

## Studies on poly(3-methylthiophene)-modified electrode for the electrochemical behavior of dopamine

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Poly(3-methylthiophene)/iodide-modified [P(3MTp)/I] electrode was used for electrochemical determination of dopamine. A platinum disc electrode was modified with an electrosynthesized P(3MTp)/I thin films which showed electrocatalytic activity toward dopamine (DA). In comparison with the bare Pt electrode, there was a response enhancement using the P(3MTp)/I-modified electrode to DA with 0.582  $\mu$ A anodic peak intensity at 160 mV potential and 0.373  $\mu$ A cathodic peak intensity at 100 mV potential. Ascorbic acid (AA) interference was greatly reduced (0.315 mA) with the modified electrode. The P(3MTp)/I film was characterized using surface analytical techniques such as X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). XPS and SEM analysis indicated the presence of DA on the surface of the film. SEM experiments provide evidence that DA is deposited in the P(3MTp)/I membrane as demonstrated by the discoloration of the almost black color to white after the film was exposed to 1 mM DA solutions.

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**Keywords:** poly(3-methylthiophene); dopamine; XPS analysis; ascorbic acid

### INTRODUCTION

In biomedical research, dopamine (DA) is an important neurotransmitter of catecholamines. It possesses very strong electrochemical activity and is one of the main objects of study in the electroanalytical chemistry of neurotransmitter [1]. The ability to detect DA with selectivity and sensitivity is of great interest to most electroanalytical researchers [2]. Measurement of DA in biological fluids serves as biological markers for diagnosis, evaluation of therapeutic response and early recognition of relapses of tumor derived from neural crest, carcinoid tumor and melanoma [3]. Patients with Parkinson's disease have been found to have low levels of DA [4].

Adams and co-workers [4] introduced the use of electrochemical techniques for the *in vivo* analysis of neurotransmitters. Presence of ascorbic acid (AA) and other easily oxidizable molecules are major problems associated with the use of electrochemical techniques for the analysis of neurotransmitter.

Biological fluids contain high level of acetaminophen and AA which are effective reducing agents, thus are interfering species on some electroactive species such as DA. Some organic and biologically important compounds like DA and AA have caught the interest of scientists because of its importance in biological and medical research [5]. Researchers are still working on methods to attenuate the electrochemical behavior of AA in the presence of minute amount of DA.

The main problem of measuring DA *in vivo* is the very low concentration of DA ( $10^{-8}$ – $10^{-6}$  M) and the large presence of interfering ions such as AA ( $10^{-4}$  M) which are always present in biological tissues [1, 6]. In most solid electrodes like glassy carbon, AA ( $E_a$  AA = 0.98 V) is oxidized at a potential close to that of DA ( $E_a$  DA = 0.83 V), resulting in an overlapping voltammetric response, complicating the interpretation of data [6].

There have been many approaches towards overcoming this problem of selectivity in the measurement of dopamine by electroanalytical technique. These approaches include the use of a specific procedure for electrode pretreatment, particularly for carbon based electrodes, which result in the separation of oxidation signals for the analyte of interest and the interfering molecule. Among the several strategies reported, coating of the working electrode with an anionic film such as Nafion and or poly(ester sulfonic acid) with or without electrochemical pretreatment is a convenient way [7].

This study aims to investigate the electrochemical behavior of DA on an electrode modified with conducting poly(3-methylthiophene) with iodide as dopant P(3MTp)/I. The study was carried out to investigate and characterize the electrochemical behavior of DA on bare platinum electrode and on P(3MTp)/I-modified electrode in the absence or in the presence of ascorbic acid as interfering species. Likewise, surface analysis was conducted on the P(3MTp)/I-modified electrode to determine electrode surface characteristics of P(3MTp)/I-modified electrode before and after exposure to DA. Surface analysis will help to understand the limitation of the modified electrode, short life span of the electrode.

## EXPERIMENTAL

**Reagents.** The 3-methylthiophene (3-MTp) monomer and the dopant tetrabutylammoniumiodide were purchased from Sigma Chemicals Co. Acetonitrile, acetic acid, phosphoric acid and sulfuric acid (ACS reagent) were obtained from Ajax Chemicals. Electropolymerization solutions were prepared fresh in every experiment and was purge with nitrogen gas for about 10 min before the polymerization step. Distilled water used was purchased from Wilkins. Analyte reagents like AA and DA as well as (tris[hydroxymethyl]aminomethane) were purchased from Sigma Chemicals Co. Boric acid, sodium chloride, sodium dihydrogen phosphate and sodium hydrogen phosphate were purchased from Merck or Ajax Chemicals. All analytical grade reagents were used as received unless otherwise stated.

**Electrochemical polymerization and characterization.** Electrochemical polymerization was performed using Metrohm VA 693 Processor. Electropolymerization was carried out in a one-compartment cell with the fabricated working electrode (Pt disc), reference electrode (Ag/AgCl, 3 M KCl) and Pt auxiliary electrode immersed in a polymerization solution containing 100 mM 3-methylthiophene monomer, 100 mM tetrabutylammoniumiodide dopant in acetonitrile solution. A repeated potential scanning at a potential window of 0 to 2500 mV was applied. Electrochemical characterization of the behavior of 5 mM DA on P(3MTp)/I-modified electrode surface was determined by cycling the potential between -1000 mV and +800 mV based on the effect of the number of measuring cycles, buffer composition, pH and presence of interfering species.

