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Hybrid bioelectrocatalyst for hydrogen peroxide reduction: Immobilization of enzyme within organic–inorganic film of structured Prussian Blue and PEDOT

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Abstract

Fabrication of structured film (on glassy carbon substrate) composed of compact Prussian Blue (that has been prepared by alternate immersions and through assembling within ultra-thin layers of 4(pyrrole-1-yl)-benzoic acid, PPyBA) and poly(3,4-ethylendioxythiophene), PEDOT, is described. This functionalized film has been characterized by fast charge propagation, and it has served as a redox conducting template for permanent attachment of a model enzyme, horseradish peroxidase, HRP. The resulting organic–inorganic system acts as an effective hybrid bioelectrocatalyst for electroreduction of hydrogen peroxide, a model reactant for biosensors and biofuel cells. Among important issues are rigidity, permanence of enzyme attachment, morphology, hydrophilicity, and attractive mediating capabilities of the PEDOT-stabilized Prussian Blue based structured film.
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Keywords: Composite film; Structured Prussian Blue film; 4(pyrrole-1-yl)-benzoic acid; Poly(3,4-ethylendioxythiophene); Horseradish peroxidase; Bioelectrocatalysis

1. Introduction

There has been growing interest in conducting polymers as matrices for immobilization of biological macromolecules, particularly with respect to the development of biosensors [1–9]. Incorporation of enzymes into a conducting polymer film (as opposed to incorporation into a polyelectrolyte or insulating polymer film) leads, in principle, to the enhancement of charge transport and better physical (and often chemical stability) of the enzyme. Conducting polymer coatings are good charge mediators, and they are not likely to be degraded through fouling by substrates and products of organic redox processes.

To improve further mediating capabilities, stability and morphology, and to increase somewhat hydrophilic properties of the conducting polymer based film, we propose fabrication of novel hybrid organic–inorganic materials by incorporation of sparingly-soluble (but hydrated) mixed-valence polynuclear cyanometallates. Thin films of their prototype, Prussian Blue or iron(III) hexacyanoferrate(II), are characterized by fast dynamics of charge propagation, and they were demonstrated to act as powerful electrocatalysts for the reduction hydrogen peroxide, an important analyte or product of the enzyme catalyzed reactions [10–21]. For example, many of glucose amperometric biosensors were constructed by immobilization of glucose oxidase within a layer of perfluorinated cation exchange membrane (Nafion) cast directly onto the Prussian Blue (PB) modified electrode [17–20]. In the present work, we refer to the recent concepts of assembling metal hexacyanoferrates within ultra-thin organic films [22–25] and generation composite (hybrid) films in which negatively charged inorganic cyanometallate species are attracted and electrostatically stabilized by positively charged conducting polymer backbone [26]. Using the alternate immersion scheme, we have assembled PB within

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ultra-thin layers of 4(pyrrole-1-yl)-benzoic acid, PPyBA and further stabilized with poly(3,4-ethylendioxythiophene), PEDOT. This polymer is one of the best known π-conjugated conducting polymers. Conducting PEDOT films have recently been considered for use as antistatic materials [27], supercapacitors [28], various electrochemical devices and biosensors [29]. PEDOT structures can be generated through oxidative electropolymerization of its monomer, 3,4-ethylendioxythiophene (EDOT), in aqueous solutions [30,31]. We are aiming at producing dense stable films in which concentration of reactive PB redox centers is high. It can be expected that, by assembling PB within PPyBA and through introduction of the polymer matrix, free space between PB grains will be minimized. It is reasonable to expect that functional carboxylate groups originating from the PPyBA organic component would form stable covalent amide bindings with amine groups from the enzyme [20,21]. Further, the PyBA caroxylate groups are likely to interact and coordinate some iron ions in the Prussian Blue lattice. Finally, the PEDOT layers should also attract electrostatically negatively charged sites of the enzyme. We demonstrate here that our composite film permits permanent attachment of a model enzyme, horseradish peroxidase, HRP. The resulting hybrid bioelectrocatalyst shows reactivity towards electroreduction of hydrogen peroxide, a model reactant for biosensors and biofuel cells.

2. Experimental

All inorganic salts and reagents were as obtained from suppliers; 4 (pyrrole-1-yl) benzoic acid, PyBA, was purchased from Aldrich. The solutions were prepared using doubly-distilled subsequently deionized (Millipore Milli-Q) water. The horseradish peroxidase (HRP) was purchased from Sigma.

