTO electrode under potentiostatic conditions. The spectra were taken at 100 mV intervals from −0.4 to −0.7 V *versus* SCE in DMSO solution containing $LiClO_4$ (0.10 mol L^{-1}) under nitrogen atmosphere.

3.2. Electrocatalytic oxidation of glucose at the GOD/$H_2BpybcBr_2/TiO_2$/FTO electrode

The electron transfer of glucose oxidase (GOD) covalently immobilized on the $H_2BpybcBr_2/TiO_2$/FTO surface was investigated

by electrochemical experiments. The carboxylic acid residues from viologen compounds immobilized on the electrode surface were functionalized to an active ester using carbodiimide reagents prior to the coupling with the GOD. Such viologen served as an anchor for the immobilization of GOD on fluorine doped TiO_2 glass with TiO_2 nanoparticles, as well as an electron mediator between the modified electrode and the enzyme.

Fig. 4 shows the changes of the open-circuit potential (OCP) values upon successive additions to glucose in phosphate buffer solution under nitrogen atmosphere to the $H_2BpybcBr_2/TiO_2$/FTO electrode before and after GOD immobilization on its surface. No change of OCP values are observed for the $H_2BpybcBr_2/TiO_2$/FTO electrode, indicating that it does not promote the glucose oxidation, while the covalent attachment of the mediator to the enzyme provides a means to facilitate electrical communication between the enzyme and the electrode, evidenced by the increase of the OCP upon glucose additions due to enhancement of viologen in the oxidized form on the electrode surface, according to the Nernst equation. The results show that the viologen has been grafted to TiO_2 film and GOD immobilized; the system can serve as an electrode material and also as a possible pathway of the electron transfer from the glucose analyte to the electrode, which can be visualized as in Scheme 2. The direct linkage of GOD via an electron mediator to the electrode is expected to increase the efficiency of electron transport, and hence the sensitivity of the GOD modified electrode [26,27]. In fact, Hale et al. has shown that viologen molecules have sufficient anodic redox potentials to reoxidize reduced glucose oxidase [28].

The bioelectrocatalytic performance for both electrode arrays GOD/TiO_2/FTO and GOD/$H_2BpybcBr_2/TiO_2$/FTO was also investigated by cyclic voltammetry experiment, in the presence of 20 mmol L^{-1} glucose dissolved in 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) at a scan rate of 50 mV s^{-1} under nitrogen atmosphere. As shown in Fig. 5, the catalytic oxidation current of glucose at the GOD/$H_2BpybcBr_2/TiO_2$/FTO electrode is much higher than that at the GOD/TiO_2/FTO electrode, indicating that the $H_2BpybcBr_2$ coating on its surface greatly enhanced the electrocatalytic current of the immobilized GOD on the nanocrystalline TiO_2 film, since it can be responsible for facilitating the electron transport from GOD enzyme [26,29]. Moreover, a high concentration of $H_2BpybcBr_2$ will also lead to a greater quantity of GOD immobilized on the electrode surface and consequently provoking an increase in the peak oxidation current.

To examine the sensitivity of the prepared GOD/$H_2BpybcBr_2/TiO_2$/FTO electrode, we investigated the amperometric response of glucose in the stirring pH 7 PBS solution. Fig. 6 shows the typical current–time curves for the modified electrode with a successive addition of glucose. The anodic oxidation currents at about +0.55 V increased linearly with the increasing glucose concentration, as shown in the inset of Fig. 6. Upon the addition of glucose, the GOD/$H_2BpybcBr_2/TiO_2$/FTO electrode reached the maximum steady-state response within 5 s, indicating a fast diffusion process and a high activity of the GOD in this system. The response was linear within the concentration range from 153 μmol L^{-1} to 1.30 mmo L^{-1}. The detection limit was 51 μmol L^{-1} with the

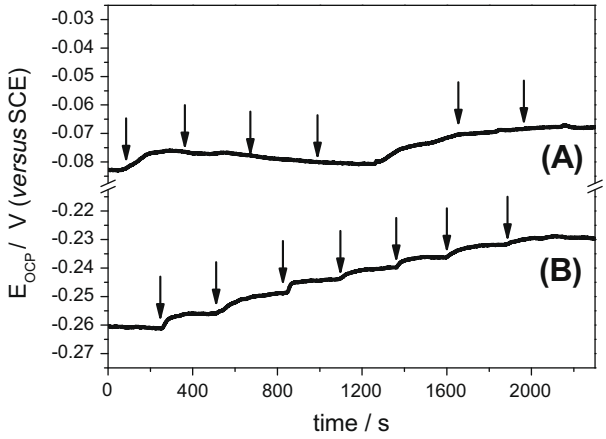
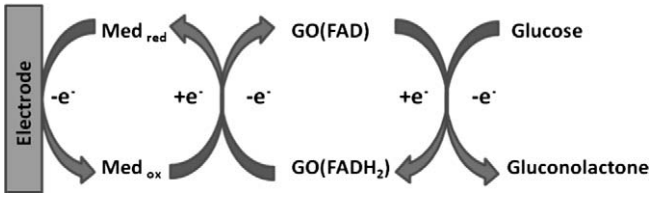


