



Preparation of triaminotriazine-based polyimide-modified electrodes and their use for selective detection of catechin in green tea samples

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Received: 9 August 2019 / Revised: 8 October 2019 / Accepted: 23 October 2019
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Abstract

An effective electrochemical sensor was developed from triaminotriazine-based polyimide (PI) films as selective membrane for the detection of catechin (CT). Firstly, triaminotriazine-based PI films were synthesized from 2,4,6-triamino-1,3,5-triazine (TAT) and pyromellitic dianhydride by thermal imidization method with different monomer ratios. Structural and morphological of synthesized PI films were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, and atomic force microscopy. Prepared polyimide films were used as membrane for the preparation of the modified electrodes. Catechin (CT) selectivity behavior of polyimide-modified Pt electrodes was investigated by means of differential pulse voltammetry (DPV). DPV voltammograms showed that peak currents of the modified electrode increased proportionally with increase in CT concentration. TAT-PI-1/1 sensor showed high selectivity, a high regression coefficient (R value = 0.9982), good repeatability (RSD of 2.15%), and limit of detection 0.0152 mM for catechin determination in the presence of multiple interferent species (1 mM coumaric acid, ascorbic acid, gallic acid, lactose, sucrose, fructose, maltose and glucose). Moreover, the TAT-PI-1/1 sensor was employed to determine CT in real sample.

Keywords Triaminotriazine-based polyimide film · Catechin · Selective membrane · Sensor

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Introduction

Catechin (CT) is present in many dietary products, fruits (such as blueberries, apples, grape seeds, gooseberries, strawberries, kiwi), plants, green tea, beer, red wine, cocoa liquor, cocoa, and chocolates, as an important polyphenol [1]. CT is also an important antioxidant which was found in very abundance in the tea leaves [2]. Catechins, which are phenolic compounds, possess features that can be useful in treatment of health problems such as cardiovascular diseases, inflammations, diabetes, viral infections, osteoporosis, and degenerative and neurodegenerative diseases. These compounds, to decrease the risk of premature aging, protect the healthy cells and also prevent the growth of cancer cells [3–5]. In recent years, various methodologies such as the high-performance liquid chromatographic (HPLC) have been reported, and UV spectrophotometric [6], capillary electrophoresis [7], electrochemical [8–10], fluorescence [11, 12], ultraviolet [13], and chemiluminescence methods [14] were used for the determination of CT content in foods and drinks. However, these methods have disadvantages such as being time consuming, costly, and laborious. When compared to other methods, electrochemical techniques have more advantages than other techniques due to high sensitivity, fast response time, lower cost, low detection limit, and simplicity for the determination of phenolic and biological compounds [15–19]. However, the electrochemical analysis of CT on traditional electrodes usually suffers from electroactive and non-electroactive interferant species [20, 21].

Polyimides are a significant type of heterocyclic polymers [22, 23]. The polyimides exhibit separation properties, biocompatibility, lightweight, insulating properties, high corrosion resistance, dimensional stability, and fluorescence properties [24, 25]. In addition, it is known that polyimides have excellent mechanical, thermal and electrical stability, and remarkable chemical resistance [26–28]. The properties such as separation, biocompatibility, good adhesion, and chemical stability of polyimides allow them to be used in sensor technology as a membrane [25, 29–31]. Due to the interesting features of polyimides as compared to other polymers, polyimide-modified electrodes are widely employed for determination of various biological compounds such as dopamine [32], uric acid [33], caffeic acid [34], hydrogen peroxide [35], glucose [36], and epinephrine [37].

In this paper, five kinds of triaminotriazine-based polyimides were synthesized from 2,4,6-triamino-1,3,5-triazine (TAT) and pyromellitic dianhydride (PMDA) with different molar ratios by two-step polycondensation method. The prepared triaminotriazine-based selective films were used for the preparation of modified electrodes by drop-casting the polyimide solution onto the surface of bare platinum electrodes. These modified electrodes were used for the detection of electroactive catechin in the presence of electroactive and non-electroactive interferences. The voltammetric behavior of CT on polyimide-modified electrodes was investigated by DPV technique in phosphate buffer pH 7 as the supporting electrolyte.

Experimental part

Materials

Pyromellitic dianhydride (PMDA) was obtained from Sigma-Aldrich. 2,4,6-Triamino-1,3,5-triazine (TAT) as a monomer was purchased from the Acros Organics Company. The *N*-methyl-2-pyrrolidone (NMP-99.5%) used as solvent during the synthesis was purchased from Merck Chemical. For voltammetric measurement, catechin (CT), *p*-coumaric acid (CU), ascorbic acid (AA), gallic acid (GA), lactose (LC), sucrose (SR), fructose (FR), maltose (ML), and glucose (GL) were the analytical grade and were obtained from Sigma-Aldrich Chemical Company.

Instrumentation

The structural and chemical characterization of the polyimides to be used in the modification of Pt electrodes was performed by Fourier transform infrared spectroscopy (FTIR) (Mattson 1000). FTIR spectra are recorded between 400 and 4000 cm^{-1} using KBr pellets. In sensor studies, electrode surface morphology was measured at 20 kV with SEM (Leo-Evo 40xVP) device as it directly affected the measurement accuracy of the sensors. For the SEM measurement, these polyimide films were coated in a spray coating (Bal-Tec SCB 050) with a layer of gold–palladium of 100 Å thickness. The PI film thickness formed on the electrode surface was also determined by SEM measurements. Surface morphology was also determined in the noncontact mode with the atomic force microscopy (AFM, XE-100E; Park Systems Corp.) device. All electrochemical tests (DPV measurements) were carried out in phosphate buffer solution (0.1 M PBS, pH 7) using BAS (Bioanalytical Systems, Inc.) 100BW electrochemical analyzer. Hanna HI 8314 pH meter was used for pH measurement of solutions. As auxiliary electrode, platinum wire electrode (MW-1032), Ag/AgCl (BASI RE-5B) electrode in 3 M KCl as reference electrode, bare platinum electrode (CHI102) as the working electrode, and Pt electrodes modified with different polyimide were used during the study. Water contact angle measurement of the prepared polyimide films was performed using sessile drop technique with SEO – Phoenix 300 Touch Automatic Contact Angle Analyzer.

