

Electrochemical study of PEDOT-PSS-MDB-modified electrode and its electrocatalytic sensing of hydrogen peroxide

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Abstract A method to fabricate poly(3,4-ethylene dioxythiophene)-poly(4-styrene sulfonate)-Meldola Blue (PEDOT-PSS-MDB)-modified electrodes had been disclosed. Firstly, the PEDOT-PSS-film-modified electrode was electrochemically prepared. Then, the PEDOT-PSS was treated as a matrix to immobilize electroactive mediator, Meldola Blue (MDB), by means of an electrostatic interaction to form the proposed film, PEDOT-PSS-MDB. Electrochemical properties of the proposed film exhibited surface confinement and pH dependence. The PEDOT-PSS-MDB electrode could electrocatalytically reduce hydrogen peroxide (H_2O_2) with a low overpotential and showed a linear response to H_2O_2 in the concentration range of 5 to 120 μM , detection limit of 0.1 μM , and sensitivity of $353.9 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ($S/N=3$). By comparison, the electrocatalytic activity of PEDOT-PSS-MDB electrode was found superior to that of PEDOT-PSS and MDB-PSS electrodes. It also has competitive potential as compared with other mediators, through the use of HRP to determine H_2O_2 . Moreover, the potential interferents such as ascorbic acid, dopamine, uric acid, and glucose were also studied for H_2O_2 determination by the proposed film.

Keywords PEDOT-PSS electrode · Meldola blue · Hydrogen peroxide · Dopamine

Introduction

There has been a continuous motivation for fabrication of electrodes with high surface area because the larger the area of the electrode–electrolyte interface is, the larger will be the rate of the electrochemical process. Electrodes with increased roughness or porosity have been prepared for that purpose [1–5] and electrodes with structure elements down to the nanometer scale have been reported [4, 5]. Electropolymerization is a good approach to prepare polymer-modified electrodes (PMEs) for adjusting electrochemical parameters to control film thickness, permeation, and charge transport characteristics. PME has many advantages in the detection of analytes due to its selectivity, sensitivity, and homogeneity in electrochemical deposition, strong adherence to electrode surface, and chemical stability of the film [6–8]. Other advantages like high density of positive charge or electrocatalytic features of electropolymerized layers have also been noticed, such as electroanalysis of NADH using conducting and redox active polymer/carbon-nanotube-modified electrodes [9].

Conducting polymers (CPs) are easily synthesized and deposited onto the conductive surface of a given substrate from monomer solutions by electrochemical polymerization with precise electrochemical control of their formation rate and thickness. Coating electrodes with CPs under mild conditions opens up enormous possibilities for the immobilization of biomolecules and bioaffinity or biorecognizing reagents, the improvement of their electrocatalytic properties, rapid electron transfer, and direct communication to produce a range of analytical signals and new analytical applications. Coimmobilization of other molecules (enzymatic cofactors or charge-transfer mediators) by entrapment within electropolymerized films or by covalent binding on these films permits straightforward fabrication

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of reagentless biosensors. The characteristics of CPs and their uses, mainly in amperometric biosensors, have been reviewed [10].

Instantly, CPs are a natural choice for preparing arrays of voltammetric sensors because they have a rich electrochemical behavior and their electrochemical properties can be modulated by introducing chemical modifications in the sensitive materials [11, 12]. Recently, the recent advances in conducting polymer-based electrochemical sensors, including chemical sensors and biosensors have also been reviewed [13].

These polymers are generally permeable to small molecules [14]; this, in principle, should allow every volume element of the electrode material at the molecular level to be in contact with the electrolyte solution, resulting in an extremely high effective surface area. However, due to their low compatibility with the electrolyte phase, the separations of the polymer chains in conducting polymers are generally small relative to the double-layer thickness [15]. This increases the electrolyte resistance in the polymer matrix [14, 16] and lowers the effective double-layer surface area. Conducting polymers with higher compatibilities have been developed in the last few years by chemical modification of the polymer units, by use of appropriate dopant counterions, and/or by using other additives [17]. Stable dispersions and/or solutions of conducting polymers are widely available [17]. Employment of such conducting dispersions for fabrication of electrodes does improve the kinetics of the electrochemical process. Nevertheless, it is then limited by the diffusion of ions in the colloidal particles of the polymer [18].