Fig. 4. OCP measurements of the $H_2BpybcBr_2/TiO_2$/FTO electrode before (A) and after GOx immobilization on surface (B) in response to successive additions of glucose in PBS solution.



Scheme 2. Reaction scheme for the oxidation of glucose under nitrogen atmosphere using a redox mediator.

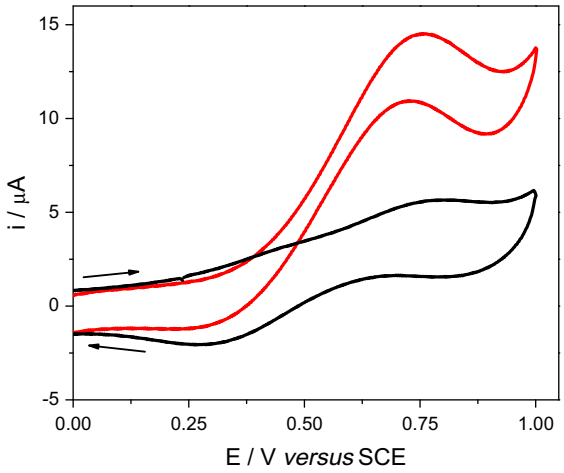


Fig. 5. Cyclic voltammograms of the GOD/TiO_2/FTO (black line) and GOD/$H_2BpybcBr_2/TiO_2$/FTO (red line) electrodes recorded in 20 mmol L^{-1} glucose dissolved in 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) at a sweep rate of 50 mV s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

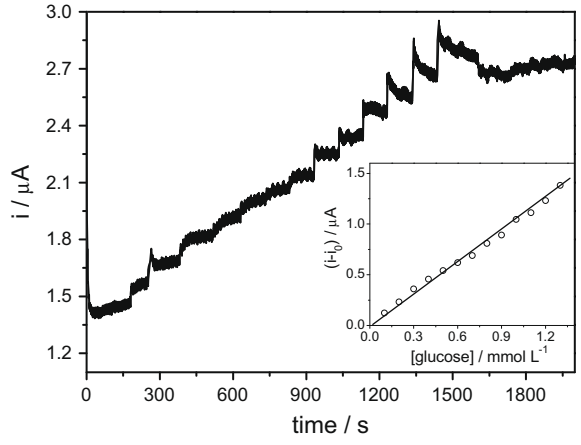


Fig. 6. Response of the modified GOD/$H_2BpybcBr_2/TiO_2$/FTO electrode to glucose concentrations, added in portions of 0.1 mmol L^{-1}. The electrode was operated at +0.55 V *versus* SCE, in 0.1 mol L^{-1} PBS (pH 7.0).

signal-to-noise ratio of three. A plateau was observed when the concentration of glucose became higher, showing the characteristics of the Michaelis–Menten kinetics. When concentration of glucose was higher than 2 mmol L^{-1}, the electrocatalytic current even decreased, implying a progressive enzyme inactivation with the increasing of substrate concentration [30]. The apparent Michaelis–Menten constant (K_m), which is an indication of the enzyme-substrate kinetics, can be calculated using the Lineweaver–Burk plot [31]. The apparent kinetic parameters of i_{max} and K_m value were found to be 4.7 μA and 3.76 mmol L^{-1}, respectively. Thus, the maximum electrode sensitivity (i_{max}/K_m) equaled to 1.25 μA mmol L^{-1}. The K_m value was two times lower than that on GOD absorbed directly on porous nanocrystalline TiO_2 film (K_m = 6.08 mmol L^{-1}) [19], and also on nanostructured TiO_2–modified Si electrodes (K_m = 7.5 mmol L^{-1}) [20], indicating an obvious evidence of high sensitivity of the glucose response on the GOD/H_2BpybcBr$_2$/TiO_2/FTO electrode. The detection sensitivity and the linear range of this developed glucose biosensor were higher than other procedures that involved immobilization of GOD on the electrode surface that have already been reported in literature involving TiO_2 film [14,19,20], but much lower than GOD immobilized on titania nanotube/titanium electrodes [12]. This result demonstrates that the viologen compound H_2BpybcBr$_2$ on the nanocrystalline TiO_2 film can provide a bridge for electron transfer between proteins and electrodes. The study proved that the combination of TiO_2 nanostructured films containing viologen compounds is able to open new opportunities for the design of enzymatic biosensors with potential applications in practice.