**Scanning Electron Microscopy (SEM).** A platinum (Pt) wire with diameter of 0.128 cm and 0.38 cm in length was soldered to a copper wire and then encased in a plastic tube and coated with P(3MTp)/I was used for SEM and XPS analysis. SEM studies of selected samples were performed using JSM - 5310 Scanning Microscope.

The P(3MTp)/I-modified sample was sputter-coated with gold prior to SEM analysis.

**X-ray photoelectron spectroscopy analysis.** XPS analysis of the Pt wire with P(3MTp)/I was performed using an ultra high vacuum ( $10^{-10}$  mbar) ESCLAB 2201 XL, VG Scientific UK, Monochromated Al K $\alpha$  (1486.6 eV), Power 120 W (10 kV, 12 mA) surface analysis system.

## RESULTS AND DISCUSSION

### Electrochemical characterization of DA on P3MTp

**Number of measuring cycles.** The intensity of the DA response using an electrode modified with P(3MTp)/I was studied to determine the effect of varying the number of measuring cycles applied over the Pt working electrode during polymerization and subsequently optimize the deposition time of P(3MTp)/I on the platinum disc.

**Table 1. Effect of number of measuring cycles to the anodic peak current intensity ( $i_a$ ) and cathodic peak current intensity ( $i_c$ ) of dopamine and hydroquinone.**

Analyte	Number of Measuring Cycles	$i_a$ ( $\mu A$ )	%RSD	$i_c$ ( $\mu A$ )	%RSD
Dopamine	1 cycle	45.00	0.867	13.33	1.282
Dopamine	2 cycles	38.33	1.291	25.00	0.916
Dopamine	3 cycles	26.67	1.368	18.33	1.114
Dopamine	4 cycles	30.00	1.500	18.33	0.0322
<b>Dopamine</b>	<b>5 cycles</b>	<b>43.33</b>	<b>0.750</b>	<b>28.33</b>	<b>1.439</b>
Dopamine	6 cycles	25.00	1.000	16.67	1.239

Table 1 summarizes the effect of measuring cycles on anodic peak intensity and cathodic peak intensity of the electrode's response. With one measuring cycle, the Pt disc was not completely covered with P(3MTp)/I; hence the 45 mA anodic peak current was generated by both the bare Pt disc and the Pt disc partially covered with P(3MTp)/I.

The response of the resulting P(3MTp)/I-modified electrode on DA was found to increase with increasing number of measuring cycles applied during the polymerization. The results (Table 1) showed that five measuring cycles gave the highest response to DA with  $i_a \sim 43$  mA.

**Effect of buffer composition.** The effect of buffer composition on the electrochemical behavior of dopamine on the P(3MTp)/I-modified surface is shown in Fig. 1. Tris buffer at pH 7.0 gave the best response because the anodic peak and the cathodic peak current intensities generated were 0.457  $\mu$ A and 0.275  $\mu$ A, respectively against the anodic peak current intensity of 0.275  $\mu$ A and negligible cathodic peak generated by phosphate buffer at pH 7.0. No response to Britton Universal Buffer at pH 7.0 was detected. Tris buffer gave the best response out of the three buffers used because both Tris and dopamine contain an amino functional group. The amino functionality of DA increased its affinity towards the tris buffer electrolyte, hence the enhanced response.

**Effect of pH.** The effect of pH level on the electrochemical behavior of DA on the P(3MTp)/I-modified surface was promising. Fig. 2a shows that at pH 3.0, there was a slight anodic peak at 200 mV and no cathodic peak. In acidic media, one

wave is observed on the cyclic voltammetric scan due to the oxidation of dopamine to *o*-quinone [8]. An anodic peak with current intensity of 0.410 mA at 190 mV and a cathodic peak with 0.360 mA peak intensity were detected at pH 5.0 (Fig. 2b). An unstable voltammogram was obtained at pH 9.0 (Fig. 2d) indicating that the polymer was slowly attacked by an alkaline medium [9]. Similar results were gathered by Oni and co-workers [8] on DA revealing that at basic medium a second cathodic peak is observed due to a two-electron reduction of aminochrome, a cyclization product of *o*-quinone. While at pH 7.0 (Fig. 2c), an anodic peak at 190 mV and cathodic peak at 90 mV were detected with intensity of 0.436 mA and 0.366 mA, respectively. At neutral pH, an improved reversibility in the oxidation-reduction of DA was observed similar to Oni and others.

**Effect of interfering species.** The responses of 0.1 mM dopamine using a bare platinum (Pt) electrode and using a P(3MTp)/I-modified electrode in the absence or presence of 1 mM AA as interfering species were compared. Electrochemical behavior of DA and AA were measured separately using a bare platinum electrode. A weak anodic peak response to dopamine was obtained at 160 mV potential was detected using bare platinum electrode (Fig. 3Aa). An anodic peak potential at 160 mV with current intensity of 0.582 mA and a cathodic peak potential at 100 mV with current intensity peak of 0.373 mA was

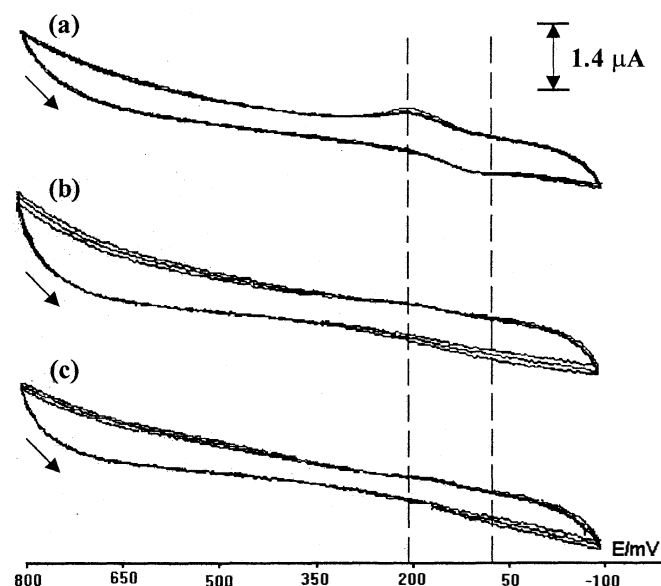


Fig. 1. Effect of buffer composition. (a) 5 mM Dopamine in Tris Buffer 7.0, (b) 5 mM Dopamine in Britton Universal Buffer 7.0, and (c) 5 mM Dopamine in Phosphate Buffer 7.0.