Among conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT), a comparatively new conducting polymer, has been attracting growing interest due to its high compatibility with other polymers, very good film-forming properties, high stability, high charge mobility, low band gap, and high degree of doping [19–21]. The use of poly(4-styrene sulfonate) (PSS) enhances the solubility of 3,4-dioxyethylenethiophene (EDOT) in aqueous media since the solubility of EDOT itself in aqueous media is not adequate to form a film [15]. The polyelectrolyte complex of PEDOT and PSS, with an excess of the latter component, is produced and negatively charged, which stabilizes them in the aqueous media [22].

Meldola Blue (MDB) is one kind of quinoid dye. Among the options of mediators when designing NADH sensors, MDB is a well-studied and extensively used compound and is one of the suitable mediators for facilitating NADH oxidation [23]. This mediator allows us to achieve high sensitivity for the amperometric determination of NADH and to detect as low as 2×10^{-6} M with good selectivity [24]. In recent years, the number of reports concerning NADH sensor was continuously increasing, and

the MDB was often a preferred modifier when designing NADH detectors [23, 25–27]. Immobilization of MDB on $\text{SiO}_2/\text{Sb}_2\text{O}_3$ binary oxide matrix [25], zirconium phosphate (MDB-ZP-CPEs) [26], layered barium, and calcium phosphates [27] was reported for fabrication of NADH sensor, and their ability to oxidation of NADH has been investigated. However, it has never been studied for H_2O_2 determination by MDB composite due to its good electrocatalytic properties.

Since several techniques have been adopted for the accurate determination of hydrogen peroxide (H_2O_2) due to it being an essential mediator in food, pharmaceutical, clinical, and environmental analysis, many techniques including titrimetry [28], spectrometry [29], and chemiluminescence [30] have been employed in the determination of H_2O_2 . However, these techniques are obviously time consuming and expensive. Recently, more attention has been paid to the electrochemistry technique owing to its intrinsic sensitivity, high selectivity, and simplicity [31]. Electrochemistry technique based on a simple and low-cost enzyme electrode has been extensively employed for accurate determination of H_2O_2 due to the intrinsic selectivity and sensitivity of enzymatic reactions [32, 33]. Although a lot of materials have been used to immobilize enzyme on an electrode for retaining the enzymatic biologic activity and electrically connecting the enzyme with the electrode surface, it was ineluctable that these materials might block the electron transfer and biologic activity of the enzyme [34, 35].

Nowadays, there is considerable interest in the development of amperometric biosensors based on electropolymerized layers and active composites (enzymeless). As NADH oxidation by MDB has already been done, other electrocatalytic properties of MDB is attractive to discuss. In this work, it is the first time to report enzymeless H_2O_2 biosensor fabricated by PEDOT-PSS-MDB. We plan to fabricate an enzymeless H_2O_2 biosensor without using horseradish peroxidase (HRP). Herein, we report a study for PEDOT-PSS-MDB electrode as a novel electrocatalyst to electrocatalytically reduce H_2O_2 without HRP, and the interference was also investigated.

Experimental

Chemicals

EDOT, PSS, and MDB were purchased from Aldrich. All reagents were of analytical grade and used without any further purification. Solutions were prepared with doubly distilled deionized water (DDDW). High-purity nitrogen was used for deaeration. The buffer and sample solutions were purged with highly purified nitrogen for at least

10 min prior to the experiments. The pH conditions (from 1 to 9) were prepared by sulfuric acid, potassium hydrogen phthalate, phosphate buffer solution (PBS; K_2HPO_4 and KH_2PO_4), Tris(hydroxymethyl)aminomethane, and potassium hydroxide in DDDW. Nitrogen atmosphere was maintained over the solutions during the experiments to prevent the reentry of atmospheric oxygen.

Apparatus

Electrochemical experiments were performed with CH Instruments using CHI-750 potentiostat. Glassy carbon electrode (GCE; geometric area of 0.07 cm^2) obtained from BAS served as the working electrode. Pt wire was used as counter electrode, and Ag/AgCl with the saturated KCl solution was used as reference electrode. All the potentials given in this paper were referred from Ag/AgCl (saturated KCl solution).