Synthesis of polyimides

For polyimide synthesis, 2,4,6-triamino-1,3,5-triazine (TAT) (5 mmol) was dissolved in 10 mL of NMP under the nitrogen gas atmosphere. Pyromellitic dianhydride (5 mmol) was dissolved in 10 mL of NMP and added to TAT solution by stirring under nitrogen atmosphere. The mixture was stirred at 30 °C for 60 min with a magnetic stirrer to give a solution of polyamic acid. Then the temperature was increased to 150 °C, and the reaction mixture was refluxed for 20 h to remove the solvent and thermal imidization. Polyimide was formed by thermal imidization of polyamic acid. The resulting product was precipitated by adding water, filtered, and

dried in a vacuum oven at 80 °C (yield approximately 89%). The synthesized polyimide solutions were used at chemical modification of bare platinum electrodes for preparation of the CT selective modified electrodes (Fig. 1).

The preparation procedure of polyimide-modified electrodes

Prior to chemical modification of electrodes, the surface of the bare platinum electrodes was carefully polished by successively finer grades of diamond polishing compounds and alumina water slurry down to 0.5 μm . The electrodes were then washed thoroughly by doubly distilled water [38]. The triaminotriazine-based modified electrodes were prepared as follows. Firstly, solutions of triaminotriazine-based polyimide were prepared by dissolving approximately 0.1 g of polyimides in 1 mL NMP. Then, the triaminotriazine-based polyimide suspension (0.5, 1, 2 μL) was drop-casted onto the polished bare platinum working electrodes for the preparation of the modified electrodes and finally dried at room temperature (for least 48 h).

Results and discussion

Five types of hyperbranched polyimide structures with different end groups were synthesized with different molar by using PMDA and TAT monomers. The resulting different structure polyimides were used in Pt electrode modification. In this study, 1/1, 1/2, 1/3, 3/1, and 2/1 mol ratios as TAT/PMDA were preferred in the scope of the study. Because of different molar ratios, amine and anhydride functional end groups on the polymer surface increase significantly [39]. These functional groups on the electrode surface increase the cumulation of the catechin molecule having

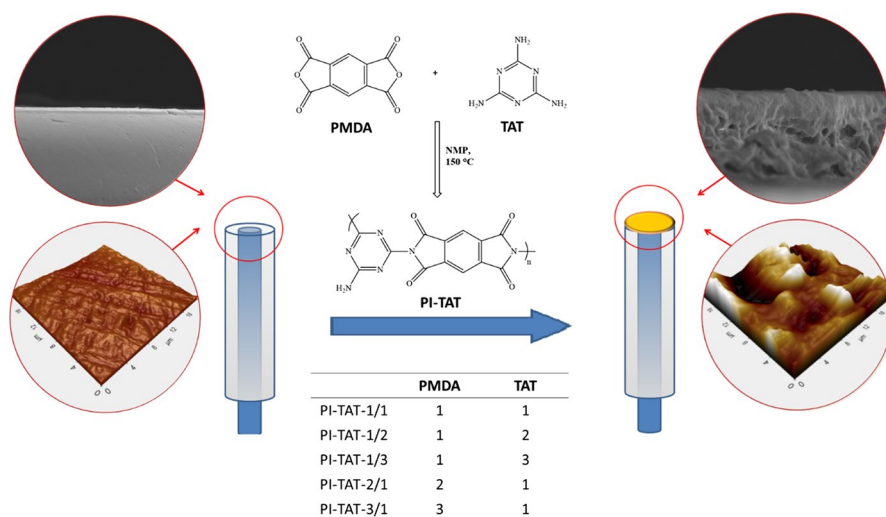


Fig. 1 Synthesis of the polyimides and preparation of the TAT-based polyimide-modified electrode

a polar character. Structural and morphological properties of synthesized PI films were investigated by FTIR, SEM, AFM, and contact angle measurements. Catechin selectivity behavior of polyimide-modified Pt electrodes was also determined by differential pulse voltammetry (DPV) technique.

Characterization of polyimide structure

For the determination of catechin, high cross-linked TAT-based PI structures were preferred. In particular, it is aimed to change the pore size and distribution of the selective membrane to be obtained on the electrode surface by varying the ratios of TAT and PMDA. For this purpose, it was studied with TAT/PMDA molar ratios of 1:1, 1:2, 1:3, 2:1, and 3:1. FTIR spectra of PI structures were used with these ratios which are given in Fig. 2. When these spectra are examined, the basic imidization peaks in all PI structures are clearly seen. For example, asymmetric imide stretching band at 1780 cm^{-1} , symmetric imidation band at

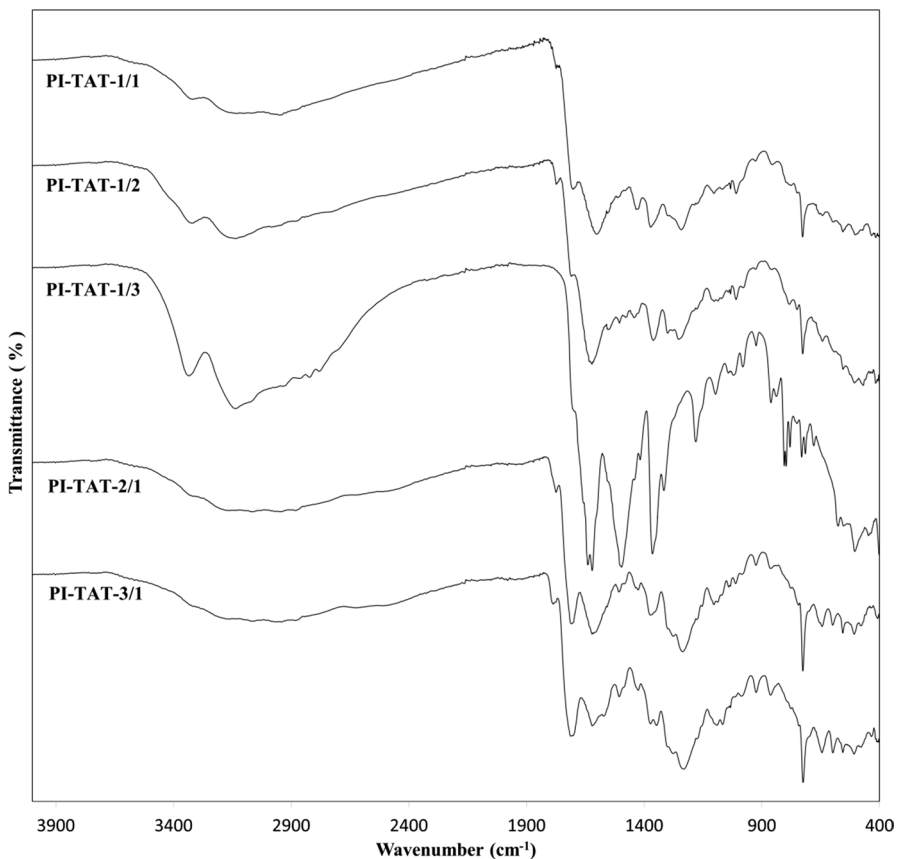


Fig. 2 FTIR spectrum of the polyimides in different TAT/PMDA ratios

1720 cm^{-1} , the C–N stretching band at 1381 cm^{-1} and the imide ring deformation peak at 725 cm^{-1} are seen. In addition, C–H stretching band in the aromatic ring at 825 cm^{-1} is also present in Fig. 2. C–N–C stretching band at 1440 cm^{-1} of triazine ring confirms the structure. These peaks show that polyimide is present in the structure.