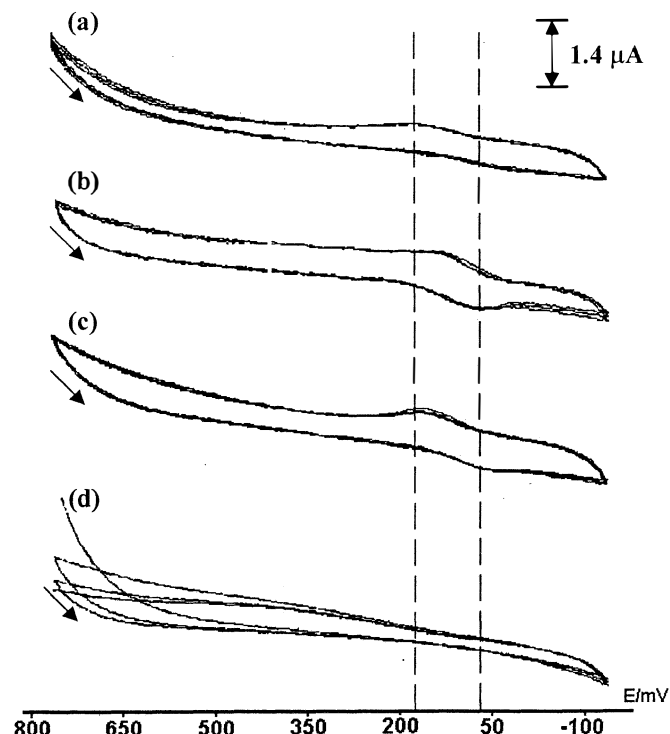


Fig. 2. Effect of pH. 5 mM dopamine dissolved in tris buffer at varying pH. (a) pH 3.0, (b) pH 5.0, (c) pH 7.0, and (d) pH 9.0.  $E_{\text{range}}$ : (+) 800 to (-) 100 mV, Scan rate = 50 mV/s, Reference Electrode = Ag/AgCl, Auxiliary Electrode = Pt rod and Working Electrode = [P(3MTp)/I]-modified Pt disc.

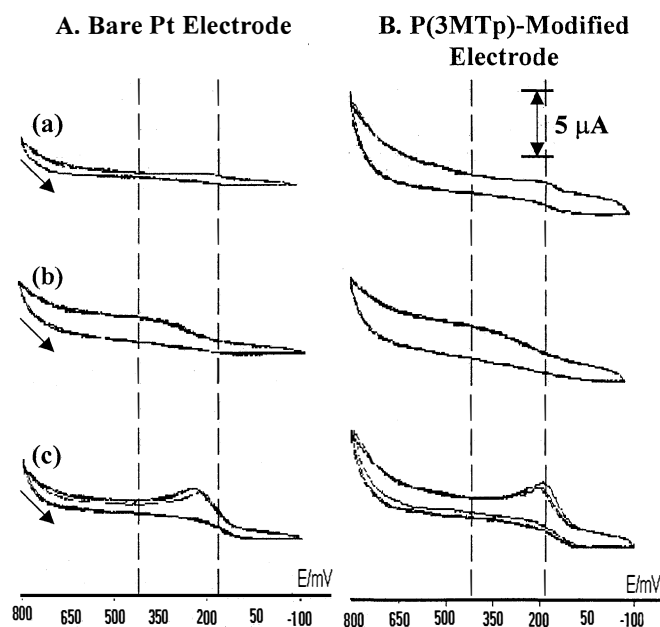


Fig. 3. Comparison of bare Pt electrode vs. P(3MTp)/I modified electrode. [A] Bare Pt electrode, [B] [P(3MTp)/I]-modified electrode. (a) 0.1 mM dopamine solution; (b) 1 mM ascorbic acid, (c.) 0.1 mM dopamine + 1 mM ascorbic acid in tris buffer. Scan rate = 50 mV/s, RE = Ag/AgCl, AE = Pt rod.

detected for DA using the P(3MTp)/I-modified electrode (Fig. 3Ab). These results showed that modifying the bare Pt electrode with P(3MTp)/I improves the response of the electrode to DA as demonstrated by the increase anodic and cathodic current peak intensities by 0.582 mA and 0.373 mA, respectively.

A notable anodic peak response with current intensity of 0.472 mA at 336 mV potential was detected for AA using bare platinum electrode (Fig. 3Ab). The P(3MTp)/I-modified electrode gave an anodic peak potential at 334 mV with current intensity of 0.740 mA (Fig. 3Bb). These results demonstrated that modifying the bare platinum electrode with P(3MTp)/I gave a slight improvement on the sensor's response to AA but only by 0.268 mA in current peak intensity on the anodic peak. A potential difference of 176 mV between the peak potential of DA and AA was observed when using bare platinum electrode or P(3MTp)/I-modified electrode on separate solutions.