Preparation of MDB, MDB-PSS, PEDOT-PSS, and PEDOT-PSS-MDB film-modified electrodes

Prior to modification, GCE was polished with $0.05\text{ }\mu\text{m}$ alumina on Buehler felt pads and then ultrasonically cleaned in water for 1 min. Finally, the electrode was washed thoroughly with doubly distilled deionized water (DDDW) to be used.

To form the MDB-modified electrode, the polished and cleaned GCE surface was dipped into 0.1 M PBS solution (pH 7) containing 1 mM MDB for 10 min. Hereafter, the electrode called as MDB/GCE-modified electrode was performed. The MDB composite electrode was thoroughly washed further with extrapure water and stored in PBS for further studies.

To form the MDB-PSS-modified electrode, the polished and cleaned GCE surface was first dipped into 0.1 M PBS solution (pH 7) containing 0.01 M PSS for 10 min and further transferred to PBS solution (pH 7) containing 1 mM MDB for 10 min. Hereafter, the electrode called as MDB-PSS/GCE modified electrode was performed. The MDB-PSS composite electrode was thoroughly washed further with extrapure water and stored in PBS for further studies.

To form the PEDOT-PSS-MDB-modified electrode, the polished GCE surface was subjected to electrochemical deposition of PEDOT film (three scan cycles within the potential range from -0.5 to 1.1 V) in 0.1 M $LiClO_4$ solution (pH 5) containing 0.01 M EDOT and 0.01 M PSS. This modified electrode was denoted as PEDOT-PSS/GCE electrode. Furthermore, the PEDOT-PSS electrode was dipped into PBS solution (pH 7) containing 1 mM MDB for 10 min. Hereafter, the electrode was called PEDOT-PSS-MDB/GCE electrode. The PEDOT-PSS-MDB composite electrode was thoroughly washed further with extrapure water and stored in PBS for further studies.

Results and discussion

Fabrication of MDB immobilized PEDOT-PSS-modified electrode

Figure 1 shows voltammograms of different kinds of MDB-modified electrodes with scan rate of 50 mVs^{-1} in PBS (pH 7). Figure 1 (a–c) shows the voltammograms representing PEDOT-PSS-MDB, MDB, and PSS-MDB-modified electrode, respectively. The cyclic voltammogram of PEDOT-PSS-MDB-modified electrode shows a pair of well-defined reversible redox peaks in the potential interest (Fig. 1, a), whereas MDB- and PSS-MDB-modified electrodes show ill-defined redox peaks (Fig. 1, b and c). On the other hand, MDB (Fig. 1, b) and PSS-MDB (Fig. 1, c) electrode do not show such reversible voltammetric response for MDB. As shown, the anodic and cathodic peaks are rather broad, and the magnitude of the peak current is significantly lower than that observed on the PEDOT-PSS-MDB electrode. The magnitude of the peak current of PEDOT-PSS-MDB electrode was 10 times higher than MDB- and PSS-MDB-modified electrodes, respectively. The peak current enhancements may be related to the electrostatic effect created by the considerable film charge density, leading to an effective accumulation of positively charged MDB in polyelectrolyte films. Furthermore, the ΔE_p value at the PSS-MDB- and MDB-modified electrodes is relatively large, suggesting sluggish electron transfer kinetics.

Electrochemical characteristics of PEDOT-PSS-MDB electrode

Figure 2 shows the cyclic voltammograms of the modified electrode at different scan rates in the potential

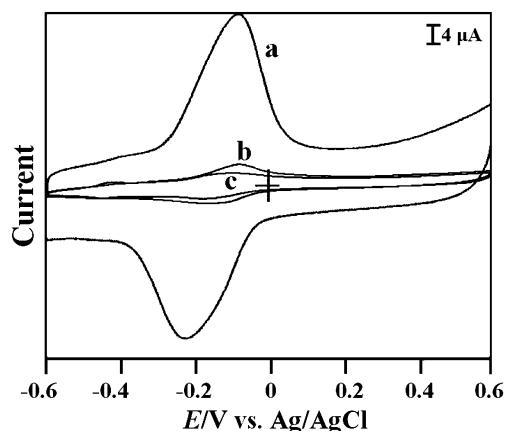


Fig. 1 Cyclic voltammograms of *a* PEDOT-PSS-MDB/GCE, *b* MDB/GCE, and *c* MDB-PSS/GCE in 0.1 M PBS solution (pH 7); scan rate: $\nu=50\text{ mVs}^{-1}$

