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Enhanced sensing of ascorbic acid, dopamine and serotonin at solid carbon paste electrode with a nonionic polymer film

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ABSTRACT

A nonionic poly(2-amino-5-mercapto-thiadiazole) film was electrodeposited on a solid carbon paste electrode via a potential scanning procedure, and used for amperometric sensing of ascorbic acid (AA), dopamine (DA) and serotonin (ST). The highly electrocatalytic activity of the sensor to the three analytes was demonstrated from the sensitive and well separated voltammetric signals. The polymer film did not show significant accumulation effect on all the three species, reducing the fouling and deactivation of the electrode surface as well as the mutual interference among the analytes. The sensor achieved amperometric sensitivities of 1.92 nA $(\text{nmol L}^{-1})^{-1}\,\text{cm}^{-2}$ to AA in the linear range of 0.025–1.95 μmol L^{-1}, 3.76 nA $(\text{nmol L}^{-1})^{-1}\,\text{cm}^{-2}$ to DA and 7.00 nA $(\text{nmol L}^{-1})^{-1}\,\text{cm}^{-2}$ to ST both in the linear range of 0.02–1.56 μmol L^{-1}. The lowest detection limits were found to be 1.5, 0.7 and 0.4 nmol L^{-1} for AA, DA and ST, respectively. This sensor was successfully employed for the successive determination of AA, DA and ST in pharmaceutical samples. The good antifouling property and reproducibility of the proposed sensor can be attributed to the nonionic polymer film without electrostatic attraction to the ionized species in the solutions.

1. Introduction

Electrochemical sensors are the subject of extensive research for developing their application in medical diagnostics, food analysis, environmental monitoring, etc. Fouling of the working electrode, resulting from the adsorption and accumulation of the interfering species, is a common and serious interference in electrochemical sensing [1–3]. Some effective strategies have been developed for minimizing electrode fouling, which is very important for achieving satisfactory repeatability of the electrochemical response. One approach to minimize fouling is the use of self-cleaning heated electrodes [1]. A combined thermal and electrochemical conditioning step was recently reported for minimizing electrode blocking in dopamine (DA) determination [2]. Electrochemically activated carbon nanotubes also exhibited an improved determination of DA with minimal electrode fouling [4]. In addition, surfactants have been used to minimize accumulation of reaction products from the conversion of the analytes such as serotonin (ST) [3]. Finally, the fouling effects can be reduced by developing novel electrode modifiers as done in the determination of ascorbic acid (AA) [5].

As a group of small biomolecules that are electroactive, AA, DA, ST, adrenalin, norepinephrine and uric acid have been attracting great interest in bioelectroanalysis because they are extremely important analytes in clinical field. AA is a soluble vitamin widely present in many biological fluids and in multivitamin preparations; DA, ST, adrenalin and norepinephrine are vital neurotransmitters distributed in the brain for message transfer in the mammalian central nervous system; and uric acid is the primary end product of purine metabolism. Recent years, many electrode modification strategies have been developed for improving the determination of them in sensitivity and selectivity [5–30], using electrode modifiers such as conducting polymers [11–17,25,26,28], nanoparticles [7–9], carbon nanotubes [7,13,16,19,22,27] and special carbon materials [22–24], and other inorganic and organic compounds [5–7,20–22]. In most cases, composite materials were prepared for the modification of electrodes [7–10,13,16,20–22,25,27,29,30]. The electrode fouling by oxidation products is still one of the main problems related to electrochemical determination of AA, DA and ST [2,3,5,17,31,32], among which ST is a more challenging analyte in this respect [3].

Conducting polymers are favorable materials for electrode-modifying, because of their straightforward preparation, good stability, high sensitivity and desirable film thickness [10,12,33]. With extended π-conjugated systems, the polymers function as redox mediators for the electron transfer between electrodes and the analytes [31]. The conducting polymers are also known to be

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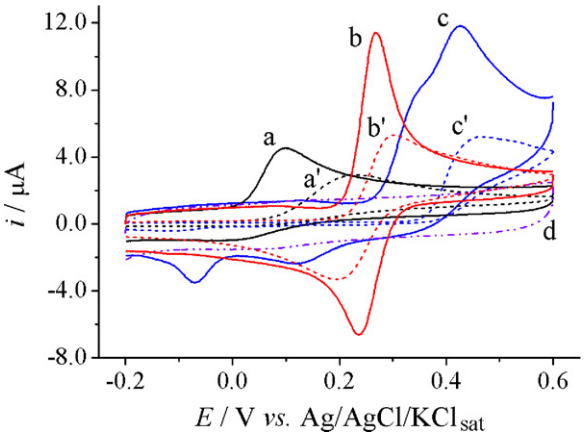