Electrochemical measurements were done with Chemical Instruments (CHI) Model 660B (Austin, TX, U.S.A.) multifunctional analyzer. Standard three-electrode cell with magnetic stirrer was used for preparation of composite films and for other electrochemical measurements. The working electrode was glassy carbon of 3 mm diameter supplied by Bioanalytical Systems (BAS), (West Lafayette, IN, USA). The counter electrode was made from Pt wire. All potentials were expressed versus saturated (KCl) Ag/AgCl reference electrode. Surface examination of films was done using JEOL Model JSM-5400 scanning electron microscope.

Before modification, glassy carbon electrodes surfaces were activated by polishing with successively finer grade aqueous alumina slurries (grain size, 0.5 μm) on a polishing cloth. The optimum composite films of Prussian Blue (PB) and polymerized 4 (pyrrole-1-yl) benzoic acid (PPyBA), were grown by chemical deposition of layers. The electrodes were alternately immersed into the appropriate solutions. Each immersion lasted for 10 minutes. The first immersion was performed into the heated (60 °C) PyBA-saturated solution (that had been freshly sonicated for 30 minutes). Here, heating aimed at improving dissolution of PyBA in water. The second solution for immersion contained 0.01 mol dm^{-3} $FeCl_3$ in 0.5 mol dm^{-3} HCl; and the third solution for immersion was 0.01 mol dm^{-3} $K_3[Fe(CN)_6]$ in 0.1 mol dm^{-3} KCl. The above procedure of alternate immersions was repeated three times. Then it was followed by potential cycling (10 full scans at 100 mV s^{-1}) in 0.1 mol dm^{-3} KCl from −0.25 to 1.1 V. KCl salt was chosen because redox reactions of PB component were supported by the flux of potassium cations. Exposure and treatments in KCl had overall conditioning effect of the composite film.

Electrochemical deposition (over-coating) with PEDOT was accomplished in the same three electrode cell. The PB based inner layers were covered with PEDOT by potential cycling (at 50 mV s^{-1}) in 0.1 mol dm^{-3} KCl containing $4 \cdot 10^{-6}$ mol dm^{-3} EDOT in the potential range from −0.4 to 1.0 V. The enzyme was subsequently immobilized by introduction of 0.5 ml of the aqueous HRP (4 mg/ml) solution onto the organic–inorganic film. The step was followed by rinsing with water, drying and overnight conditioning in refrigerator.

Unless otherwise stated, electrochemical (voltammetric, amperometric) measurements were performed in 0.1 mol dm^{-3} KCl solutions in the absence or presence of hydrogen peroxide (at 0.1 mmol dm^{-3} level).

3. Results and discussion

Modification of a glassy carbon electrode with ultra-thin films of polymerized 4 (pyrrole-1-yl) benzoic acid (PPyBA) was achieved in a manner described in the Experimental section. Exposure to the saturated solution of PPyBA was

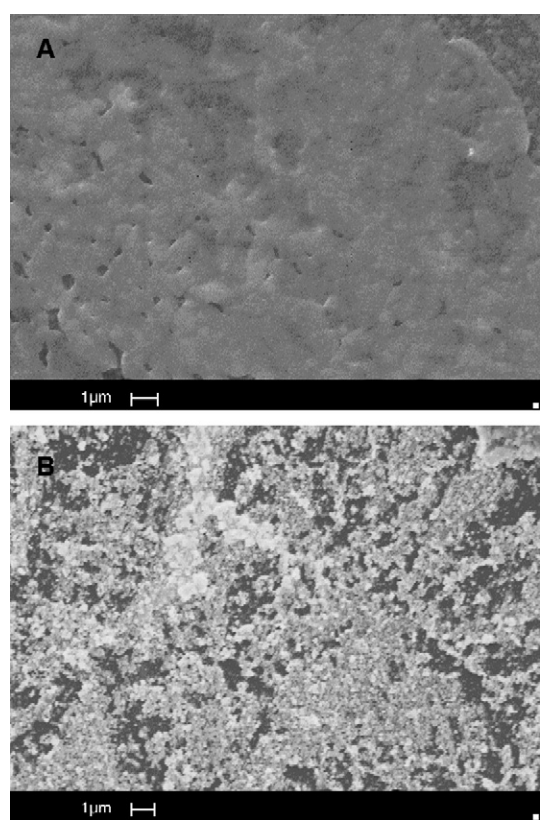

Fig. 1. Scanning electron micrographs of (A) PPyBA-assembled PB layer and (B) conventionally electrodeposited PB film [25]. Electrode substrate, glassy carbon.