Electrochemical behavior of combined 0.1 mM DA and 1 mM AA solution was also measured using bare platinum electrode and comparing the response of the bare platinum electrode to the P(3MTp)/I-modified electrode. Figure 3Ac shows that using bare platinum electrode only the anodic peak at 252 mV potential with current intensity of 2.10 mA current intensity was detected. The peak at 252 mV potential indicates the overlapping of DA and AA anodic peak. Using P(3MTp)/I-modified electrode, an anodic peak at 190 mV potential with 2.62 mA current intensity and a cathodic peak at 90 mV with 1.36 mA

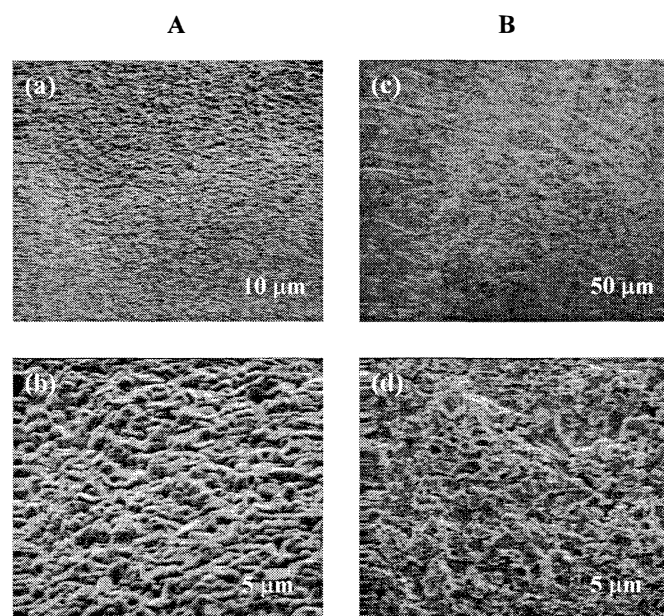


Fig. 4. SEM micrographs of [A] fresh [P(3MTp)/I] at (a) 750x magnification, (b) 3500x magnification; and [B] [P(3MTp)/I] after exposure with dopamine at (c) 500x magnification, (d) 3500x magnification.

current intensity was detected. Results as shown in Fig. 3Bc reveals that only DA was detected when P(3MTp)/I-modified electrode is used.

#### Surface properties of P(3MTp)/I film

Surface analysis is a sensitive method of performing chemical analysis on very small quantities of material in the first 5–10 atomic layers of the surface of a solid [10]. Studies on surface properties using XPS, SEM, and TOFSIMS have been utilized to enhance understanding of the electrodes behavior [11–13]. Surface analysis of P(3MTp)/I will provide understanding of the characteristics of the surface where the site of the electrochemistry of DA takes place. Electrochemical properties of DA on P(3MTp)/I surface is correlated with examination of the membrane structure and composition using XPS and SEM. Surface analysis facilitates a means for understanding the performance of the modified electrode [14].

**SEM on P(3MTp) after exposure to DA.** The morphology of fresh P(3MTp)/I film surface was a homogeneous rough film that looked like a rough carpet (Fig. 4a and b) that turned sponge-like after 5 min exposure to 1 mM DA solution and discoloration of the film surface was also noted. Fig. 4c and d shows the SEM micrographs of the film surface after exposure to DA solution.

The change in the morphology of P(3MTp)/I after it was exposed to DA solution indicates that DA solution adheres to the surface of the film where discoloration occurs and slowly poisons the surface of the film.

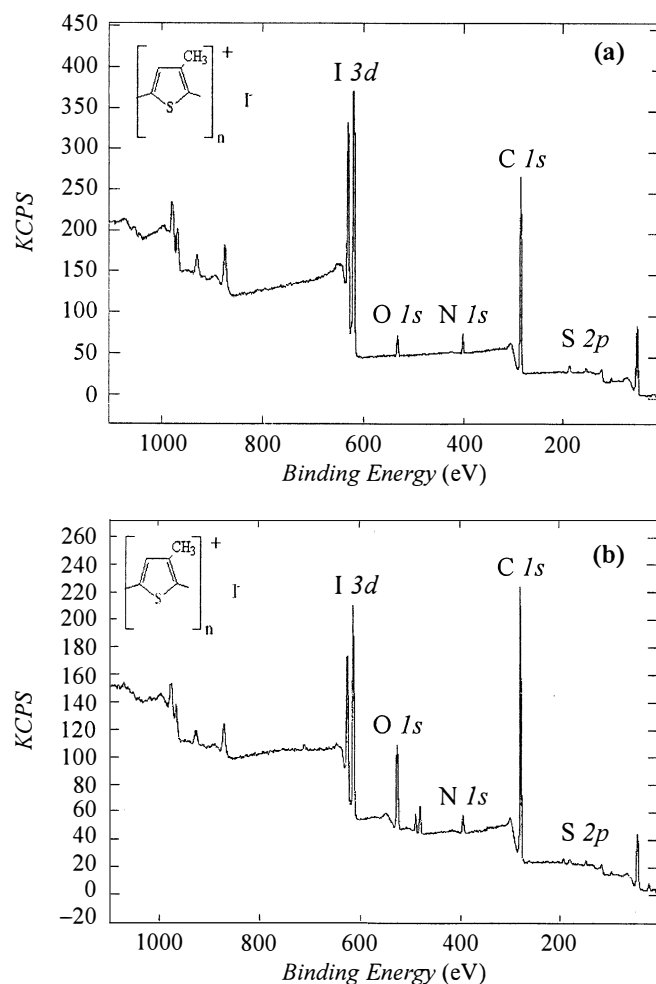


Fig. 5. XPS wide scan spectrum of (a) fresh [P(3MTp)/I] film over binding energy range 1200 to 0 eV. Peaks are identified as iodine (I 3d), oxygen (O 1s), nitrogen (N 1s), carbon (C 1s) and sulfur (S 2p), and (b) [P(3MTp)/I] film exposed to 1 mM dopamine over binding energy range 1000 eV to 0 eV. Peaks are identified as iodine (I 3d), oxygen (O 1s), nitrogen (N 1s), and carbon (C 1s).