range from -0.6 to 0.6 V in PBS solution (pH 7). The peak currents of redox couples are directly proportional to scan rates up to 500 mVs^{-1} (Fig. 2, inset A) as expected for surface-confined process. As can be seen in inset B of Fig. 2, the logarithmic regressing equation of anodic peak current and concentration can be expressed as $\log(I_{pa})(\mu\text{A}) = 0.8636\log(v)(\text{Vs}^{-1}) - 4.4818$, $R^2 = 0.9994$. Moreover, the ratio of oxidation-to-reduction peak currents is near unity and formal potentials did not change with increasing scan rate in this pH condition. This result reveals that the electron transfer kinetics is very fast on the electrode-modified surface.

We have estimated the apparent surface coverage (Γ) by using Eq. 1:

$$\Gamma = Q/nFA_c \quad (1)$$

Where Q is charged from the area under the PEDOT-PSS-MDB composite electrode oxidation peak corrected for the baseline (at the scan rate of 10 mVs^{-1}); A_c is the area of the electrode surface (0.07 cm^2); n is the number of electron transfer; F is Faraday constant ($96,485$ C/mol). In the present case, the calculated surface coverage (Γ) was 1×10^{-10} molcm^{-2} for assuming a two-electron process.

Figure 3 displays the pH-dependent voltammetric response of PEDOT-PSS-MDB composite electrode. In order to ascertain this, the voltammetric responses of PEDOT-PSS-MDB electrode were obtained in the solutions of different pH values varying from 1 to 9. As can be seen in Fig. 3, the formal potential ($E^{0'}$) of the redox couples were pH dependent, and it was negatively shifted by increasing pH value of the solution. The pH dependence suggests that the electroactive sites on the PEDOT-PSS-MDB composite electrode behave as true surface active groups influenced by specific solution

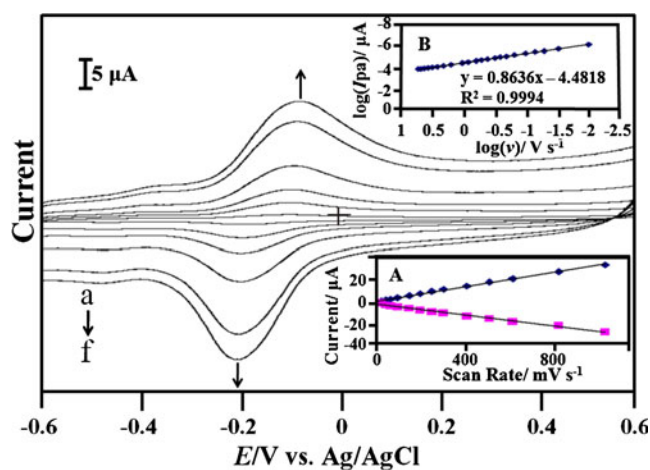


Fig. 2 Cyclic voltammograms of PEDOT-PSS-MDB/GCE in PBS solution (pH 7) with different scan rates (from inner to outer correspond to $v=(a)$ 10, (b) 50, (c) 100, (d) 200, (e) 400, and (f) 500 mVs^{-1}). Insets: a plot of $\text{Log}(v)$ versus $\text{Log}(I_{pa})$; b plot of current versus scan rate

