

Selective Determination of Serotonin on Poly(3,4-ethylenedioxy pyrrole)-single-walled Carbon Nanotube-Modified Glassy Carbon Electrodes

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An electrochemically-modified electrode [P(EDOP-SWNTs)/GCE] was prepared by electropolymerization of 3,4-ethylenedioxy pyrrole (EDOP) single-walled carbon nanotubes (SWNTs) on the surface of a glassy carbon electrode (GCE) and characterized by SEM, CV, and DPV. This modified electrode was employed as an electrochemical biosensor for the selective determination of serotonin concentrations at pH 7.4 and exhibited a typical enhanced effect on the current response of serotonin with a lower oxidation overpotential. The linear response was in the range of 1.0×10^{-7} to 1.0×10^{-5} M, with a correlation coefficient of 0.998 on the anodic current. The lower detection limit was calculated as 5.0 nM. Due to the relatively low currents and difference of potentials in the electrochemical responses of uric acid (UA), ascorbic acid (AA), and dopamine (DA), the modified electrode was a useful and effective sensing device for the selective and sensitive serotonin determination in the presence of UA, AA, and DA.

Key Words : 3,4-Ethylenedioxy pyrrole, Single-walled carbon nanotubes, Serotonin, Modified electrode, Biosensor

Introduction

Serotonin (5-hydroxytryptamine, 5-HT) is an important biomolecule in physiological systems, a neurotransmitter widely dispersed throughout the central nervous system, playing a vital role in the regulation of mood, sleep, emesis, sexuality, and appetite. Low levels of 5-HT are associated with several disorders, including depression, anxiety, and migraines.^{1,2} Extremely high levels of 5-HT can manifest toxicity and potentially fatal effects known as serotonin syndrome.³ It is well known that 5-HT and DA influence each other in their respective releasing given their coexistence in biological systems.⁴ Determination of 5-HT is often complicated by the presence of DA, with the oxidation potential of 5-HT (0.38 V) close to that of DA (0.22 V). Furthermore, accurate determination of 5-HT often proves difficult because of interference from AA and UA, as both are often in high concentration and capable of oxidation at a potential close to that of 5-HT at the bare electrode. Several methods have been employed for accurate determination of 5-HT, such as liquid chromatography, fluorometry, coulometry, capillary electrophoresis, mass spectrometry, and electrochemical methods.⁵⁻¹⁵ With the exception of electrochemical methods, there exists several difficulties that render the methods overly time-consuming, such as high cost and requisite sample manipulations. Conducting polymers such as polypyrrole and polyaniline possess many attractive features as molecular recognition systems. Such polymers can be used to construct solid-state ion selective electrodes¹⁶⁻²⁰ and composites with various nanomaterials and nanotubes,²¹⁻²⁸ imparting superior selectivity and sensitivity toward neurotransmitter analytes.⁴ Research in the field of voltammetric

sensors based on polymers are focused on three areas: (a) greater reproducibility in the formation of the electrode surface; (b) stable polymerizations that enables an acceptable durability of the sensors; (c) increase in the electrode surface in order to obtain greater levels of sensitivity. Additionally, the importance of the 5-HT level in usual matters requires a simple cost effective method for its rapid monitoring. Electro-analytical methods meet the above requirements, but normally possess lower sensitivity than conventional electrodes. However, low sensitivity and poor selectivity of electrochemical methods can be overcome through electrode modification. Nanogold, carbon nanotubes (CNTs) and fullerene-modified electrodes have been used by several research groups for simple, fast, and sensitive voltammetric determination of various compounds of physiological importance;²⁹⁻³³ an enhanced sensitivity has been observed with shifts of the peak potential to less positive potentials. Carbon nanotubes have stimulated increasing interest in the application of fabricated electrochemical sensors due to their unique combination of excellent mechanical, electrical, and electrochemical properties.³⁴⁻³⁶ Many applications of CNTs in electrochemical sensors for different biomolecules have been reported.^{37,38} In recent years, CNT-modified electrodes made using electropolymerization as a binder for analytical purposes have been reported in many studies; this gives new capabilities to electrochemical sensors by combining the advantages of both a copolymer and CNTs. Due to their attractive performance, CNT-copolymer composite materials have been utilized to fabricate electrochemical sensors for selective detection of various biomolecules.³⁹