Table 2. XPS elemental analysis of fresh P(3MTp)/I film and P(3MTp)/I film after exposure to 1 mM dopamine solution.

Elemental Peaks	Binding Energy (eV)	% AT Fresh Film	% AT After Dopamine
C 1s			
1) C=O	289.01	0	1.258
2) C-O	286.44	19.566	14.568
3) C-C	284.98	63.696	65.801
O 1s			
1) C-O	532.66	2.620	5.624
2) O-H	531.60	0	1.510
3) N-O	533.79	0.524	2.363
N 1s			
1) N-H <sub>4</sub>	402.04	4.580	2.680
2) N-H <sub>2</sub>	400.09	0	1.025
I 3d			
1) I 3d <sub>5/2</sub>	618.89	6.333	3.626
2) I 3d <sub>3/2</sub>	620.68	2.683	1.546

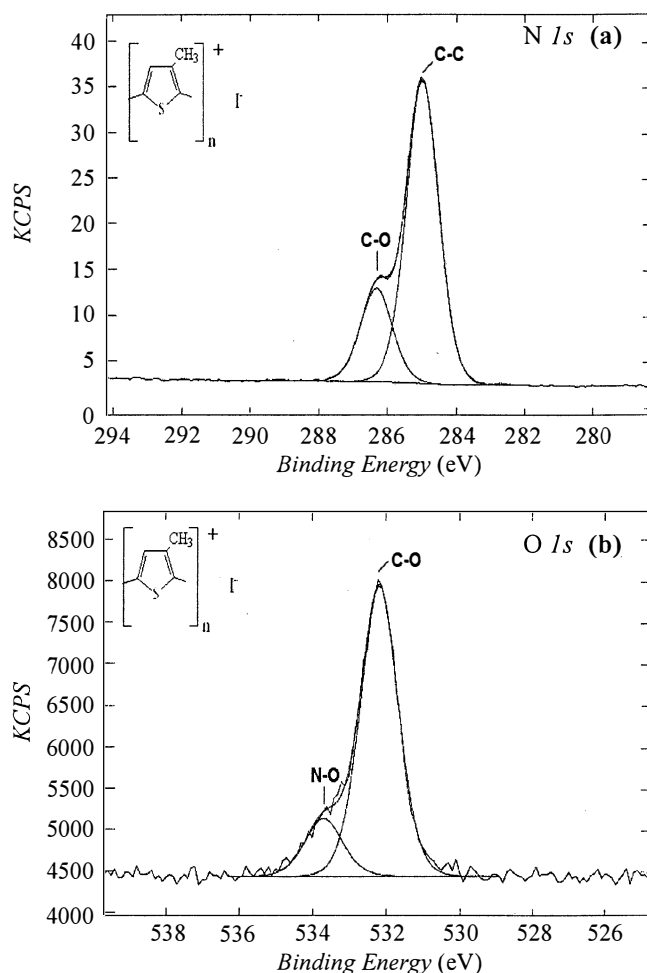


Fig. 6. XPS core level spectrum of the fresh P(3MTp)/I film (a) C 1s ( $E_B = 286.32$  eV &  $284.98$  eV) XPS core level spectrum, and (b) O 1s ( $E_B = 532.18$  eV &  $533.70$  eV).

**XPS analysis on fresh P(3MTp)/I film.** The Poly(3-methylthiophene) structure is composed of a chain of 3-methylthiophene monomers, while structure of tetrabutylammoniumiodide (TBAI) consists of tertiary hydrocarbon chain with one hydrogen substituted by an ammonium iodide. These elemental compositions of the polymer film are shown in a typical XPS wide scan spectrum as shown in Fig. 5 of the P(3MTp)/I film. The elemental peaks for C 1s, N 1s, I 3d, and S 2p are indicative of the poly(3-methylthiophene) and TBAI. Similar XPS wide scan spectra of P(3MTp)/I grafted on Pt wire was obtained by Tourillon [13] except that  $N(Bu)_4PF_6$  was used as dopant instead of TBAI. While the O 1s reveals the presence of oxidized carbon and nitrogen component. The binding energies ( $E_B$ ) of the observed peaks are shown in Table 2.