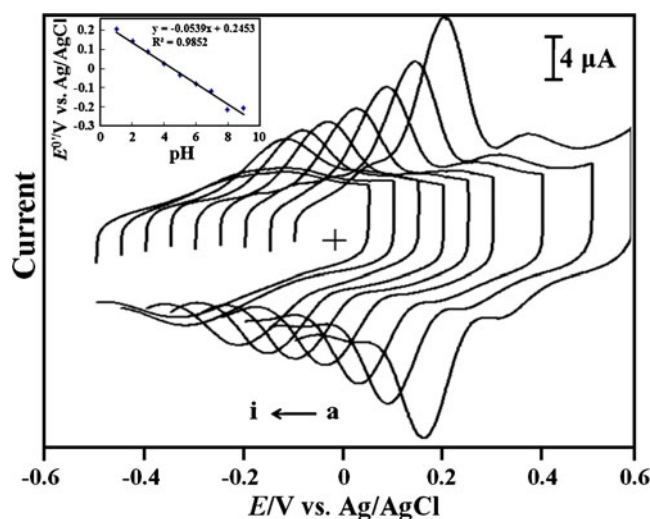
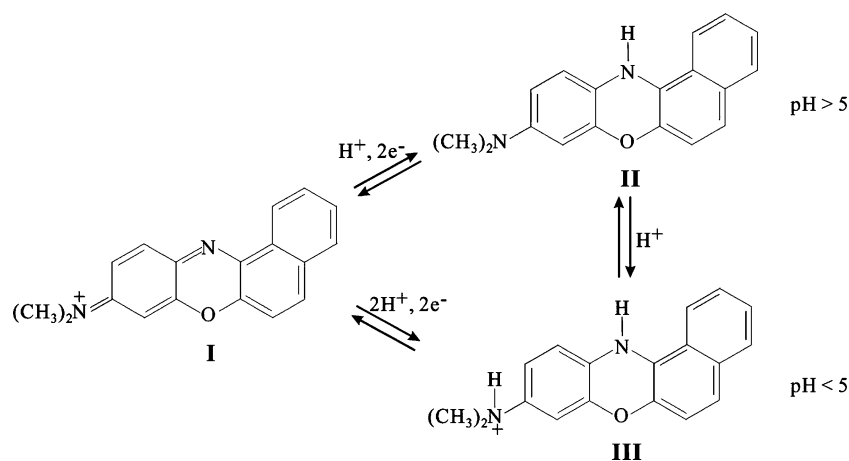


Fig. 3 Cyclic voltammograms of PEDOT-PSS-MDB/GCE tested in different pH solution including: a pH 1, b pH 2, c pH 3, d pH 4, e pH 5, f pH 6, g pH 7, h pH 8, and i pH 9, respectively. Scan rate: $v = 50$ mVs^{-1} ; slope = -0.0539

conditions and not shielded within the electrode interior. The plot of formal potential ($E^{0'}$) versus pH yields a straight line with a slope of about -54 mV per pH change in the solution as shown in the inset of Fig. 3, which was very close to the anticipated Nernstian value of -59 mV for processes in which equal numbers of electrons and protons were involved in the electrode reactions. As shown in Scheme 1, the structure of I and II represents the reduction and oxidation states of Meldola Blue in pH 7 solution. As the experimental result, the slope of -54 mV/pH close to Nernstian value (-59 mV/pH) implies two-electron/two-proton process. Further considering the previous reference [36], the structure of I and II represents the reduction and oxidation states of Meldola Blue in PBS solution (pH 7) as shown in Scheme 1. It involved the process of one-proton and two-electron transfer.

Electrocatalytic properties of PEDOT-PSS-MDB electrode towards the reduction of hydrogen peroxide

Electroanalytical application of the PEDOT-PSS-MDB composite electrode was studied for the analysis of H_2O_2 . The electrochemical responses to the reduction of H_2O_2 were shown in Fig. 4, where the current response was recorded by the PEDOT-PSS-MDB composite electrode in 0.1 MPBS solution (pH 7) in the (a) absence and presence of H_2O_2 : (b) 1×10^{-5} M, (c) 2×10^{-5} M, and (d) 3×10^{-5} M, respectively. The PEDOT-PSS-MDB modified electrode with an addition of H_2O_2 to PBS solution (pH 7), and change in the cyclic voltammogram occurs with an increase in cathodic current and a concomitant decrease in the anodic current. The catalytic reduction occurs at a much lesser potential of -0.16 V at the PEDOT-PSS-MDB