The surface properties of these structures were studied using SEM (Figs. 3, 4) analysis. Figure 3 presents SEM photographs of the bare electrode. Figure 4 also shows SEM images of TAT-based polyimide surfaces at a magnification of 5000 $\times$. Polyimide films with different properties and morphology can be obtained by polymerizing TAT and PMDA at different molar ratios. The SEM images in Fig. 4 show that the morphology of the polyimide films has changed. While PI-TAT-1/1 showed a homogeneous structure, PI-TAT-1/3 and PI-TAT-2/1 showed a fractal structure. The change in mole ratios not only changes the surface morphology but also the hydrophilicity of the surface. To determine the change in surface hydrophilicity of polyimide films, contact angle measurements were performed by sessile drop technique. Measurements were performed in four replicates at room temperature. The obtained standard deviation results are given in the graph in Fig. 5. In addition, images of the highest contact angle measurement results for polyimides are given in Fig. 5. When different ratios of TAT and PMDA are used, amine or anhydride functional groups increase significantly on the polyimide surface.

In SEM analysis, suitable film character and morphology were observed in PI-TAT-1/1. In addition, the contact angle measurement results in Fig. 5 support this result.

The surface areas and surface roughness of the modified electrodes have grown compared to the bare electrode. This change increases the sensitivity of the electrodes. In Fig. 6, this change is given by AFM images. AFM images of the bare (a, b, c) and the PI-TAT-1/1-modified Pt (d, e, f) electrode structure show that the surface roughness increases with modification. Figure 7 shows SEM photographs of the film thickness of the PI-TAT-1/1-modified electrode compared to the bare electrode. The film thickness of the PI-TAT-1/1-modified electrode was determined as 64.39 μm .

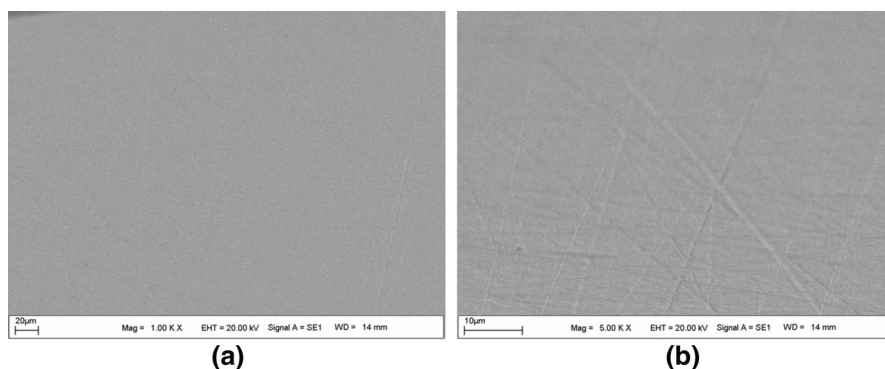


Fig. 3 SEM photographs of the bare electrode (**a** $\times 1000\times$ and **b** $\times 5000\times$)

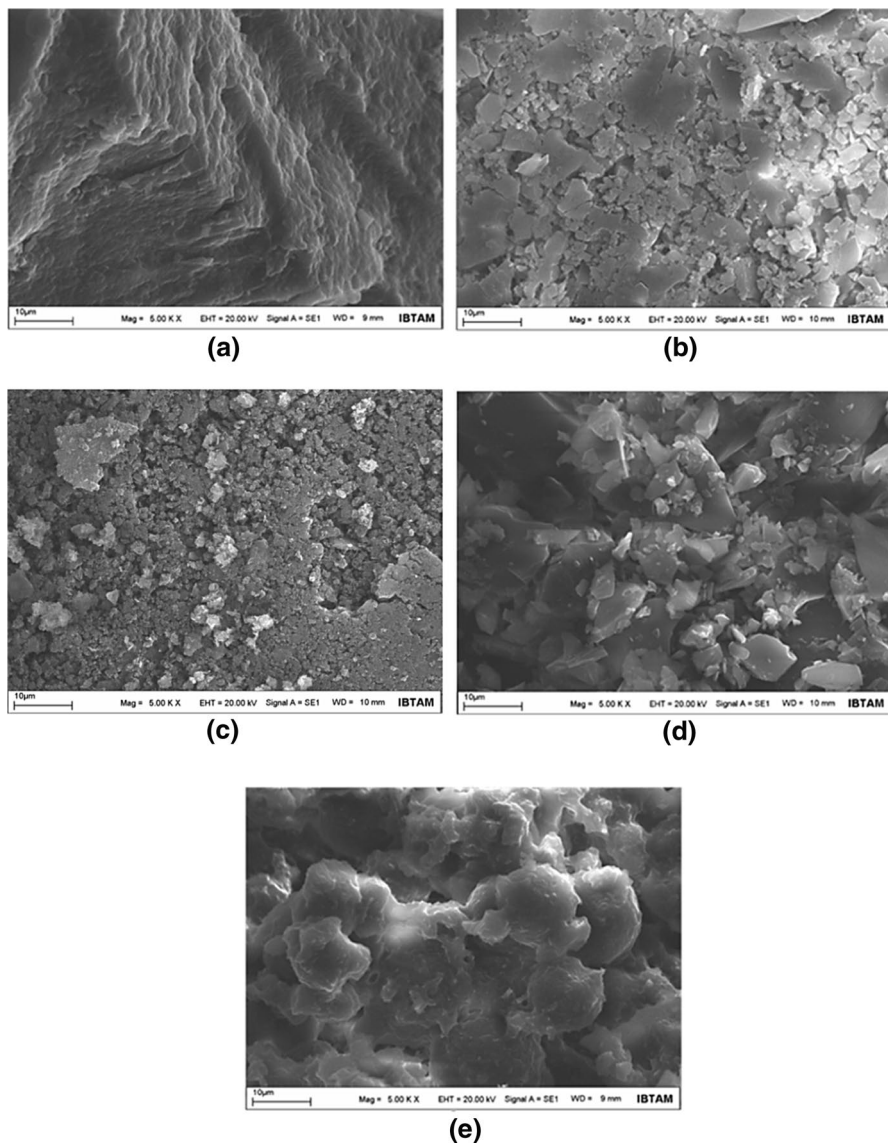


Fig. 4 SEM photographs of the TAT-based polyimide surfaces at a magnification of $\times 5000$. (**a** PI-TAT-1/1, **b** PI-TAT-1/2, **c** PI-TAT-1/3, **d** PI-TAT-2/1 and **e** PI-TAT-3/1)