Fig. 1. CV responses of bare sCPE (a′–c′) and PAMT/sCPE (a–d) to 100 μmol L^{-1} AA (a′ and a), 100 μmol L^{-1} DA (b′ and b), 100 μmol L^{-1} ST (c′ and c) and no analytes (d) in the buffer of 0.2 mol L^{-1} BRS (pH 5.0) + 0.5 mol L^{-1} KCl, scan rate 50 mV s^{-1}.

compatible with biological molecules in a neutral aqueous solution [33]. As a general strategy for improving the selectivity and sensitivity, the polymer films can be positively or negatively charged by introducing ionizable groups onto the polymer backbones [25]. The ionized films adsorb the analytes with the opposite charge by the electrostatic attraction, while electrostatically blocking access of the species with the like charge. A representative case is the electropolymerized film of Eriochrome Cyanine R with a large number of negative charge groups ($-SO_3^-$ and $-COO^-$) in pH 7 solution, which was used for enrichment and determination of the cationic species ST and norepinephrine, without the interferences from the anionic species UA and AA [26]. The same was also achieved at the Nafion membrane with sulfonic groups [25] and the poly(3,5-dihydroxy benzoic acid) film with carboxylic groups [16]. On the contrary, the polymer film of N,N-dimethylaniline with positive charge in its backbone was used for amperometric determination of the anionic species AA [34]. Simultaneous determination of these differently charged analytes can still be realized at such ionized polymer electrodes by selecting the proper pH of the electrolytes according to their pK_a values [11,12]. However, the electrostatic adsorption of the charged species on the film surface probably aggravates the fouling of electrodes, so this strategy is more suitable for the disposable sensors.

Recently, we fabricated a polymer film sensor by electrodepositing poly-2-amino-5-mercapto-1,3,4-thiadiazole (PAMT) on a

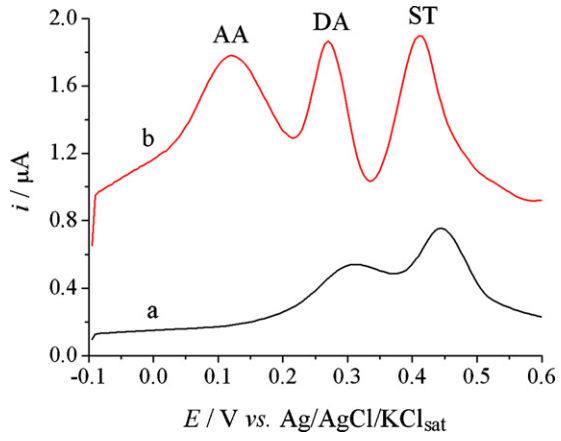

Fig. 2. DPV responses of bare sCPE (a) and PAMT/sCPE (b) to 30.0 μmol L^{-1} AA, 5.0 μmol L^{-1} DA and 5.0 μmol L^{-1} ST mixed in the buffer of 0.2 mol L^{-1} BRS (pH 5.0) + 0.5 mol L^{-1} KCl, pulse amplitude 50 mV, pulse width 50 ms, sample width 40 ms and pulse period 100 ms.