In this study, a poly(EDOP-SWNTs)-modified GCE was prepared by electrochemical polymerization *via* a cyclic

voltammetry method. This modified electrode was employed for electrochemical selective determination of 5-HT in the comparable presence of DA, UA, and excess AA, with a linear response range of 1.0×10^{-7} to 1.0×10^{-5} M, under a biologically and analytically significant pH of 7.4; this was comparable to recent literature values.^{4,5,40} The respective detection limit and correlation coefficient were calculated as 5.0 nM and 0.998 on the anodic current.

Experimental

Chemicals. The EDOP, tetrabutyl ammonium perchlorate (TBAP), 5-HT, DA, UA, and AA were purchased from Aldrich. The SWNTs [diam. \times length: 1.2-1.5 nm \times 2.0-5.0 μ m (bundles), produced by an arc method, purity 50-70%] were also purchased from Aldrich. All other reagents used were of analytical grade and used without further purification. All electrochemical experiments were carried out at room temperature. The pH of the PBS was adjusted with 0.1 M H_3PO_4 and 0.1 M NaOH. High purity argon was used for deaeration. Doubly distilled water with a resistivity exceeding 18 M Ω cm in a quartz apparatus was used to prepare all aqueous electrolyte solutions. Testing solutions of 5-HT, DA, UA, and AA were prepared by adding required volumes of the respective stock PBS solution.

Apparatus. A three-electrode assembled cell was employed, which consisted of the modified glassy carbon electrode (3.0 mm diameter) as the working electrode. A platinum-wire electrode was used as an auxiliary electrode. An Ag/AgCl (3.0 M NaCl) electrode supplied by BAS (Model MF-2052) was used as the reference electrode. All potentials were reported with respect to the Ag/AgCl electrode at room temperature and under an argon atmosphere. Electrochemical techniques, including cyclic voltammetry (CV), differential pulse voltammetry (DPV), and chronoamperometry (CA) were performed using a BAS 100B/W voltammetric analyzer (Bioanalytical Systems, West Lafayette, IN, USA) in a grounded Faraday cage. All pH measurements were performed with a pH glass electrode with a JENCO meter. Field emission scanning electron microscopic (FE-SEM) images of the modified electrode were obtained by a JSM-600 field emission scanning electron microanalyzer

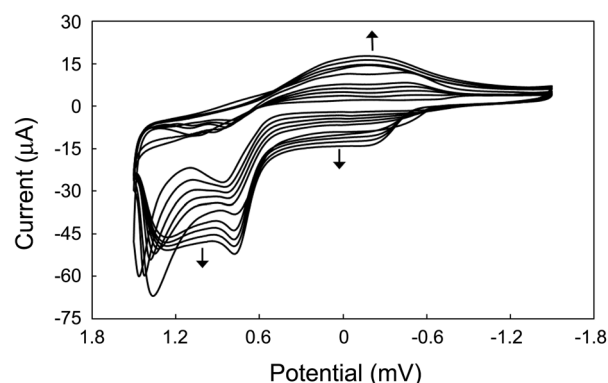


Figure 1. CVs of the electropolymerization of EDOP in the presence of SWNTs on GCE; Scan rate of 0.1 V/s for 10 cycles.

(JEOL).

Preparation of the Modified Electrode. The GCE surface was highly polished with alumina paste, followed with a wash in a 1.0 M HCl solution, rinsed several times with distilled water, and finally rinsed with methanol. First, 1.0 mM EDOP, 1.0 mg of SWNTs, and 0.05 M TBAP/MeCN solution was mixed by ultrasonication for 5 min; the P(EDOP-SWNTs)-modified GCE was then made by electropolymerization with EDOP in the prepared solution with a cyclic sweeping from 1.5 to -1.5 V at 0.1 V s^{-1} for 10 cycles (Fig. 1).