The P(3MTp)/I carbon 1s photoelectron spectrum was deconvoluted into two component peaks as shown in Fig. 6a. The largest peak centering at  $E_B \sim 285$  eV corresponds to aromatic carbons of the P(3MTp) ring system [16], while the peak at  $E_B \sim 286$  eV is assigned to C-O [16], indicative of the presence of oxidized carbon. The oxygen 1s spectrum (Fig. 6b)

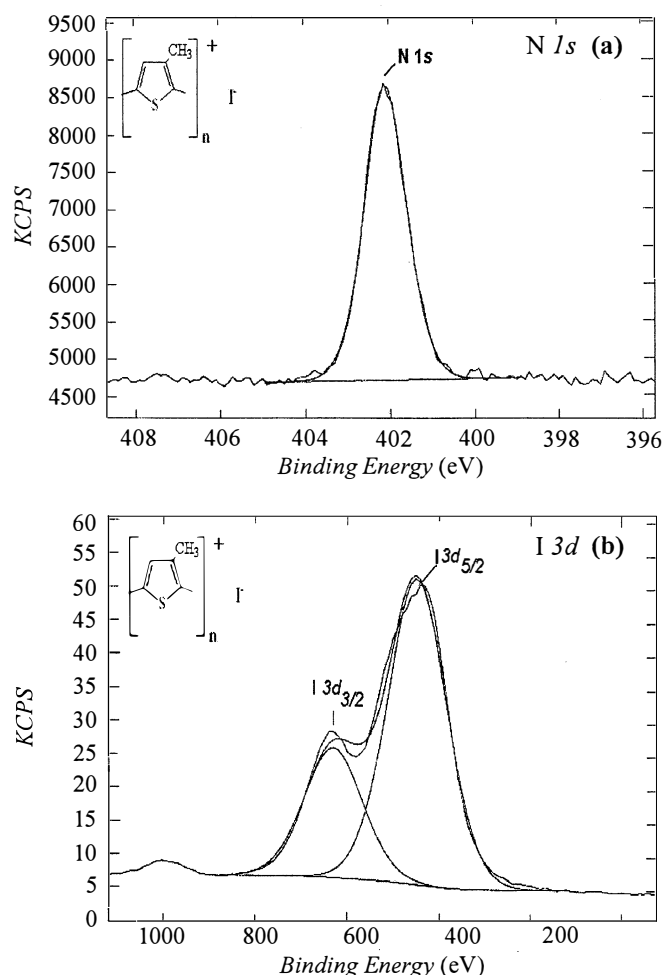


Fig. 7. XPS core level spectrum of the fresh P(3MTp)/I film on the Pt wire (a) N 1s ( $E_B = 402.09$  eV) XPS core level spectrum, and (b) I 3d ( $E_B = 620.31$  eV & 618.48 eV).

was deconvoluted into two component peaks: a peak at  $E_B \sim 534$  eV assigned to N-O species revealing that nitrogen components are oxidized to nitrates and a peak at  $E_B \sim 532$  eV assigned to C-O species indicative of the oxidation of the carbon component.

The nitrogen 1s photoelectron spectrum was deconvoluted into a single component peak as shown in Fig. 7a with peak centering at  $E_B \sim 402$  eV indicating the presence of nitrogen as ammonium ion from tetrabutylammoniumiodide (TBAI) dopant. The Iodine 3d photoelectron spectrum was deconvoluted into a doublet peak with centers at  $E_B \sim 620$  eV and 618 eV (Fig. 7b). The strong doublet peaks of I 3d<sub>5/2</sub> and I 3d<sub>3/2</sub> indicates the presence of iodine from the tetrabutylammoniumiodide (TBAI) dopant on the surface of the P(3MTp)/I film.

The Sulfur 2p photoelectron spectrum was not subjected to a curve fitting because the peak was too weak which only indicates that the S component from poly(3-methylthiophene) is

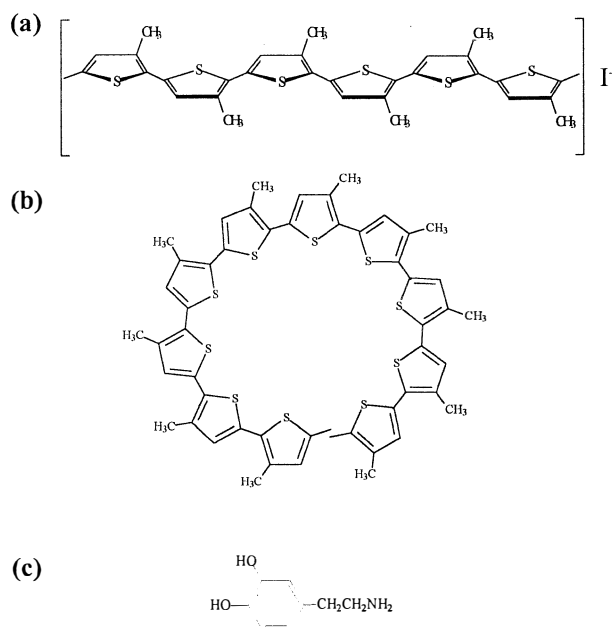


Fig. 8. Structures of [P(3MTp)] and dopamine. (a) Linear structures of [P(3MTp)/I], (b) Coil structure of [P(3MTp)/I], and (c) structure of dopamine.

not found on the surface of the film but could be in the bulk of the film or covered by the dopant.

These XPS results conform to the sequence previously published by Tourillon [15] that P(3MTp) polymer may have two models. One model would lead to a linear structure for the polymeric structure as shown in Fig. 8a. Another model corresponds to a coil structure Fig. 8b. The diameter of the coil and the number of monomeric units can be theoretically calculated and lead to 11 3-methylthiophene units for one loop of the coil. In this coil configuration, the iodide ( $I^-$ ) from TBAI dopant intercepts between the 3-methylthiophene molecular planes of two superimposed loops, the inner hole of the coil remaining empty. The sulfur-atom in the 3-methylthiophene monomer is oriented towards the inner coil as shown in Fig. 8b [15]. There is a high concentration of dopant present on the surface as shown by the high intensity of the typical doublet iodine peak which covers the film thus account for the weak S atom peak intensity.