Scheme 1 Structural formula of Meldola Blue (MDB)

composite electrode. A significant improvement in the magnitude of the cathodic current at a lower potential reflects the high electrocatalytic activity of the PEDOT-PSS-MDB composite electrode. Besides, the electrocatalytic activity for H_2O_2 by MDB-PSS (curve e) and PEDOT-PSS (curve f) electrode was also shown by comparison (inset of Fig. 4). It confirms that PEDOT-PSS-MDB-modified electrode gave higher catalytic current than MDB-PSS or PEDOT-PSS electrode. The higher electrocatalytic current response for H_2O_2 by PEDOT-PSS-MDB-modified electrode might be due to the cooperation of PEDOT, and MDB lowers the activation of electrode surface and it gives larger surface area. After 10 repeated experiments, the lower overpotential of electrocatalytic reduction for H_2O_2 by PEDOT-PSS-MDB remains the same. Base on both positively charged PEDOT and MDB in the PEDOT-PSS-MDB film, this kind of lower potential shifting could be explained by rich positive charge of electrode surface lowering the activation energy of H_2O_2 .

Amperometric determination of H_2O_2 at PEDOT-PSS-MDB electrode

Quantitative determination of H_2O_2 was also carried out amperometrically in a stirred solution of PBS (pH 7) with sequential additions of H_2O_2 from 1 to 270 μM (electrode rotation rate of 400 rpm). Figure 5 depicts the typical amperometric response of the PEDOT-PSS-MDB electrode recorded at an applied potential of -0.15 V for successive addition of 1 mM H_2O_2 solution. A rapid and well-defined response was observed for each addition of H_2O_2 . The sensor responds quickly to the concentration of H_2O_2 , a response current being reached within less than 6 s. Under optimum conditions, the modified electrode showed a linear concentration range of 5 to 120 μM , detection limit of 0.1 μM , and sensitivity of $353.9 \mu\text{A mM}^{-1}\text{cm}^{-2}$ ($S/N=3$) for sensing H_2O_2 at the proposed composite electrode. As a result, the linearly regressing equation of peak current and concentration can be expressed

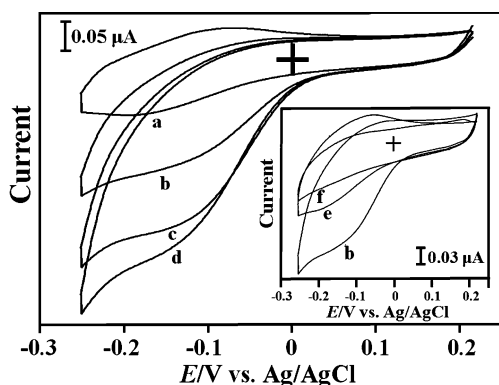


Fig. 4 Cyclic voltammograms of different H_2O_2 concentrations tested by PEDOT-PSS-MDB/GCE in PBS solution (pH 7) containing H_2O_2 of a 0 M, b 10^{-5} M, c 2×10^{-5} M, and d 3×10^{-5} M, respectively. Inset: cyclic voltammograms of 10^{-5} M H_2O_2 tested by b PEDOT-PSS-MDB/GCE, e MDB-PSS/GCE, and f PEDOT-PSS/GCE, respectively. Scan rate: $\nu=50 \text{ mV s}^{-1}$

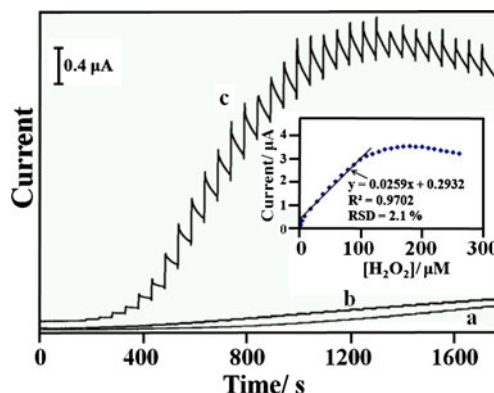


Fig. 5 Amperometric responses of a MDB/GCE, b PEDOT-PSS/GCE, and c PEDOT-PSS-MDB/GCE individually tested in PBS solution (pH 7) with the addition of 100 μL of 10^{-4} M H_2O_2 applied potential: $E_{\text{app}}=81\text{--}150$ mV, rotation rate of 400 rpm. Inset: plot of current versus H_2O_2 concentration by PEDOT-PSS-MDB/GCE. Linear concentration range of 5 – 120 μM