Also, the SWNTs/GCE surface was coated with 5.0 μ L of the black SWNT suspension (1.0 mg/mL) in distilled water. The solvent was evaporated in air at room temperature. The modified electrode was washed with distilled water before and after each experiment. All experiments for determination of 5-HT were carried out in a 15 mL electrolytic cell with 5.0 mL PBS, whereby oxygen was removed by a continuous purging with high-purity argon.

Results and Discussion

Electropolymerization of EDOP-SWNTs on GCE. The P(EDOP-SWNTs)-modified GCE was made by electropolymerization of 1.0 mM EDOP and 1.0 mg SWNTs in 0.05 M TBAP/MeCN, with a cyclic sweeping as outlined in Figure 1. The reduction peak at -0.2 V and the oxidation peaks at -0.2 and $+0.7$ V were increased with subsequent cyclic

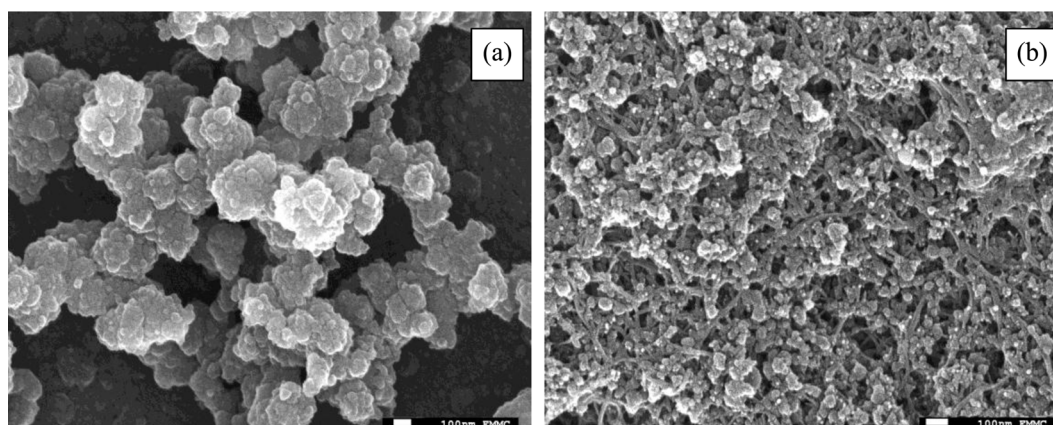


Figure 2. SEM image of electropolymerized P(EDOP)/GCE (a); P(EDOP-SWNTs)/GCE (b), in 0.05 M TBAP/MeCN.

sweeping; this oxidation and reduction wave increased due to formation of a conducting polymer layer around the electrode, provoking broadening of the electronic surface.

Surface Morphology of the P(EDOP-SWNTs)/GCE. The SEM image of the surface of the modified GCE is shown in Figure 2. After electropolymerization of EDOP and (EDOP-SWNTs), the GCE bore variations in their structures, clearly indicating the existence of polymeric EDOP on the SWNTs. In Fig. 2(a), the EDOP was polymerized on the GCE surface in a crystalline form, though not completely homogeneous. Nevertheless, the EDOP was polymerized with SWNTs as a net-like structure and was homogeneously compact (Fig. 2(b)). The image illustrates the uniform dispersion of the poly (EDOP-SWNTs) on the GCE surface.

Electrochemical Behavior of 5-HT at the Modified Electrode. The voltammetric response of 5-HT on the modified electrode was performed *via* CV. Figure 3 demonstrates a typical CV of 3.0×10^{-6} M 5-HT in PBS at pH 7.4, recorded at: bare GCE (a); completely modified electrodes (b, absence of 5-HT and c, presence of 5-HT); partially modified electrodes (d and e). At the bare electrode, a weak oxidation peak was observed near 0.39 V, as shown in Figure 3(a). At the partially modified electrode were shallow (low current response) peaks at 0.34 and 0.39 V, as shown in Figure 3(d) and 3(e), respectively. Under the same conditions, the anodic peak of 3.0×10^{-6} M 5-HT at the completely modified electrode P(EDOP-SWNTs)/GCE appeared as a deep peak at 0.37 V; the peak current increased significantly (Fig. 3c) and there was no signal at P(EDOP-SWNTs)/GCE due to absence of 5-HT (Fig. 3b). The remarkable enhancement in the current response of the oxidation potential provided clear evidence of the catalytic effects of the modified electrode acting as a promoter to enhance the electrochemical reaction and thus, considerably accelerating the rate of electron transfer. The scan rate was 0.1 V s^{-1} , with the accumulation time of only 10 s.