We have also investigated the dependence of applied potentials on the amperometric response of the GOD/H_2BpybcBr$_2$/TiO_2/FTO electrode to glucose detection (see Fig. 7). The biosensor response increased with increasing potentials from 0.25 to 0.65 V, indicating that the biosensor response is controlled by both kinetics of the enzyme catalytic reaction and the electrochemical process. When the potential was more positive than +0.55 V, the response changed slightly, indicating that the biosensor response was controlled by the diffusion of substrate and product. At +0.55 V and more positive potentials, there are interfering reactions from other electroactive species in the solution, such as: ascorbic and uric acid. However, the biosensor developed in this work was suitable for non-clinical samples, due to high signal-to-noise ratio. For biomedical diagnosis, other positive potentials lower than +0.55 V could be chosen in order to avoid oxidation of different interfering compounds, but presenting lower sensibility to glucose detection. Especially, the sensitivity of the GOD/H_2BpybcBr$_2$/TiO_2/FTO electrode at +0.35 V (0.70 μA $mmol^{-1}$ L) is higher than that obtained for other biosensors such as GOD trapped inside an electropolymerised film (0.28 μA $mmol^{-1}$ L cm^{-2}) [32], GOD immobilized onto carbon film electrodes (0.28 μA $mmol^{-1}$ L cm^{-2}) [33] and GOD immobilized onto copper hexacyanoferrate nanoparticles by using the electrostatic deposition layer-by-layer technique (LbL) [34]. On the other hand, it has to be taken into account that sensitivities here obtained are of the same order than those obtained with electrodes where the amount of enzyme used is much higher.

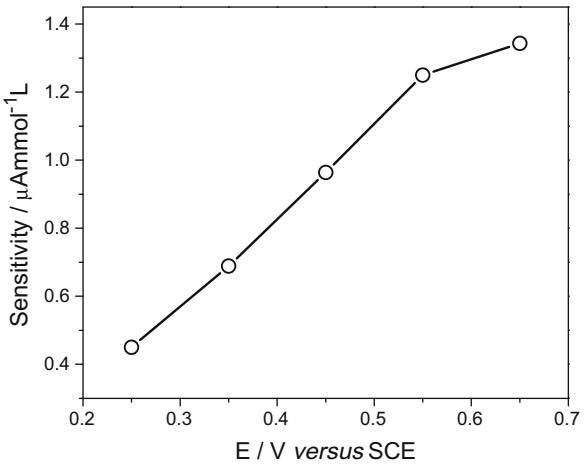


Fig. 7. Effect of the applied potential on the sensitivity of the modified GOD/H_2BpybcBr$_2$/TiO_2/FTO electrode, in 0.1 mol L^{-1} PBS (pH 7.0).

Further studies also showed that this biosensor is very stable when compared to GOD covalently linked to the H_2BpybcBr$_2$/APTES/Si electrode [15]. When it was stored at 4 °C for two weeks and used for measurements intermittently, the sensor retained more than 85% of its initial response to the oxidation of 0.5 mmol L^{-1} glucose. The good microenvironment caused by the synergistic effect of this hybrid film might have contributed to the improvement of the affinity and good performance of the biosensor.

4. Conclusion

In this paper, we have demonstrated the electron transfer between GOD and the electrode in the presence of the viologen mediator covalently linked to the nanocrystalline TiO_2 film. The catalytic oxidation current of glucose at the GOD/H_2BpybcBr$_2$/TiO_2/FTO electrode is much higher than that at the GOD/TiO_2/FTO electrode, indicating that the coated H_2BpybcBr$_2$ on the electrode surface greatly enhances the electrocatalytic current of the immobilized GOD on the nanocrystalline TiO_2 film, since it lead to a greater quantity of GOD immobilized on the electrode surface and consequently provoking an increase in the peak oxidation current. The sensor exhibits good performance for electrocatalytic oxidation of glucose, such as sensitivity, detection limit, and linear range. The improved electrode coverage and high sensitivity are important steps towards further miniaturization of biosensors. As a result, the methodology described here can be applied to improved enzyme immobilization for enhanced bioelectrocatalytic activity of porous electrodes.

Acknowledgments

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