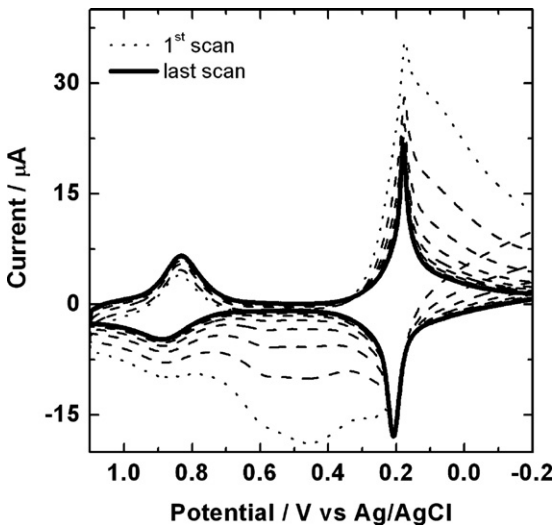

Fig. 2. Voltammetric conditioning of composite PB/PPyBA film by repetitive potential cycling. Electrolyte, 0.1 mol dm^{-3} KCl. Scan rate, 100 mV s^{-1}. Electrode substrate, glassy carbon.

accompanied by the formation of the system's monolayer type film on glassy carbon. To produce ultra thin films of iron(III) hexacyanoferrate(II), i.e. PB, we utilized the ability of carboxylate groups within PPyBA to attract iron(III) ions. In this context, our approach paralleled other attempts aiming at producing self-assembled films of PB and its analogues by multiple sequential adsorption or attachment of metal cations and hexacyanoferrate anions [22–25]. Here PB films were assembled by exposing (for 15 min) the PPyBA-modified electrode first to 10 mmol dm^{-3} $FeCl_3$ (in 0.5 mol dm^{-3} HCl), then to 10 mmol dm^{-3} $K_3Fe(CN)_6$. It is apparent from scanning electron microscopic measurements that morphology of PPyBA-assembled PB layer (Fig. 1A) is less granular, much more uniform and compact in comparison to the conventionally electrodeposited PB film (Fig. 1B).

For practical purposes stable, dense, and sufficiently thick films that contain three-dimensionally distributed PB have to be produced. Therefore, the procedure involved three cycles of alternate immersions mentioned above. Consequently, a multi-layer film of PB (assembled within PPyBA layers) was formed. As a rule, the electrode was rinsed with 0.1 mol dm^{-3} KCl after each step. Fig. 2 illustrates voltammetric conditioning of the resulting organic–inorganic PB-based film. During repetitive potential cycling from 1.1 to −0.25 V in 0.1 mol dm^{-3} KCl, currents tended to initially decrease until they reached steady values. The appearance of two sets of reversible and well defined peaks at about 0.9 and 0.2 V (Fig. 2) implied the presence of PB in the film. These two sets of voltammetric peaks originated from the following reactions [21,25]: the oxidation of PB (Eq. (1)) to iron(III) hexacyanoferrate(III), Prussian Yellow, at about 0.9 V, and the reduction of PB to iron(II) hexacyanoferrate(II), Prussian White (Eq. (2)) at about 0.2 V

$$KFe^{III}[Fe^{II}(CN)_6] - e^- - K^+ \Leftrightarrow Fe^{III}[Fe^{III}(CN)_6] \quad (1)$$

$$KFe^{III}[Fe^{II}(CN)_6] + e^- + K^+ \Leftrightarrow K_2Fe^{II}[Fe^{II}(CN)_6] \quad (2)$$

The important issue was that presence of the functional organic component had no inhibiting effect on the voltammetric behavior of PB.

The film was further subjected to over-coating and stabilizing with PEDOT polymer due to its high electrical conductivity [32], good stability in the p-doped state [33], and ability form well-behaved composite films with anionic polynuclear inorganic compounds [30,34]. In the presence of EDOT monomer, the characteristic current increases (at potentials higher than 0.95 V in Fig. 3) were consistent with the system's electropolymerization during positive potential scans. It is also reasonable to expect that positively charged conducting polymer (PEDOT) structures were attracted by the negatively charged PB layers.