Electrochemical Response of 5-HT at the Modified Electrode. DPVs of 5-HT at the P(EDOP-SWNTs)/GCE (Fig. 4) showed a dynamic response due to increased con-

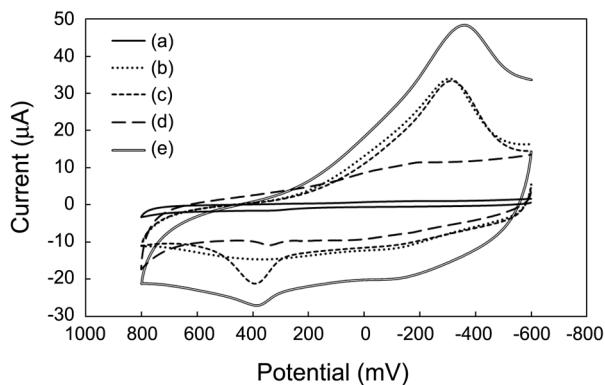


Figure 3. CVs at the bare GCE (a); P(EDOP-SWNTs)/GCE (b) and (c); SWNTs/GCE (d); P(EDOP)/GCE (e), each in PBS at pH 7.4; all electrodes were tested in the presence of 3.0×10^{-6} M 5-HT, except (b).

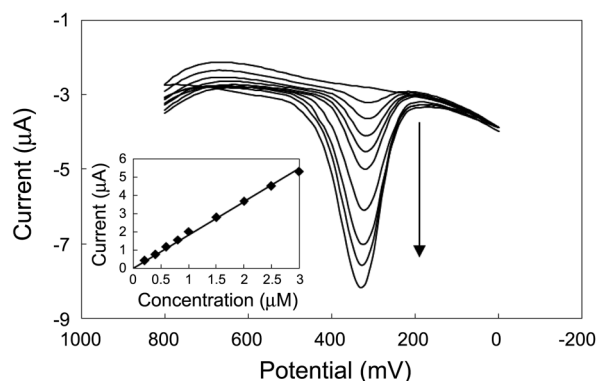


Figure 4. DPVs of 0.0 to 3.0×10^{-6} M 5-HT at the P(EDOP-SWNTs)/GCE in PBS, the plot of peak current *versus* 5-HT concentration (Inset).

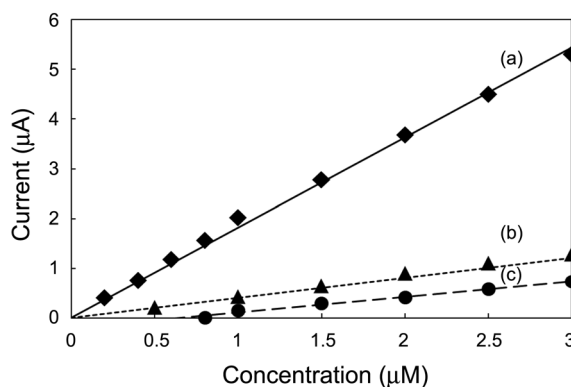


Figure 5. Plot of peak current *versus* concentration of 5-HT (a); DA (b); UA (c), all obtained from DPVs.