**XPS analysis on P(3MTp) film exposed to DA.** The structure of DA as shown in Fig. 8 consists of a benzene ring with two hydroxyl group at *ortho* position attached to the ring and an amino substituted ethyl group also attached to the ring at *para* position to one of the hydroxyl group.

The elemental XPS peaks for C 1s, O 1s, N 1s, and I 3d are indicative of similarities in elemental analysis of the near surface region of the fresh P(3MTp)/I film and the one exposed to 1 mM DA solution are shown in Table 2. The increase in the intensity of the C 1s and O 1s peaks are characteristics of the presence of DA at the surface of the film as shown in Fig. 5b.

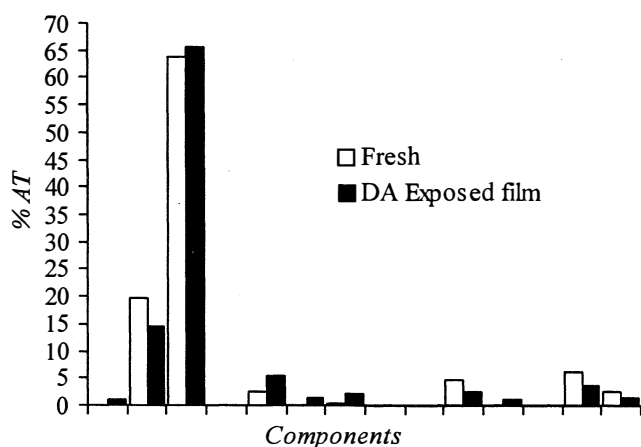


Fig. 9. Chart of elemental components comparing before and after exposure to 1 mM dopamine solution.

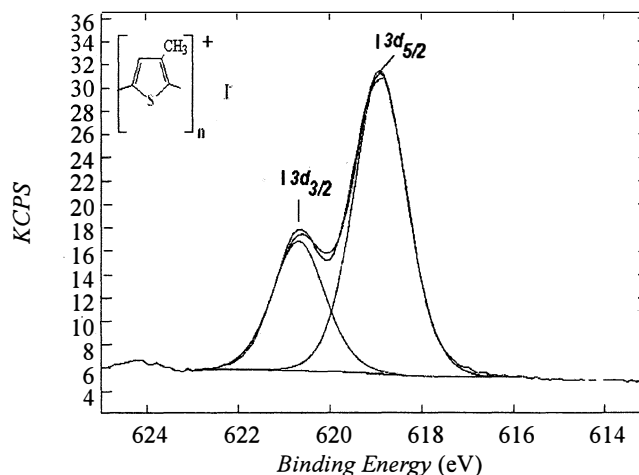
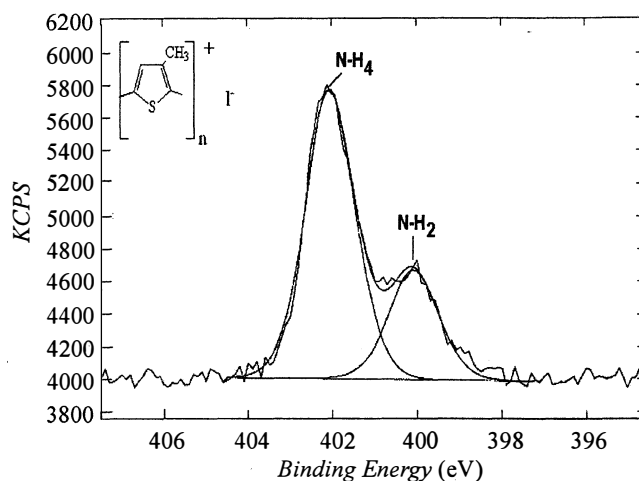


Fig. 11. [P(3MTp)/I] film on Pt wire exposed to 1 mM dopamine. (a) N 1s XPS core level spectrum and (b) I 3d XPS core level.

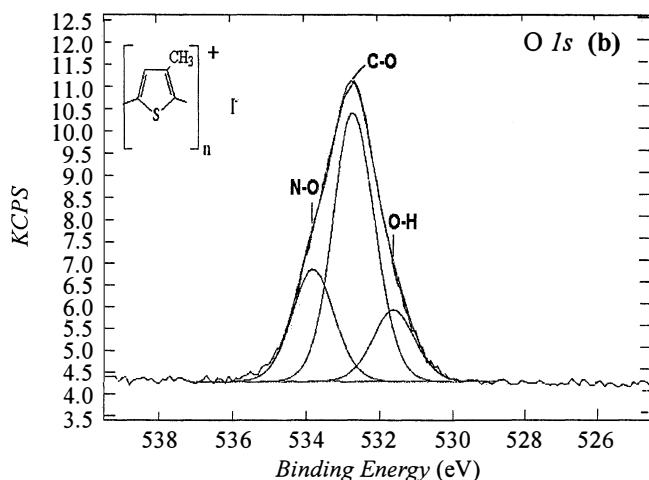
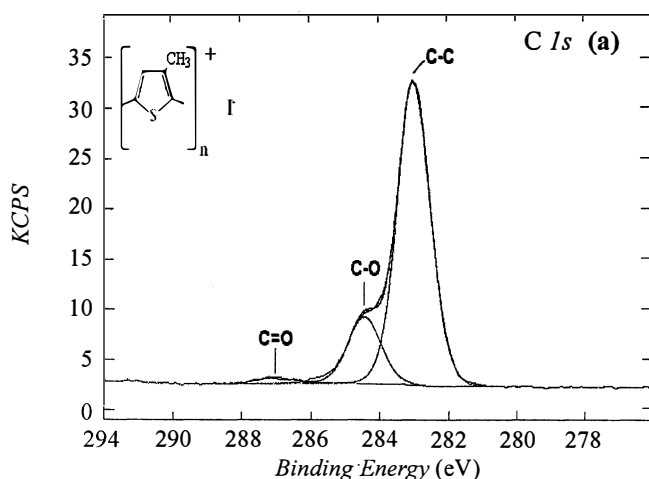


Fig. 10. [P(3MTp)/I] film on Pt wire exposed to 1 mM dopamine. (a) C 1s XPS core level spectrum with contributions from C-C, C-N and C-O atoms and (b) O 1s core level spectrum curve fit with contributing oxygen species.