Table 1 Comparison of electrochemical sensing of H₂O₂ with various modifiers

Modifiers	Working potential (V) (vs. Ag/AgCl)	Linear range/ μM	LOD (μM)	Sensitivity ($\text{mAM}^{-1}\text{cm}^{-2}$)	Ref.
5,2':5,2'' -Terthiophene-3-carboxylic acid/HRP ^a	-0.2	300–1,500	200	6	[37]
PEDOT/PSS/HRP ^a	0.025	0–30	1	130	[38]
PANI/HRP ^a	-0.4	250–5,000	2.5×10^{-4}	1627	[39]
PANI/carbon nanotubes/HRP ^a	-0.1	0.2–19	1	130	[40]
2-Methoxyaniline-5-sulfonic acid/poly(L-lysine)/HRP ^a	-0.1	10–100	10	24.91	[41]
nanostructured Prussian Blue ^a	0.05	10^{-3} – 10^4	0.001	700	[42]
conventional (unstructured) Prussian Blue ^a	0.05	0.1–1000	0.001	500–700	[42]
Prussian Blue ^a	-0.05	0.1–100	0.10	600	[43]
Cerium oxide nanoparticles ^a	0.2	1–50	1	15	[44]
Polymer/Pt nanoparticle ^b	0.6	0.042–160	0.042	500	[45]
Pt nanowire ^a	0	100 – 6×10^4	0.050	540	[46]
CNT/nano-Pt ^b	0.55	0.025–2,000	0.025	3,886	[47]
Carbon film/nano-Pt ^b	0.6	0.5–2,000	7.5×10^{-3}	56	[48]
Ensembles of nano-Pt ^b	0.5	5×10^{-4} –4000	500	21	[49]
PEDOT-PSS-MDB ^a	-0.15	0.1–120	0.10	353.9	This work

^a Sensing of H₂O₂ by its reduction

^b Sensing of H₂O₂ by its oxidation

as $I_{pc}(\mu\text{A}) = 0.0259[\text{H}_2\text{O}_2](\mu\text{M}) + 0.2932$, $R^2=0.9702$. The relative standard deviation for determining H₂O₂ is 2.1%. It indicates that the sensor had very good reproducibility at pH 7. The results indicate that the modified electrode maintained a good sensitivity and had a stable amperometric response under hydrodynamic condition.

The main goal of this work is to perform an enzymeless H₂O₂ sensor. To understand the ability of PEDOT-PSS-MDB, some other methods including HRP-based [42–46] and HRP-less-based [47–49] modifiers for H₂O₂ determination are compared. In comparing detection potential, linear range, limit of detection (LOD), and sensitivity in Table 1, the proposed film (PEDOT-PSS-MDB) has competitive potential as compared with other HRP-based H₂O₂ sensors [42–46]. By further comparing the proposed film with other enzymeless H₂O₂ biosensor [47–49], PEDOT-PSS-MDB also has developed potential due to its fast detection result (because most of these H₂O₂ sensors are performed in flow injection

analysis (which is time consuming). Furthermore, it also can be envisaged that MDB might improve the electrocatalytic property for H₂O₂ by further considering the electrocatalytic result of PEDOT-PSS and PEDOT-PSS-MDB (in Fig. 4 of the “[Electrocatalytic properties of PEDOT-PSS-MDB electrode towards the reduction of hydrogen peroxide](#)”). The main goal of enzyme-less sensors is proceeded by PEDOT-PSS-MDB. It is worth mentioning that not using any enzyme

Table 2 H₂O₂ recoveries at various concentrations determined with the biosensor (PEDOT-PSS-MDB)

H ₂ O ₂ (μM)	[H ₂ O ₂] Found ^a (μM)	Recovery/%
1	1.01	101.0
1.5	1.48	98.7
2	1.98	99.0
2.5	2.47	98.8
5	4.90	98.0