Electrochemical catechin measurements with the modified electrodes

The CV technique is less sensitive than the DPV technique for detection of electro-active molecules because of the background current that can unclear the Faradaic current of the attached (related) redox species [40]. Therefore, in order to investigate the voltammetric behavior of CT, the DPV technique was used as a more sensitive

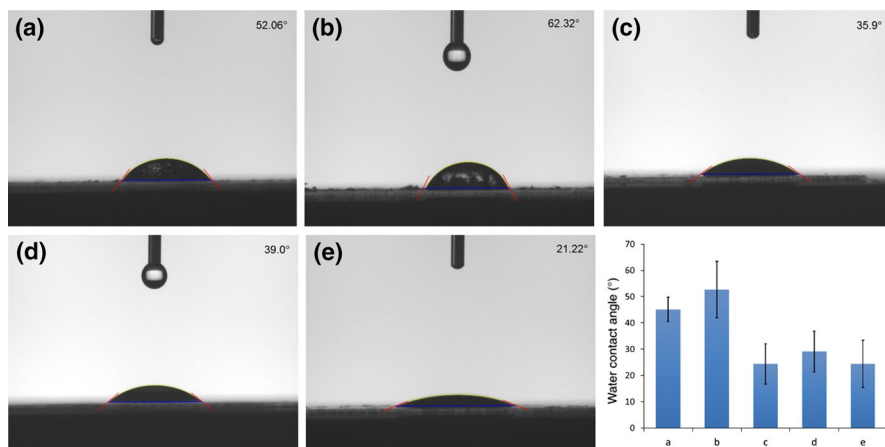


Fig. 5 Contact angle images and contact angle values of the polyimide membranes with different TAT/PMDA ratios. (a) PI-TAT-1/1, b PI-TAT-1/2, c PI-TAT-1/3, d PI-TAT-2/1, and e PI-TAT-3/1)

a method for the electrochemical experiments. Figure 8 shows the voltammetric behaviors of 2 mM CT, 2 mM AA, 2 mM GA, and 2 mM CU at 0.1 M PBS (pH 7.0) at the bare electrodes. A clear and significant peak potential of CT was determined as +0.13 V.

In order to determine the polyimide type, the electrochemical behaviors toward 2 mM CU, 2 mM CT, 2 mM AA, and 2 mM GA of five different polyimide films were investigated at a scan rate of 100 mV/s in 0.1 M PBS as the supporting electrolyte. Figure 9 shows the DPV results toward 2 mM CU, 2 mM CT, 2 mM AA, and 2 mM GA of five different polyimide electrodes. From these electrochemical results, it is seen that the TAT-based PI electrodes modified with 1 μ L PI-1 allowed CT oxidation while eliminating unwanted responses from GA, CU, and AA interferences. Considering the situation of the interferant species and related peak intensities, it has been determined that the most ideal polyimide type is TAT-PI-1/1 structure. In other polymers excluding TAT-PI-1/1 polymer, it is seen that there are GA and AA responses that can perform very high peak interference. Therefore, TAT-PI-1/1 polyimide was preferred as the optimum polymer type for further studies (Fig. 10).

For the purpose of investigating the film thickness effect on the responses of PI-TAT-1/1 polyimide, three different film thicknesses were examined. The voltammetric responses to CT of the electrodes chemically modified by dropping 0.5 μ L, 1 μ L, and 2 μ L of polymer solutions on the bare platinum electrode surface are displayed in Fig. 8. From Fig. 11, it is easily seen that the electrochemical response toward CT of the modified polyimide electrode by 2 μ L PI-TAT-1/1 suspension was higher than other polyimide electrodes. Based on these results, the optimum film thickness of chemically modified electrodes was chosen as 2 μ L PI-TAT-1/1 solution for advanced CT sensor applications.

Under optimized conditions, the DPV curves of TAT-PI-1/1 electrode in various CT concentrations were also recorded in the presence of electroactive (CU, GA, and AA) and non-electroactive interferences (LC, SR, FR, ML, and GL).