The carbon 1s photoelectron spectrum of the film exposed to 1 mM DA was deconvoluted into three component peaks as shown in Fig. 10a. The largest peak centering at  $E_b \sim 285$  eV corresponds to the aromatic carbon [13] of the P(3MTp) ring system similar to the fresh film surface. The peak at  $E_b \sim 286$  eV is assigned to C-O specie [14], the third peak centering at  $E_b \sim 289$  eV corresponds to C = O component which is indicative of the presence of DA on the surface causing the film to be oxidized. The oxygen 1s photoelectron spectrum of the film exposed to 1 mM DA was deconvoluted into three component peaks as shown in Fig. 10b. There was a considerable increase in the intensity of the oxygen peaks on the P(3MTp)/I film exposed to the DA solution (Fig. 9) than on the fresh film. The peak centering at  $E_b \sim 534$  eV corresponds to N-O species while the peak at  $E_b \sim 533$  eV is assigned to C-O components indicating oxidation of the P(3MTp)/I film. The third peak at  $E_b \sim 532$  eV corresponds to O-H species indicating the presence of DA on the surface of the film.

The nitrogen 1s photoelectron spectrum was deconvoluted into two components as shown in Fig. 11a. The largest peak at  $E_b \sim 402$  eV corresponds to N-H<sub>4</sub> specie [14] indicating nitro-

gen coming from the ammonium ion ( $\text{NH}_4^+$ ) of the dopant. The second peak centering at  $E_B \sim 400$  eV is assigned to  $\text{NH}_2$  specie [14] indicating the presence of amino group ( $\text{NH}_2$ ) from DA. The iodine  $3d$  photoelectron spectrum was deconvoluted to a doublet peak (Fig. 11b) with binding energies centering at  $E_B \sim 619$  eV corresponding to  $\text{I } 3d_{5/2}$  and at  $E_B \sim 621$  eV assigned to  $\text{I } 3d_{3/2}$  [14], indicating the presence of iodine on the surface of the film similar to the fresh P(3MTp)/I film but the intensity of the peak was reduced to half revealing that iodine on the surface maybe partially covered by DA after soaking, or the possible leaching out of iodide from the surface of the film to the solution. DA deposited on the surface of the film is trap on the crevices at the surface leading to poisoning or fouling of the film. This is clearly demonstrated by the change in the surface morphology and discoloration of the film as shown in Fig. 4b and d.

## CONCLUSION

Modifying electrodes with poly(3-methylthiophene) film by cyclic voltammetry has been investigated to study the electrochemical behavior of DA on the surface of the conducting film. The electrode was modified using the following optimized electrochemical polymerization parameters summarized in Table 3.

This study deals with the development of an electrode modified with P(3MTp)/I for electrochemical characterization of DA. The electrode is made of 3 mm platinum disc coated with P(3MTp)/I film doped with tetrabutylammoniumiodide. Increasing the number of measuring cycles to five cycles during polymerization gave the highest peak intensity to DA. Optimized polymerization conditions include: 0.1 M tetrabutylammonium iodide dopant, 0.05 M 3-methylthiophene monomer, five measuring cycles and freshly prepared polymerizing solution is needed for every polymerization.

**Table 3. Optimum electrochemical polymerization parameters.**

<b>Polymerization Solution:</b>	
Dopant	0.10 M tetrabutylammoniumiodide
Monomer concentration	0.05 M 3-methylthiophene
Solvent	Acetonitrile
<b>Polymerization Condition</b>	
Purging Gas	Without stirring
Purging time	Nitrogen gas
$E$ window	10 min
Scan rate	0.0 V to 1800 mV
Solution	50 mV/s
Measuring cycles	Fresh solution
Buffer Composition	Five cycles
Buffer pH	Tris buffer
	pH 7.0

The modified electrode's response on DA is enhanced when tris buffer at pH 7.0 is used as an electrolyte. Use of P(3MTp)/I as an electrode modifier increases the peak intensity of the electrode for DA while decreasing the electrode response to AA interferant.

SEM micrographs of the P(3MTp)/I film revealed that a change in surface morphology was observed after exposure to DA from dark or almost black color to white discoloration was observed after the film was exposed to 1mM DA solutions. XPS studies also verified that the presence of DA on the surface of the film causes the film to be oxidized based on the increase of elemental peak intensities of C  $1s$  component and O  $1s$  component and the decrease in I  $3d$  as compared to the elemental analysis done on the fresh P(3MTp)/I film. The presence of the C = O component, O-H component, the  $\text{NH}_2$  component are indicative of the presence of DA on the P(3MTp)/I film surface. The low electrode reproducibility and short electrode lifetime are due to the gradual poisoning of the electrode surface as it is exposed to DA. There is a need to use fresh film surface for every measurement to maintain high sensitivity and reproducibility.

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