centration (0.0 to 3.0×10^{-6} M) of 5-HT; the sharp peak was found at 0.34 V. The calibration curve for the 5-HT was measured using DPV. The catalytic peak current was found to increase as the concentration of 5-HT increased linearly (Fig. 4, inset). For 5-HT, the plot of the peak current (μA) *versus* concentration (comparison with DA and UA, Fig. 5a) was linear in the range of 1.0×10^{-7} to 3.0×10^{-6} M, at pH 7.4. The linearity of the plot was reasonable, with a correlation coefficient of 0.996 [$i_p (\mu\text{A}) = 1.816C (\mu\text{M})$] on the anodic current, indicating that 5-HT could be estimated in the given concentration range. The voltammetric behaviors of UA, DA, and 5-HT mixture were investigated by DPV. While the plot of the peak current (μA) for DA (Fig. 5(b), 0.990) and UA (Fig. 5(c), 0.988) *versus* concentration was also linear, it still could not provide interference based upon 5-HT determination. On the basis of the slope (Fig. 5), the electrochemical response of the 5-HT was significantly larger than that of DA and UA.

Furthermore, Figure 6 illustrates the chronoamperometric response of the modified electrode to subsequent additions of 5-HT in PBS at an applied potential of 0.38 V, using CA. The inset of Figure 6 represents the plot of the response current *versus* 5-HT concentration. The linearity of the plot proved very reasonable. The linear regression equation is: $i(n\text{A}) = 0.214C (\text{nM})$, with a correlation coefficient of 0.998.

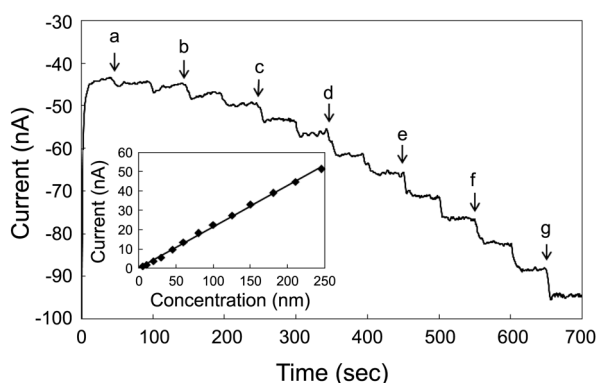


Figure 6. Amperometric response of 5-HT at the P(EDOP-SWNTs)/GCE in PBS at a constant potential of 380 mV. (a \rightarrow b, 5.0×10^{-9} M; b \rightarrow c, 1.0×10^{-8} M; c \rightarrow d, 1.5×10^{-8} M; d \rightarrow e, 2.0×10^{-8} M; e \rightarrow f, 2.5×10^{-8} M; f \rightarrow g, 3.0×10^{-8} M; g \rightarrow , 3.5×10^{-8} M step). Inset: plot of response currents versus 5-HT concentration.

This result suggests that 5-HT could be easily detected at very low concentrations using the chronoamperometric method, indicating a detection limit (S/N = 3) of 5.0 nM.

Differential pulse voltammetry was used for determination of 5-HT in the presence of AA and UA at the P(EDOP-SWNTs)-modified GCE, given its higher sensitivity and improved resolution over CV. As the aforementioned results indicated, the electrochemical response of 5-HT was stable in the successive DPV scan, with the well-separated oxidation peak of the 5-HT. Thus, a DPV scan for one cycle from 0 to 0.8 V or -0.1 to 0.8 V at 50 mV/s was performed with the mixture sample, containing different concentrations of 5-HT, DA, AA, and UA. However, as shown in Figure 7, in the presence of a constant concentration (5.0×10^{-6} M) of UA, DPV was performed at different concentrations (0.0 to 3.0×10^{-6} M) of 5-HT, yielding a peak near 500 mV for UA. Accordingly, there was a peak near 0.34 V for 5-HT that increased (current response) upon increase in 5-HT concentration. The peak was still in the previous position (0.34 V), indicating that the UA could not interfere with 5-HT electrolytic determination. No interference, even at 10-fold UA, affected determination of the 5-HT level; a 10-fold peak current intensity of UA proved less than 5-HT.