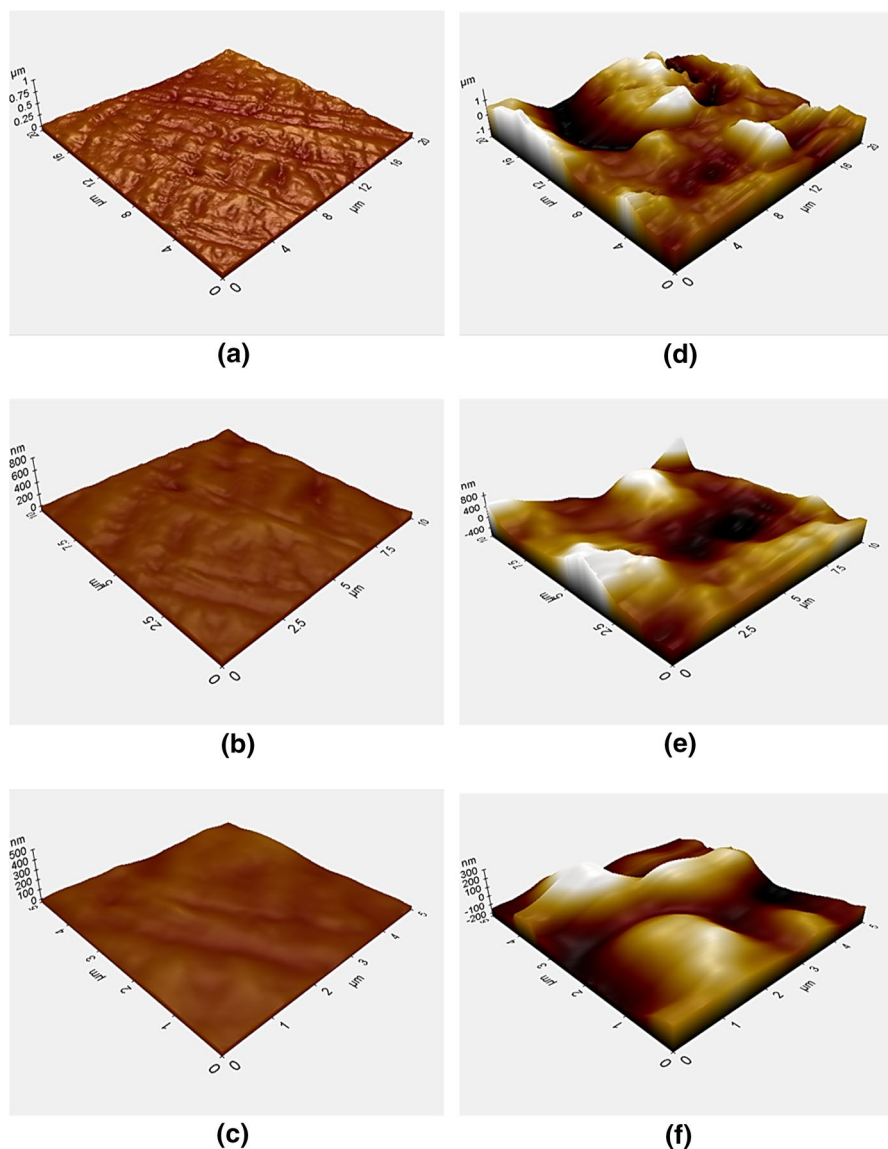


Fig. 6 AFM photographs of the bare (a, b, c) and the PI-TAT-1/1-modified Pt (d, e, f) electrode structure

The optimized electrode showed excellent electrocatalytic activity for the oxidation of CT. DPV voltammograms of the optimized TAT-PI-1/1 sensor is given in Fig. 12. Experiments performed with the TAT-PI-1/1 sensor in 0.1 M PBS at pH 7.0, displayed that increasing the CT concentration in the range of 0.5–5 mM resulted in an increase in the peak current intensity. Consequently, it was demonstrated that the oxidation peak currents of TAT-PI-1/1 sensor increased proportionally with increase in CT concentration, even in the presence of multiple

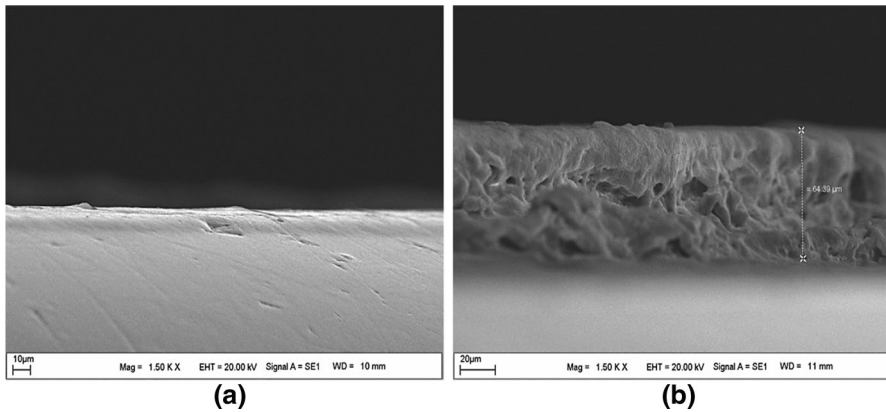


Fig. 7 SEM photographs of the bare (a) and Pt-modified PI-TAT-1/1 (b) electrode structure for investigation of film thickness

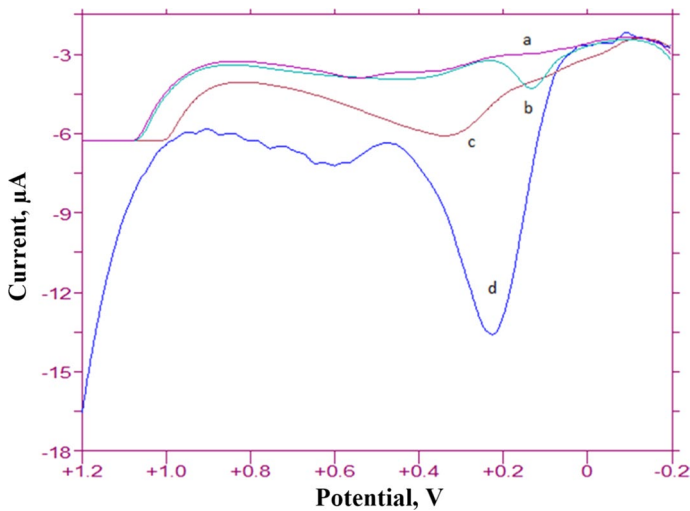


Fig. 8 Bare electrode responses in PBS at pH 7.0. (a: CU, b: CT, c: AA, d: GA)

interference. On plotting the oxidation peak current versus different CT concentration, the corresponding calibration curve was obtained (Fig. 13). As it could be clearly seen from the DPV results of the optimized TAT-PI-1/1 sensor, the oxidation peak currents were proportionally dependent on the CT concentrations in the range from 0.05 to 0.35 mM with a regression coefficient of 0.9982 and in the range from 0.5 to 5 mM with a regression coefficient of 0.9968. The TAT-PI-1/1 sensor showed limit of detection 0.33 mM for the determination of CT in the presence of 2 mM multiple interferent species.