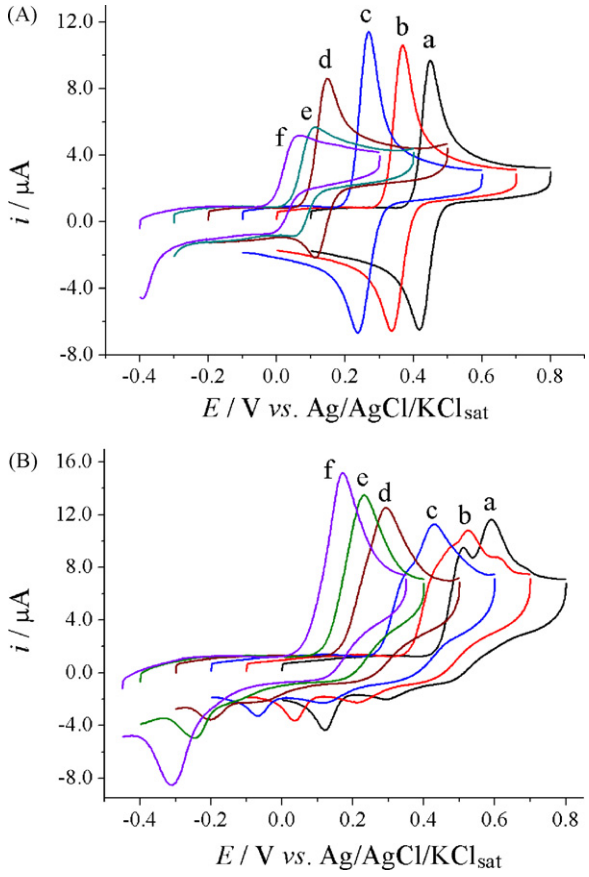

Fig. 3. CVs of 100 μmol L^{-1} DA (A) and 100 μmol L^{-1} ST (B) at PAMT/sCPE in the buffers with different pHs (a → f): 1.8, 3.3, 5.0, 7.4, 8.4, 9.3, scan rate 50 mV s^{-1}.

solid carbon paste electrode (sCPE) for the selective determination of two flavonoid isomers with the same electroactive moiety [35]. The electropolymerized polymer showed no accumulation or repulsion effect on the anionic redox couple $[Fe(CN)_6]^{3-/4-}$, indicating the absence of ionized groups at the polymer backbone. This nonionic polymer film displayed outstanding electron-transfer properties providing a possibility to accelerate the sluggish charge-transfer kinetics of some organic/biomolecules, whether positively or negatively charged. The film electroneutrality might hopefully contribute to antifouling property and therefore to sensitivity and reproducibility of the sensors, since no electrostatic attraction exists between the film itself and the analytes or their electrolysis products. The objective of this work is to assess the antifouling property of a nonionic polymer film against ionized species present in electrolyte or produced at electrode surface. AA, DA and ST are selected as the model analytes assayed at PAMT/sCPE, because they are prone to foul electrode due to adsorption of their oxidation products, and exist in differently charged forms in near neutral pH solution (pK_a: AA 4.1, DA 8.9 and ST 9.8).

2. Experimental

2.1. Chemicals and solutions

Spectrograde graphite powders (320 mesh) and spectrograde paraffin wax (solidification point 46–48 °C) were purchased from Shanghai Chemical Works for preparing the solid carbon paste electrode. Reagent-grade AMT was from Alfa Aesar, a Johnson Matthey Company (Ward Hill, MA, USA). AA, DA and ST (99% pure each) were purchased respectively from Chemical Regent Company of Shanghai (Shanghai, China), Acros Organics (Geel, Belgium) and