To investigate the electrochemical response when 5-HT

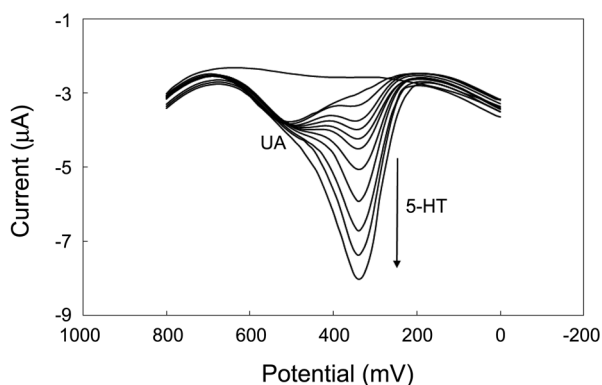


Figure 7. DPVs of 0.0 to 3.0×10^{-6} M 5-HT in the presence of 5.0×10^{-6} M UA at the P(EDOP-SWNTs)/GCE at pH 7.4 in PBS.

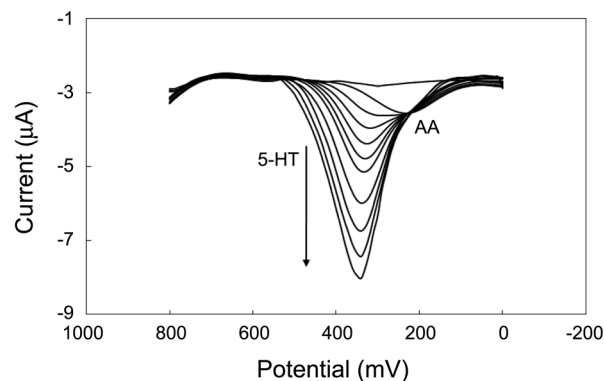


Figure 8. DPVs of 0.0 to 3.0×10^{-6} M 5-HT in the presence of 5.0×10^{-4} M AA at the P(EDOP-SWNTs)/GCE at pH 7.4 in PBS.

co-existed with AA, its voltammetric behavior was examined by DPV in the presence of a substantial excess of AA. All experiments were carried out by varying concentration (0.0 to 3.0×10^{-6} M) of the 5-HT in the presence of 5.0×10^{-4} M (166-fold) AA (Fig. 8). Acceptable linearity was obtained between the anodic DPV peak currents of the 5-HT concentration in the mixture. Clearly, the competitive adsorption equilibrium of 5-HT could be overcome at a suitable concentration. Hence, this proposed method was suitable for concentration determination of 5-HT, since the amount of AA in the biological system was larger than the monoamine neurotransmitters. Interference of the high concentration of AA should be taken into account prior to determination of 5-HT. From the above discussion, it is apparent that AA does not interfere with measurement of 5-HT at pH 7.4 in PBS, at a scan rate of 50 mV/s, and the accumulation time of 10 s.

Figure 5 represents the variation in peak current observed at different concentrations of 5-HT, DA, and UA. The i_{pa} was found to increase linearly with concentration, with a correlation coefficient of 0.990 on the anodic current of DA and within a measuring range of 1.0×10^{-7} to 3.0×10^{-6} M for 5-HT. On the basis of the slope, the electrochemical response of 5-HT was significantly larger than that of DA and UA at the P(EDOP-SWNTs)/GCE. A possible reason for such a response can be that oxidation of the analyte was subject to substrate modification on the GCE or morphology of the modified electrode. Until now, the modified electrodes demonstrated the electrochemical response of 5-HT to be smaller than that of DA.^{4,40} These results suggest that, in the presence of DA, the concentrations of 5-HT can be selectively determined with excellent sensitivity. It is possible that the amino group of the 5-HT is more electroactive than that of DA, according to structure. The oxidative electrochemistry of 5-HT is, however, complex. In Figure 9, different concentrations (0.0 to 3.0×10^{-6} M) of 5-HT were measured with 1.0×10^{-5} M DA, without any interference with the determination of 5-HT. Under identical conditions, DA and 5-HT yielded two well-defined oxidation peaks with respective potentials of 0.18 and 0.34 V at the P(EDOP-SWNTs) film-coated GCE; they did not interfere with each other. Consequently, the electron transfers of DA and 5-HT at the