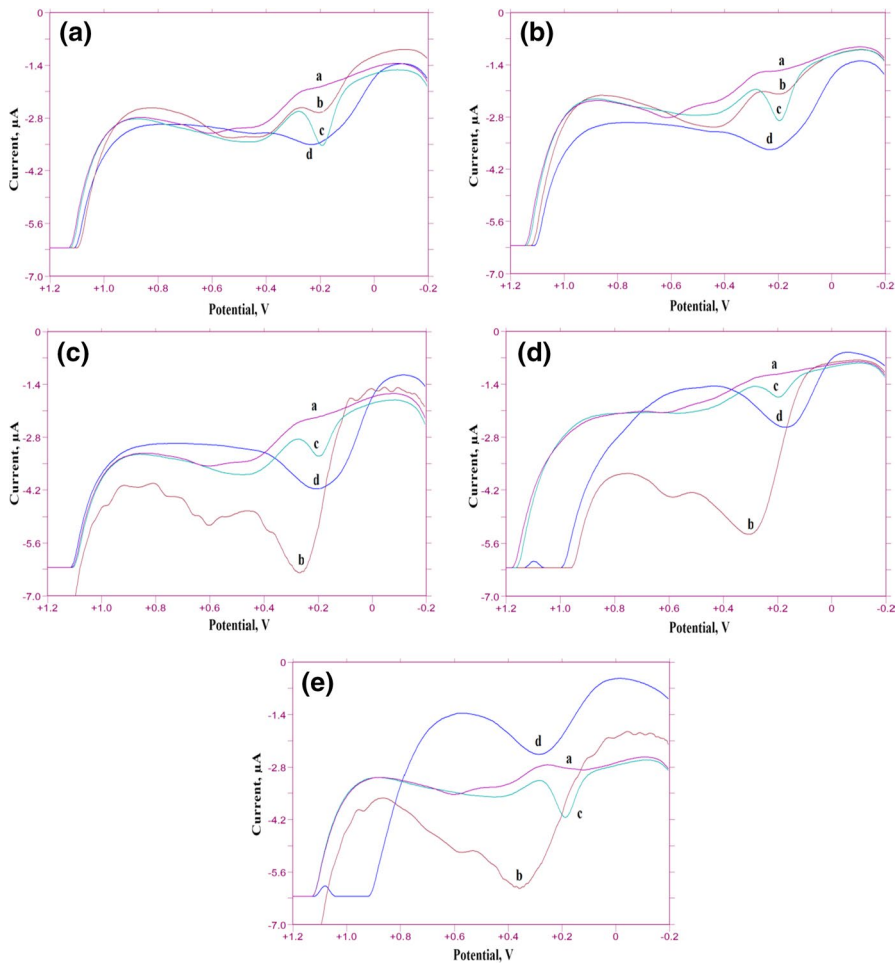


Fig. 9 DPV results obtained from TAT-based PI-modified electrodes with 1 μ L of PI-1 for 2 mM CU (a), 2 mM GA (b), 2 mM CT (c) and 2 mM AA (d) in PBS at pH 7.0. (a PI-TAT-1/1, b PI-TAT-1/2, c PI-TAT-1/3, d PI-TAT-2/1, e PI-TAT-3/1)

Electrochemical repeatability of optimized TAT-PI-1/1 sensor

Using optimized conditions, the repeatability of TAT-PI-1/1 sensor for six replicates was also examined for 2 mM CT in the presence of the multiple interferences (GA, AA, CU, LAC, FRU, and GLU). Figure 14 shows DPV curves recorded on the TAT-PI-1/1 sensor in the presence of the multiple interferences. As it could be easily seen from Fig. 14, quite similar peak currents (98% stable) were obtained for 2 mM CT at optimized TAT-PI-1/1 electrode. The relative standard deviation (RSD) was 2.15% for twelve replicates determination of CT in the presence of mentioned interferent species.

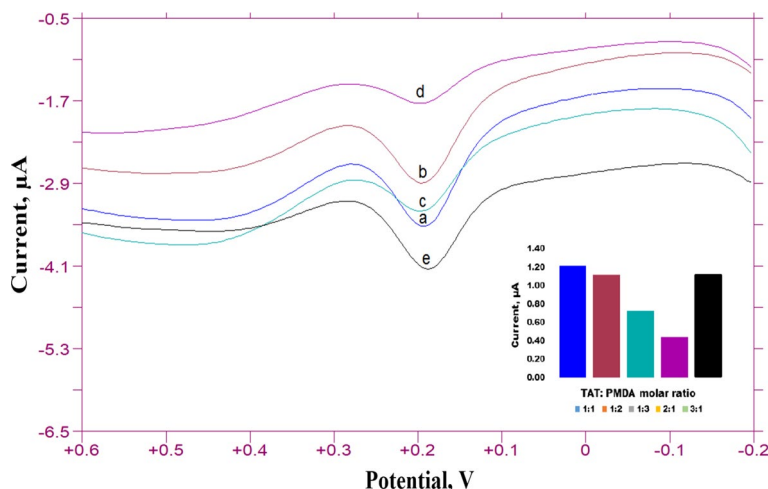


Fig. 10 DPV results obtained from TAT-based PI-modified electrodes with 1 μ L of PI-1 for 2 mM CT

The determination of CT in real sample

The TAT-PI-1/1 electrode successfully also was employed to determine CT in real sample such as green tea. The method of standard addition was used for the determination of CT concentration in green tea. Four grams of three parallel green tea samples was weighed. 40 mL of PBS (pH 7.0) at boiling temperature was added and infused for 2 h at room temperature. This mixture was filtered and completed with 40 mL PBS. Four milliliters of PBS was added to 1 mL of mentioned the solution. Five milliliters of prepared test solution was transferred in the electrochemical glass cell, and the CT content was measured. Then, 0.5 mM CT standard was added in the glass cell including 5 mL test solution. DPV curves toward CT of TAT-based PI-1/1 sensor were examined (Fig. 15). From Fig. 12, the average concentration of CT in green tea was detected as 2.10 mM. Using this value, the amount of catechin in green tea was calculated as $0.609 \pm 0.078\%$. These results indicate that it is practicable to apply the TAT-PI-1/1 sensor for the determination of CT in green tea sample.

The comparison of the properties of this sensor that was developed in presented work with those mentioned in the literature is shown in Table 1. When Table 1 is examined, it can be stated that analytical parameters of the developed sensor are compatible with the data reported in the literature. Consequently, the practically analytical application of proposed sensor was demonstrated by using green tea samples.