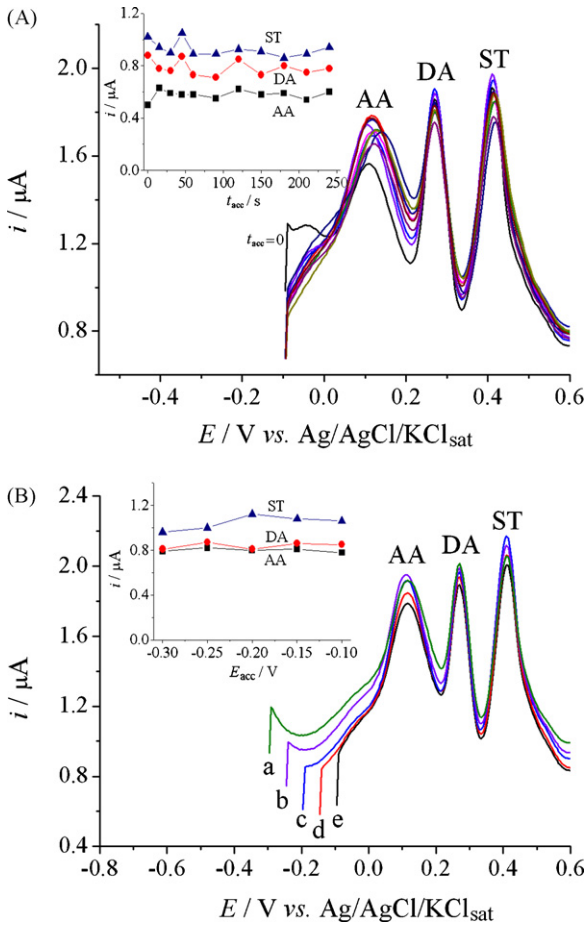

Fig. 4. Effects of t_{acc} (A, E_{acc} = –0.1 V) and E_{acc} (B, t_{acc} = 60 s) on the DPV responses of PAMT/sCPE to 30.0 μmol L^{-1} AA, 5.0 μmol L^{-1} DA and 5.0 μmol L^{-1} ST mixed in the buffer of pH 5.0. The insets show the plots of DPV peak current *vs.* t_{acc} (A) or E_{acc} (B). The pulse parameters are the same as in Fig. 2.

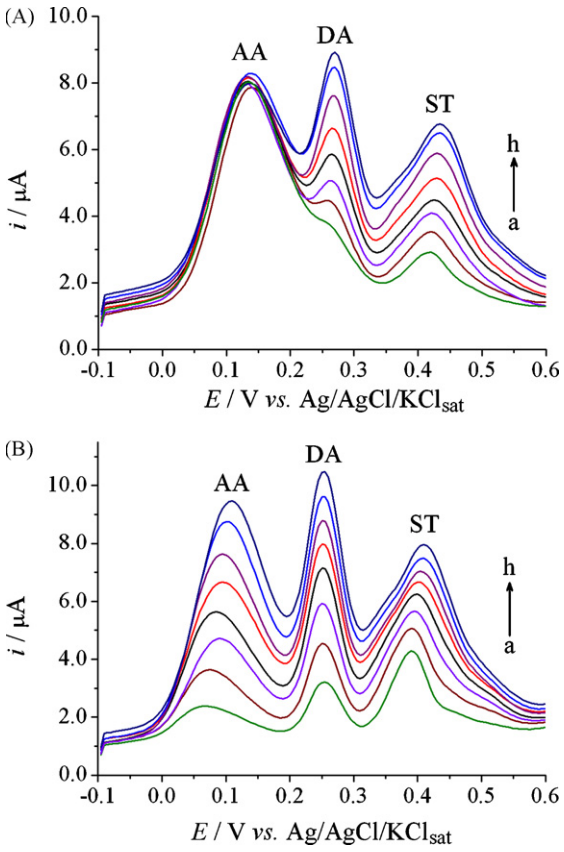

Fig. 5. DPV responses of PAMT/sCPE to AA, DA and ST mixed in the buffer of 0.2 mol L^{-1} BRS (pH 5.0) + 0.5 mol L^{-1} KCl. *c*(DA) and *c*(ST) (a → h): 5, 10, 15, 20, 25, 30, 35, 40 μmol L^{-1}; (A) *c*(AA) = 240 μmol L^{-1}; (B) *c*(AA): 30, 60, 90, 120, 150, 180, 210, 240 μmol L^{-1} (a → h). The pulse parameters are the same as in Fig. 2.

Alfa Aesar, and were used as received. All the other chemicals were of analytical grade. High pure N_2 was used to deaerate the solutions. Doubly-distilled water from an all-glass distillatory apparatus was used.

The modifier of the electrode was an aqueous solution containing 0.5 mmol L^{-1} AMT and 0.1 mol L^{-1} H_2SO_4. The supporting electrolytes for sensing measurements were 0.2 mol L^{-1} Britton–Robinson buffer (BRS) plus 0.5 mol L^{-1} KCl with different pHs. Stock solutions of 1.0 mmol L^{-1} AA, DA and ST were prepared in double distilled water, respectively, and mixed and diluted to various desired concentrations with the supporting electrolytes before being used. All the stock solutions were kept at 4 °C in a refrigerator.

2.2. Electrode preparation

The carbon paste was made from dry graphite powders and paraffin wax (5:2, w/w). The resulting 'solid' CPE have some advantages such as low residual currents, improved reproducibility, robust in operation and better stabilization against organic solvents than oily liquids [36]. The wax portion of the electrode provides an organic surface for easy stretch of the conducting polymer film growing on the electrode [35].