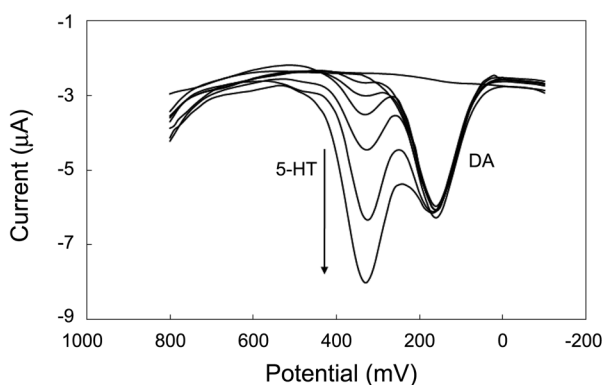


Figure 9. DPVs of 0.0 to 3.0×10^{-6} M 5-HT in the presence of 1.0×10^{-5} M DA at the P(EDOP-SWNTs)/GCE in PBS.

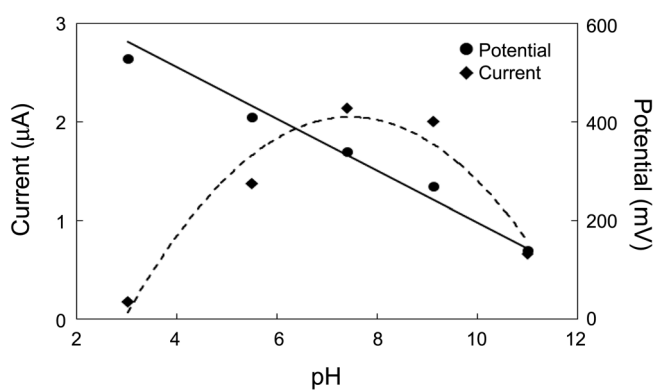


Figure 10. Effect of pH on 1.0×10^{-6} M 5-HT oxidation at the modified electrode by CV.

P(EDOP-SWNTs)/GCE were facilitated. Thus, DA and 5-HT yielded two separate and sensitive oxidation peaks.

Effect of pH on P(EDOP-SWNTs)/GCE. The effect of pH on the electrode response for the oxidation of 5-HT was investigated using the CV mode in a pH range 3-11, and in the presence of 1.0×10^{-6} M 5-HT. The peak currents of the 5-HT increased with an increase in pH, indicating the proportion of the electrons and protons involved in the oxidation of 5-HT. Finally, the highest oxidation peak currents were observed at pH 7.4 PBS, as shown in Figure 10. The physiological pH of 7.4 in PBS was chosen as the supporting electrolyte for the experiment. The slope for the 5-HT was -52.55 mV/pH, which was in agreement for the $2e^-$ transfer reaction.⁴¹

Effect of Scan Rate and Adsorption of 5-HT on P(EDOP-SWNTs)/GCE. The influence of the scan rate on the oxidation peak current of 5-HT at the P(EDOP-SWNTs)/GCE was also studied *via* CV in the presence of 2.0×10^{-6} M 5-HT. As demonstrated in Figure 11(a), there were a wide-ranging linear peak currents of the 5-HT and a square root of the scan rate from 25 to 400 mV/s, a linear regression equation of: $I_{pa} (\mu A) = 1.10V^{1/2} - 3.83$, and a correlation coefficient of 0.997, indicating a diffusion-controlled process in the electrochemical reaction.

Under a different accumulation time, responses of 5-HT (3.0×10^{-6} M) at P(EDOP-SWNTs)/GCE were also investi-