^a Average of three measurements

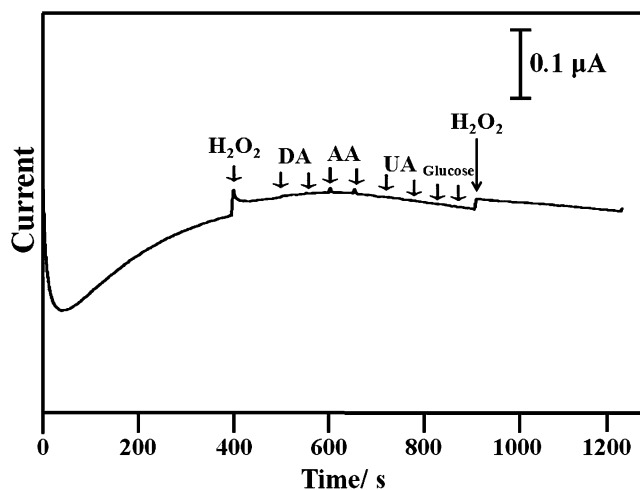


Fig. 6 Amperometric responses for interferences tested by PEDOT-PSS-MDB/GCE-modified electrode with 100 μL of various electroactive biomolecules additions of: 10^{-4} M H₂O₂ (at 400th s), 10^{-3} M DA (at 500th s and 550th s), 10^{-3} M AA (at 600th s and 650th s), 10^{-4} M UA (at 700th s and 750th s), 10^{-3} M glucose (at 800th s and 850th s), and 10^{-4} M H₂O₂ (at 900th s) applied potential, $E_{app}=-150$ mV, rotation rate of 400 rpm

(HRP) would be an extreme advantage which would make possible the manufacturing of H₂O₂ biosensors with low cost, easy fabrication, and wide storage condition.

Stability study of PEDOT-PSS-MDB film

Repetitive potential cycling experiments to test redox peaks intensity of the proposed film were performed to determine the extent of stability relevant to PEDOT-PSS-MDB-modified GCE in 0.1 MPBS solution (pH 7). This investigation indicated that the peak heights of the redox couple decreased less than 5% after 100 continuous scan cycles with scan rate of 100 mVs⁻¹. On the other hand, the PEDOT-PSS-MDB-modified GCE kept its initial activity for more than 1 month as kept in 0.1 MPBS solution (pH 7). A decrease of 5% was observed in the current response of the electrode at the end of 30th day. And the electrocatalytic response current of PEDOT-PSS-MDB for H₂O₂ can keep more than 90% of the original current response with a lifetime of 30 days at least.

The analytical applicability of the biosensor was evaluated by determining the recoveries of five H₂O₂ samples with different concentrations by the standard addition method. The results were satisfactory, with an average of 99.1%, as listed in Table 2.

Interferences study

In order to understand if other factors can affect the analytical estimation, we have finally studied the effect of the potential interferents such as dopamine, uric acid, and glucose in the determination of H₂O₂ with PEDOT-PSS-MDB-modified electrode. Figure 6 shows the typical amperometric responses of DA, UA, NADH, glucose, and ascorbic acid at -0.15 V in PBS solution (pH 7) under stirring condition. No evident oxidation current was observed upon the addition of DA, UA, AA, and glucose. However, if H₂O₂ was successively added to the electrolyte solution, an increase in current response was observed. Also, the magnitude of the currents was proportional to the concentration of AA. The main target of H₂O₂ determination to present no interference with interferents (AA, DA, UA, and glucose) can proceed although the background currents are not good. These observations also indicate that PEDOT-PSS-MDB-modified electrode could be used to design sensors for the selective detection and determination of H₂O₂ in the presence of interferents.

Conclusion

The PEDOT-PSS-MDB electrode had been successfully fabricated by electropolymerization of PEDOT-PSS and further immobilization of MDB by an electrostatic interac-

tion. Electrochemical properties of PEDOT-PSS-MDB-modified electrode exhibited surface confinement and pH dependence. The PEDOT-PSS-MDB-modified electrode could electrocatalytically reduce hydrogen peroxide (H₂O₂) and had lower overpotential and higher current response in the absence of HRP. In addition, electrocatalytic activity of PEDOT-PSS-MDB was superior to that of PEDOT-PSS and MDB-PSS for H₂O₂ detection. Particularly, the proposed film has competitive potential as compared with other HRP-based H₂O₂ sensors. Furthermore, the potential interferents such as ascorbic acid, dopamine, uric acid, and glucose were not found for H₂O₂ determination using PEDOT-PSS-MDB.

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