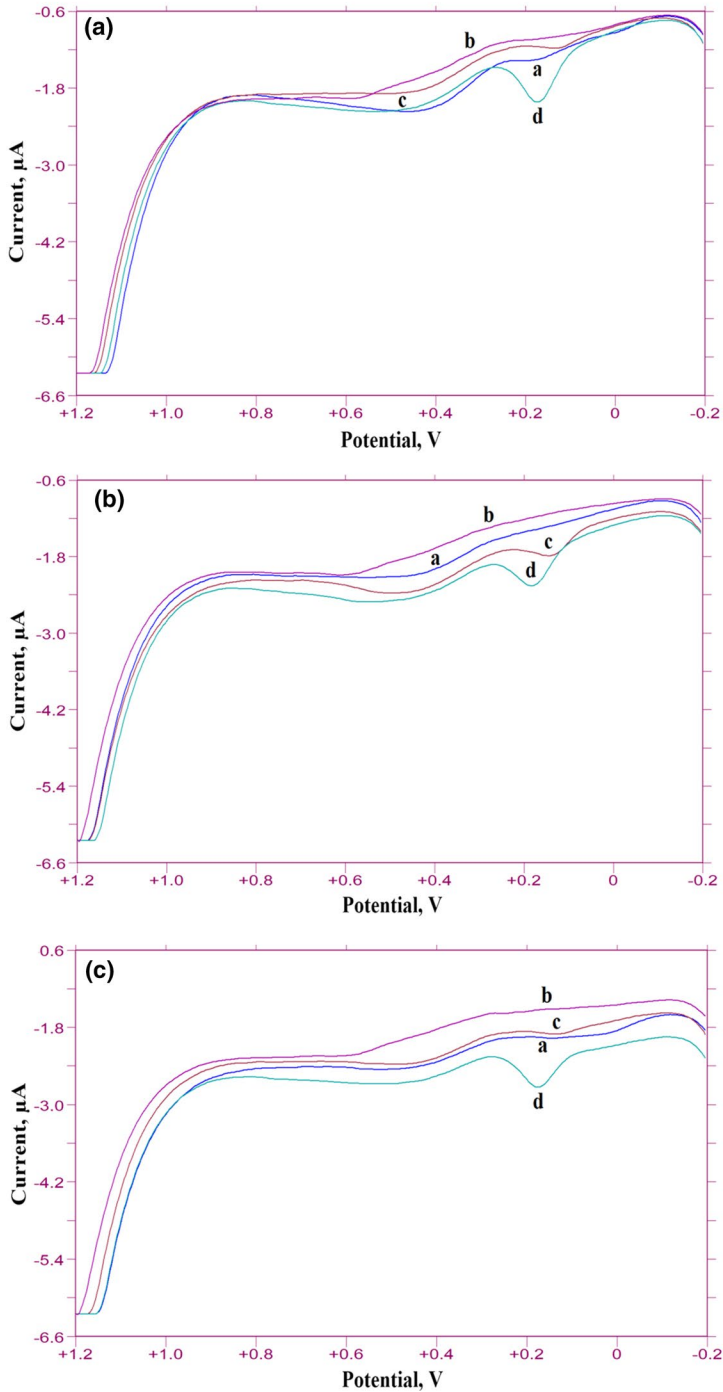


Fig. 11 Effect of film thickness on CT responses of electrode modified with TAT-PI-1/1 (2 mM AA (a), 2 mM CU (b), 2 mM GA (c), and 2 mM CT (d) solutions) (a 0.5 μ L, b 1 μ L, c 2 μ L TAT-PI-1/1)

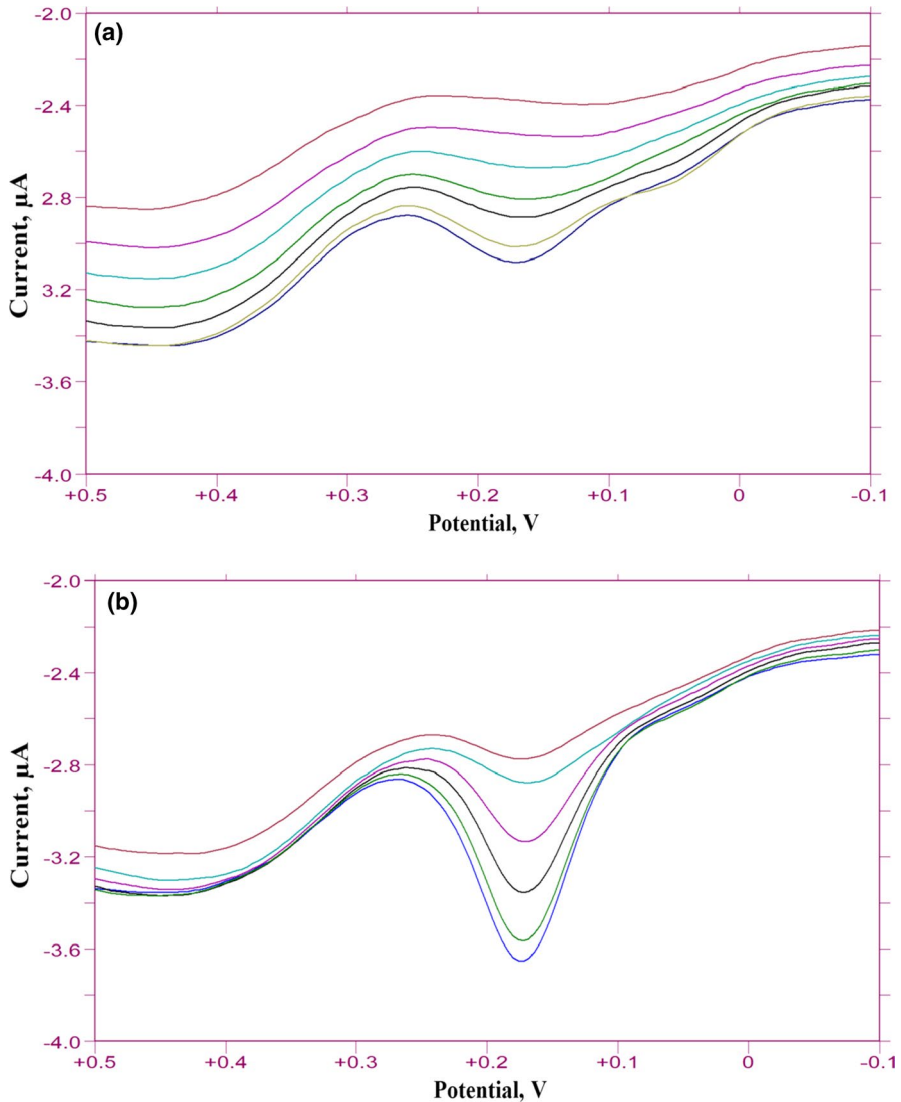


Fig. 12 DPV responses obtained from the PI-TAT-1/1 sensor to the increased concentrations of CT in the presence of the multiple interferences. CT concentration **a** 0.05 mM, 0.10 mM, 0.15 mM, 0.20 mM, 0.25 mM, 0.30 mM, 0.35 mM; CT concentration **b** 0.5 mM, 1.00 mM, 2.00 mM, 3.00 mM, 4.00 mM, 5.00 mM; (interferences: CU, GA, AA, LC, SR, FR, ML, GL each having a concentration 2 mM)