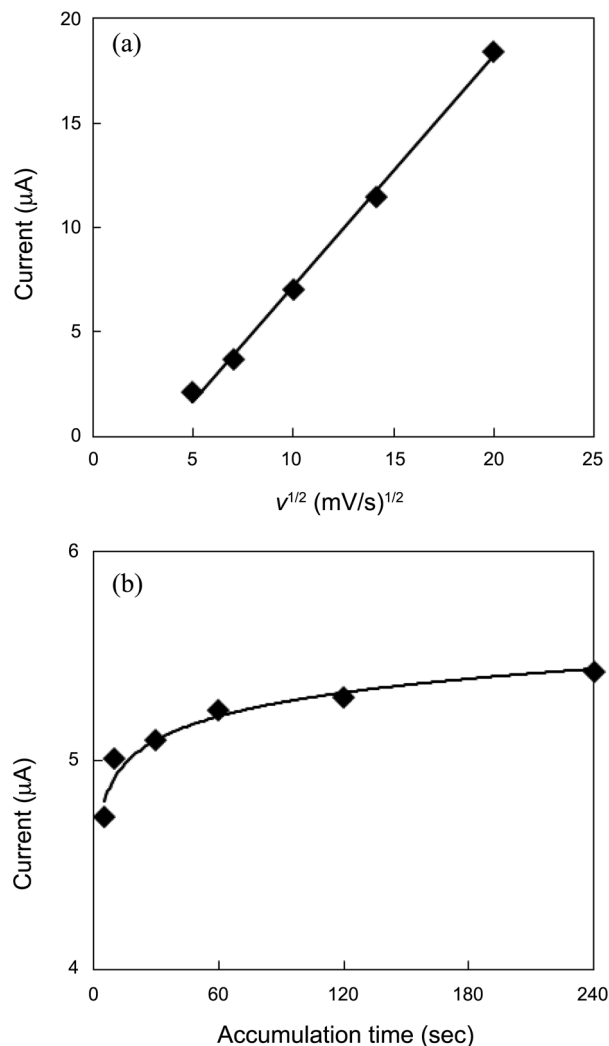


Figure 11. Effect of the scan rate of 3.0×10^{-6} M (a); adsorption of 2.0×10^{-6} M 5-HT (b) on P(EDOP-SWNTs)/GCE by CV, investigated in PBS at pH 7.4.

gated. As shown in Figure 11(b), if the accumulation time was longer, the serotonin peak currents increased minimally from 10 s ($5.006 \mu A$) and 240 s ($5.423 \mu A$). However, the oxidation of serotonin is known to produce hydroxylated products, dimers, and other species that can irreversibly adsorb to the electrode, thus fouling the surface.⁷ Ten seconds of accumulation time proved sufficient to obtain a good current response for serotonin with the P(EDOP-SWNTs)/GCE. Thus, this short accumulation time showed reduced fouling and increased reproducibility. Accordingly, the accumulation time chosen was 10 s.

Stability. The limit of detection (defined as the concentration leading to a signal three times the standard deviation of the baseline noise) was 5.0 nM. To characterize the reproducibility of the modified electrode, repetitive measurements were carried out in 1.0×10^{-6} M 5-HT. The results from five successive measurements demonstrated a 1.01% relative standard deviation (RSD), suggesting good reproducibility. The long-term stability of the modified electrode was estimated by measuring the current response at a fixed

concentration of 1.0×10^{-6} M 5-HT, over a period of 30 d, with the modified electrode undergoing daily use. The experimental results showed that the current response deviated only 4.2%, implying that the P(EDOP-SWNTs)/GCE possesses long-term stability. As a result, it could be stored in PBS (pH 7.4) at approximately 20 °C.

Conclusions

The P(EDOP-SWNTs)-coated GCE exhibited outstanding electrocatalytic effects towards the oxidation of 5-HT, improving oxidation peak currents and lowering oxidation overpotential. Electrocatalysis by the P(EDOP-SWNTs)/GCE toward 5-HT was mainly attributed to a stereo-porous interfacial layer. The single-walled carbon nanotubes provide many active sites, enhancing the sensitivity of 5-HT. At the bare GCE, the oxidation signal of the 5-HT merged and could not be sensitively determined. However, the P(EDOP-SWNTs)/GCE permitted a favorable voltammetric resolution of 5-HT in the pH 7.4 phosphate buffer. The modified electrode demonstrated efficacy in detecting 5-HT selectively and exhibited excellent stability and reproducibility. Furthermore, a large excess of AA and UA had minimal influence over the oxidation signal of 5-HT. Thus, 5-HT could be easily and selectively oxidized in the presence of a certain amount of DA. These properties indicate the P(EDOP-SWNTs)/GCE as promising for *in vitro* 5-HT measurements.

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