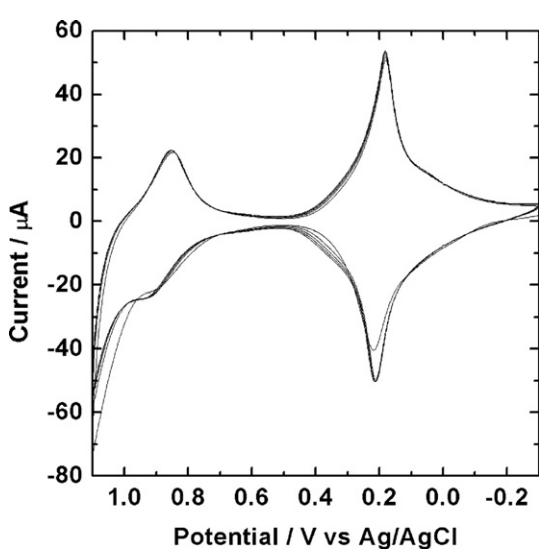

Fig. 3. Generation of PEDOT within PB/PPyBA composite film through application of 10 potential cycles in EDOT-saturated solution. Other conditions as for Fig. 2.

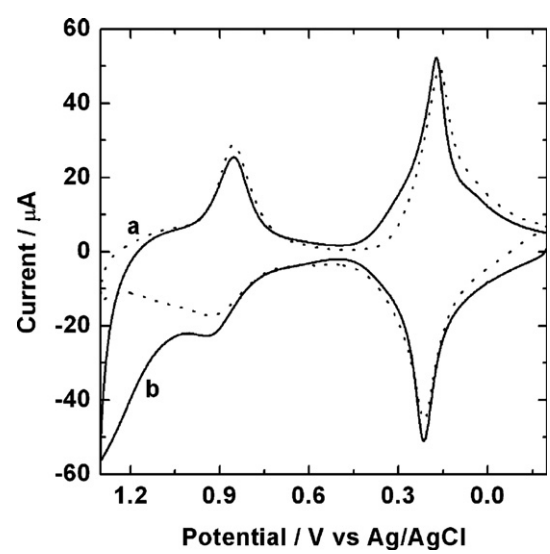

Fig. 4. Comparison of cyclic voltammetric responses of (a) PB/PPyBA and (b) PEDOT-containing PB/PPyBA films. Other conditions as for Fig. 2.

Cyclic voltammetric responses of PPyBA-assembled PB (PB/PPyBA) films, (a) bare and (b) subjected to electropolymerization in the presence of EDOT, are shown in Fig. 4. The appearance of fairly large voltammetric currents at potentials higher than 0.9 V clearly implies the presence of sizeable amounts of PEDOT in the hybrid PB-based film. In view of the recent reports describing redox intercalative polymerization of pyrrole, aniline and thiophenes in various inorganic materials leading to the formation of well-ordered compound with enhanced electrical properties [35,36], it is reasonable to expect that PEDOT is also inserted into gallery space of PB.

The PEDOT over-coated electrode showed long-term stability to storage under dry ambient conditions. For example, after 7 days of storage, the electrode did not change its voltammetric characteristics (Fig. 4b) during potential cycling in 0.1 mol dm^{-3} KCl supporting electrolyte. On the whole the system was electrochemically well behaved and stable during prolonged potential cycling (at least 2 h) under the experimental conditions of Fig. 4. The fact that formal potentials of PB redox processes lied in the potential range where PEDOT is conductive [30], allowed the PB redox species to operate reversibly and reproducibly in the electrolyte containing potassium cation. We have also found from our preliminary potential step chronocoulometric experiments (involving potential steps from 0.5 to −0.25 V) that effective (apparent) diffusion coefficient, D_{eff}, characteristic of PEDOT over-coated PB/PPyBA film (Fig. 4b) is on the level $1 \cdot 10^{-8}$ cm^2 s^{-1}, i.e. it is somewhat higher than that obtained for the PEDOT-free PB/PPyBA film ($6 \cdot 10^{-9}$ cm^2 s^{-1}) of comparable loading (Fig. 4a). In the study, D_{eff}'s were estimated by usual means [37] using integrated Cottrell equation. In the above estimations, we have assumed the concentration of PB redox centers on the level 0.6 mol dm^{-3}. In spite of large uncertainties in the estimation of D_{eff}'s (e.g. due to existence of two types of redox active fragments in the PEDOT-over coated composite film), the above results are consistent with the view that ohmic limitations, which are typically complicating redox behavior of polymer-stabilized films on electrodes, are practically negligible in our composite structure. Furthermore, the composite film is expected to retain the PB's hydration sphere and to be porous and hydrophilic enough to permit the unimpeded flux of counterions (K^+).