The electrode body was a polystyrene hollow tube with inner diameter of 2.5 mm, which was tightly impacted with a copper rod leaving a cavity with a depth of 2 mm at one end of the tube. The solid wax was heated until molten, and then mixed with the graphite powders in an agate mortar with a glass rod until a well blended paste was obtained. The paste was firmly pressed into the cavity of the electrode body forming a bare sCPE with a geometric area of 4.9 mm^2.

The bare sCPE was polished successively with 800–4000 grit emery papers, and then ultrasonically washed in double distilled water for 5 s, followed by repetitive potential cycling between −0.4 and 1.6 V at a scan rate of 0.5 V s^{-1} in 1.0 mol L^{-1} KCl until the background current was obtained. Afterwards, the cleaned substrate was modified by 100 cycle potential scan between −0.2 and 1.7 V (*vs.* Ag/AgCl/KCl_{sat}) in the AMT (+H_2SO_4) solution, at a scan rate of 50 mV s^{-1}. In this way, PAMT film was electrodeposited on the substrate forming PAMT-modified carbon paste electrode (PAMT/sCPE). The prepared electrode was rinsed with doubly-distilled water and cleaned by potential cycling in 1.0 mol L^{-1} KCl to remove adsorbed substances.

2.3. Apparatus and procedures

Electrochemical experiments including cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry were carried out on a CHI660B electrochemical analyzer (Chenhua, Shanghai, China). A three-electrode system was used, which was composed of a working electrode (either bare sCPE or PAMT/sCPE), a saturated Ag/AgCl/KCl reference electrode, and a platinum coil counter electrode. All experiments were conducted at room temperature (21 ± 1 °C). Before measurement the electrolyte was bubbled with high pure N_2 for about 10 min to remove dissolved oxygen.

3. Results and discussion

3.1. Comparison of PAMT/sCPE and bare sCPE in electrocatalytic activity

The voltammetric behaviors of AA, DA and ST were individually investigated at bare sCPE and PAMT/sCPE. The CV responses obtained at the two electrodes show some significant differences in electrocatalytic activity to the three analytes (Fig. 1). The bare sCPE showed three oxidation peaks at 0.23 V, 0.30 V and 0.47 V, successively corresponding to AA, DA and ST. At PAMT/sCPE, the peak potentials of AA, DA and ST negatively shifted to 0.10 V, 0.27 V and 0.43 V, respectively. Thus the small peak separation of 0.07 V between AA and DA was increased up to 0.17 V with the modification of the electrode. Meanwhile, the peak currents at the PAMT/sCPE were enhanced 1.5-fold, 2.2-fold and 2.2-fold for AA, DA, and ST, respectively, in comparison with those at the bare sCPE.

An interesting observation is the broad oxidation peak of ST (Fig. 1, curves c′ and c), which is an overlapping signal suggesting that ST was subjected to successive oxidation. It has been thought that the oxidation product of ST (a corresponding ketone) could undergo chemical reaction to form an intermediate that is easily oxidizable, and this intermediate is believed to be the reduced hydroquinone [37]. According to this mechanism, 4 electrons are involved in the oxidation reaction of ST, favorable to sensitive determination of ST.

The bare sCPE and PAMT/sCPE were compared also in a mixture of the three analytes by DPV (Fig. 2). The DPV response obtained at the bare sCPE presented only two peaks with relatively low peak currents (curve a), one at around 0.31 V being the overlapping signal of AA and DA, and another at around 0.44 V corresponding to ST. In the case of PAMT/sCPE (curve b), three greatly increased peaks appeared at around 0.12 V, 0.27 V and 0.41 V attributed to AA, DA and ST, respectively. The peak separations were 0.15 V between AA-DA and 0.14 V between DA-ST, allowing simultaneous determination of the three analytes.

3.2. Effects of pH, accumulation time, accumulation potential and concentration

The pH effect of the buffer on the oxidation of the analytes at PAMT/sCPE was examined. The oxidation peak potentials of AA, DA and ST shifted negatively with increasing pH (CVs of DA and ST shown in Fig. 3), due to their oxidation mechanisms all involving both electron and proton transfer [20,37,38]. The oxidation peak currents of DA in acidic buffers were higher than in basic buffers with a maximum at about pH 5.0 (Fig. 3(A)). This is contrary to the result reported for nano-Pd/poly(3-methylthiophene)/Pt electrode, at which the DA showed the minimum oxidation peak current at pH 5.0 [17], indicating different electrocatalytic mechanisms between the two modified films. Similarly, basic buffer was also unfavorable to the oxidation of AA at PAMT/sCPE (not shown). As for the oxidation of ST, the peak current showed little change in the acidic media but increased with increasing pH in the alkaline range (Fig. 3(B)). The peak of ST was broadened or even split in acidic buffers showing two separated oxidation steps, unfavorable for sensitive voltammetric determination; nevertheless, this would not affect the sensitivity of amperometric determination at a moderately positive potential. On an overall consideration of the three analytes, the pH 5.0 buffer was selected in this work.