Conclusion

In this study, TAT-based polyimide structures were synthesized by polycondensation and thermal imidization methods. The chemical structure and morphology of these TAT-PI structures were characterized by FTIR, SEM, and AFM. The polyimide-modified electrodes were prepared by drop casting of obtained

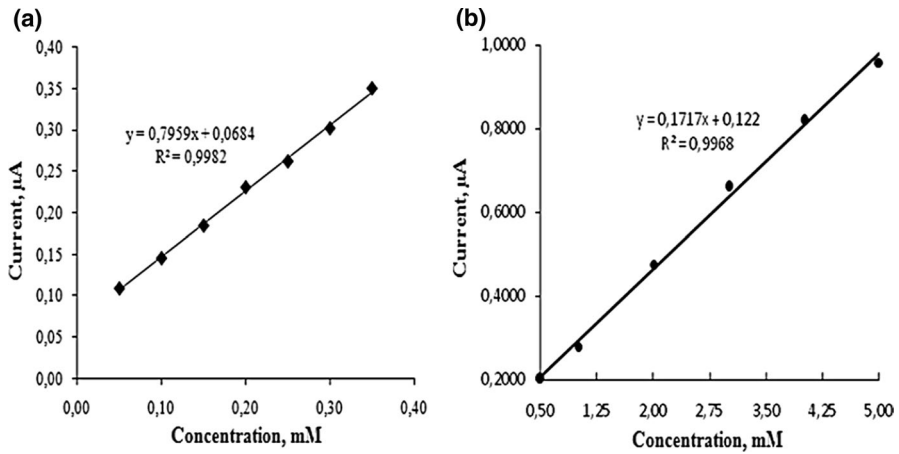


Fig. 13 Calibration curve of optimized TAT-PI-1/1 sensor for CT response

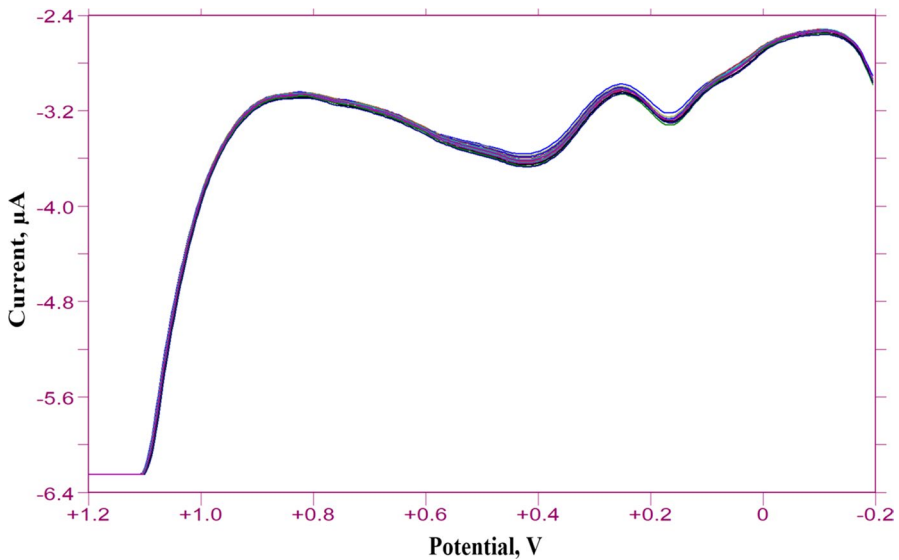


Fig. 14 Electrochemical repeatability of optimized TAT-PI-1/1 sensor for the 2 mM CT in the presence of interferences (interferences: CU, GA, AA, LC, SR, FR, ML, GL each having a concentration 1 mM)

TAT-based polyimide solutions on the bare platinum electrode surface. Moreover, the work also investigated whether these TAT-PI films could be used as selective membranes for CT detection in the presence of multiple interference species. The TAT-PI-1/1-modified electrode absolutely eliminated the unwanted responses from GA, CU, and AA. The TAT-PI-1/1 polyimide electrode was also applied for the CT detection in real sample such as green tea. The DPV results displayed that the developed sensor had selectivity, easy preparation, low detection limit

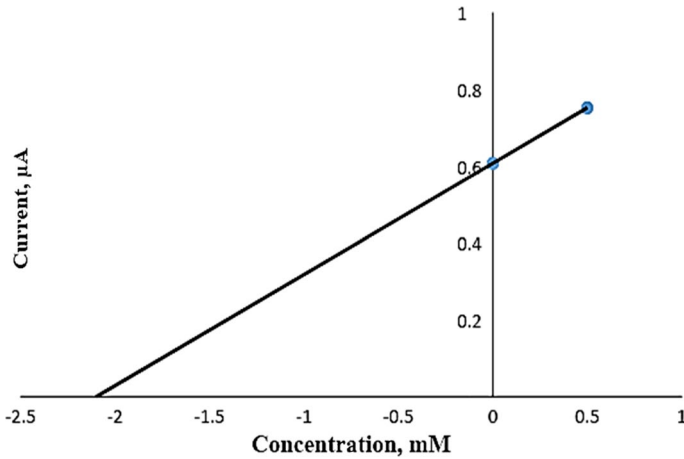


Fig. 15 DPV results of TAT-PI-1/1 sensor toward different CT concentrations in green tea

Table 1 The comparison of the properties of presented sensor with the literature

Classical methods	Electrode	Linear range	LOD	R^2	RSD (%)	Reference
BIA-MPA	GCE	20–100 μM	0.03 μM	0.999	–	[41]
SWV	GCE	23–58 μM	2.89 μM	0.988	2.5	[42]
DPV	MWCNT/CPE	0.10–2.69 μM	0.017 μM	–	–	[43]
CE	–	35–10,335 μM	–	0.996	–	[44]
SWV	Modified Au	4.95–32.7 μM	0.28 μM	0.9993	3.5	[45]
HPLC	–	345–2067 μM	0.04 μM	0.9990	–	[46]
DPV	Modified Pt	50–350 μM	15.2 μM	0.9982	2.15	This work

BIA-MPA batch injection analysis with multiple-pulse amperometry, *CPE* carbon paste electrode, *CE* capillary electrophoresis, *SWV* square-wave voltammetry, *MWCNT/CPE* multiwalled carbon nanotube paste electrode

(0.0152 mM), high regression coefficient (R value = 0.9982), and good repeatability (RSD of 2.15%). As a result, it has been used to develop a rapid, effective, stable, low cost, sensitive, selective electrochemical biosensor for detection of CT through TAT-PI-1/1-modified electrode.

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