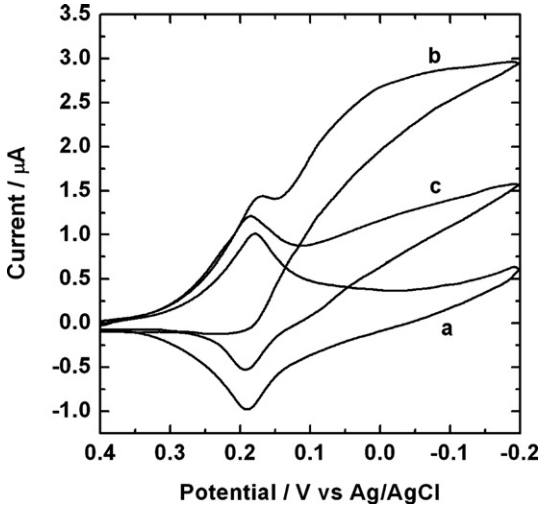

Fig. 5. Cyclic voltammograms of the HRP-covered PEDOT-containing PB/PPyBA films in the (a) absence and (b) presence of 0.1 mmol dm^{-3} hydrogen peroxide. Curve c refers to the electrocatalytic reduction of H_2O_2 at HRP-free PEDOT-containing PB/PPyBA film. Scan rate, 5 mV s^{-1}. Other conditions as for Fig. 2.

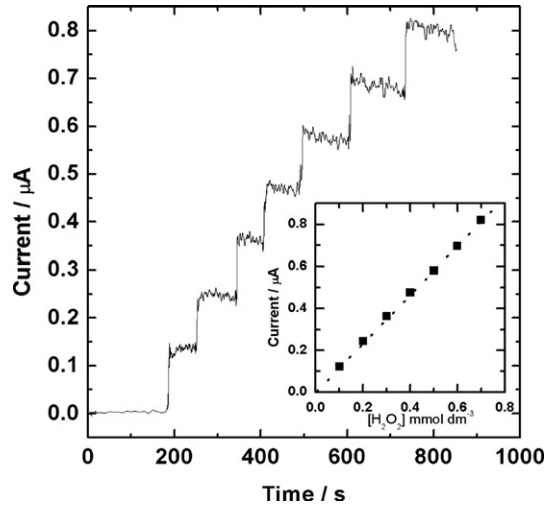

Fig. 6. Amperometric detection (at 0.2 V) of successive additions of hydrogen peroxide using the electrode modified as for Fig. 5. Each addition increased H_2O_2 concentration by 0.1 mmol dm^{-3}. Other conditions as for Fig. 2.

Provided that we were operating with stable, electroactive and porous hybrid organic–inorganic) film, immobilization of HRP was achieved by introducing its aqueous aliquot on the electrode surface. In order to make a clear distinction of the electrocatalytic response (H_2O_2 reduction) originating from the enzyme from the activity of PB, the concentration of HRP in the aliquot was fairly high, 4 mg/ml. Because the system containing HRP behaved virtually identical to that of Fig. 4b, for simplicity, no additional cyclic voltammogram is presented here. An important issue is that the presence of HRP did not affect mediating capabilities of the composite PEDOT-containing film. The systems voltammetric peak currents at about 0.2 V (characteristic of PB/Prussian White redox transition) were found to be proportional to scan rate up to at least 500 mV s^{-1}. Such dependence is consistent with the surface type behavior of PB redox centers and fast charge propagation within the film.

Fig. 5, curve a shows cyclic voltammogram of the PEDOT-containing PB/PPyBA film in H_2O_2-free solution after HRP has been introduced onto its surface. Curve b results when the electrode is subsequently transferred into H_2O_2-containing solution. The reduction of hydrogen peroxide now proceeds at potentials where HRP is catalytically active and PB is in the reduced form. For comparison, we provide the response to hydrogen peroxide of the PEDOT-containing PB/PPyBA modified electrode with no HRP immobilized on its surface (curve c). The results are consistent with the view that, while PB existing within hybrid organic–inorganic film shows some

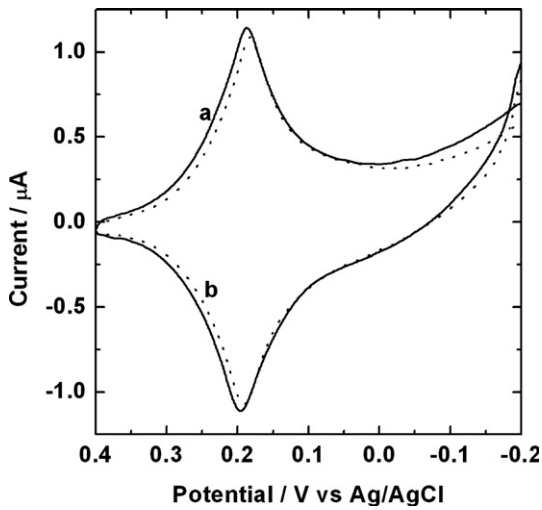

Fig. 7. Cyclic voltammetric responses of HRP-covered PEDOT-containing PB/PPyBA films (a) before and (b) after amperometric experiments with H_2O_2 of Fig. 6. Other conditions as for Fig. 5.

electrocatalytic properties, the high system's reactivity shall be mostly attributed to the presence of HRP.

The presence of HRP on surface of the electrode (modified with organic–inorganic film as for Fig. 5) was verified by performing the colorimetric enzyme assay [38]. Approximately 100 μl of the solution of syringaldazine (5 mg/ml) containing H_2O_2 (1 mmol dm^{-3}) was transferred onto the electrode surface. Contrary to the HRP-free system, introduction of HRP onto the PEDOT-containing PB/PPyBA led to the coloring of the solution mentioned above. The result provided evidence for the presence of active HRP on the surface.

Some applications, including electrochemical detection in a flow system, would require measurements to be done in the controlled potential electrolysis mode. Fig. 6 shows the amperometric responses recorded upon consecutive additions of hydrogen peroxide (in time). The modified electrode responded very rapidly and produced steady-state signal within less than 5 s. A working curve is presented in the inset. A 7-point linear least squares working curve over the investigated concentration range yielded the following: slope, 1.15 ± 0.01 μA dm^3 $mmol^{-1}$; correlation coefficient, 0.9998; current axis intercept, 12.2 ± 4.4 nA; standard error of current estimate, 5.2 nA; standard error of concentration estimate, $5 \cdot 10-^{-6}$ mol dm^{-3}. The detection limit, using the criterion of the concentration that yields a current of twice the uncertainty of the measurement on a blank solution, was $3 \cdot 10^{-5}$ mol dm^{-3}. The latter parameter was certainly not as low as one would like to have but it should be remembered that the system had not been optimized in terms of the film thickness and composition. The hybrid bioelectrocatalytic film was very stable, and there was no significant change in its catalytic activity during repetitive measurements over a period of at least a week (after which the modified surface was intentionally destroyed). High electrocatalytic activity of the enzyme-modified electrode was certainly facilitated by good mediating capabilities of the organic–inorganic film that contained N-coordinated iron(III,II) redox sites (in PB component) capable of fast electron transfers and the conducting polymer (PEDOT) intermediate layer.

The stability of hybrid biocatalytic film was diagnosed by executing comparative cyclic voltammetric measurements before and after the series of electrocatalytic reductions of hydrogen peroxide (performed as for Fig. 6). The fact, that the system's voltammetric currents did not decrease following long-term experimentation with H_2O_2 (Fig. 7), implies both physicochemical stability of the PEDOT-containing PB/PPyBA mediator film and permanence of the HRP immobilization on its surface.

4. Conclusions

We demonstrate here the possibility of preparation of robust three-dimensional PEDOT-containing PB/PPyBA composite (hybrid) films that are capable of fast delivery of charge to the three-dimensionally distributed PB redox centers. The attractiveness of the composite system concerns the fact that formal potential of PB redox processes lies in the potential range where PEDOT is conductive. Morphology of the hybrid film is fairly dense, and it does not resemble granular electrodeposited PB layers. Excellent stability of the hybrid organic–inorganic film may originate from the existence of electrostatic and chemical interactions between PEDOT, PB and PPyBA components. Another important issue is high electrocatalytic activity and permanence of attachment of the enzyme. Finally, the whole concept of fabrication of such hybrid bioelectrocatalytic films is of potential importance to the construction of electrodes for biosensors and biofuel cells.

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