Fig. 4(A) presents the DPV curves of a mixed sample recorded after different accumulation times (t_{acc}). The adsorptive accumulation of the analytes on the electrode surface was performed at the starting scanning potential (E_{acc}). The result shows that the increase of t_{acc} did not induce a significant change in the peak currents (background subtracted) of the three species (Fig. 4(A), the inset). The

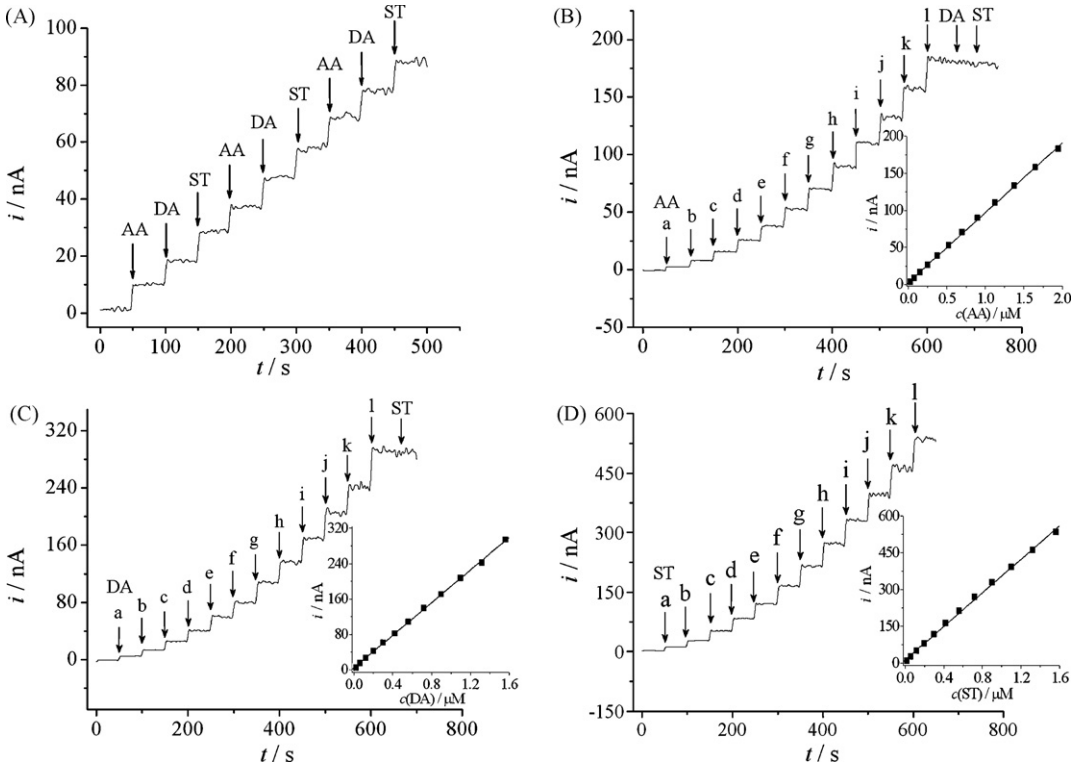

Fig. 6. Amperometric responses of PAMT/sCPE to successive addition of AA, DA and ST to the stirred 0.2 mol L^{-1} BRS solution (20 mL, pH 5.0, 0.5 mol L^{-1} KCl), along with the resulting calibration plots (insets). (A) E_{app} = 0.55 V, c(AA/DA/ST) was increased by 50/40/30 nmol L^{-1} upon each addition; (B) E_{app} = 0.20 V, c(AA) = 0.025, 0.075, 0.15, 0.25, 0.375, 0.525, 0.70, 0.90, 1.125, 1.375, 1.65, 1.95 μmol L^{-1} (a → l); (C) E_{app} = 0.32 V, c(DA) = 0.02, 0.06, 0.12, 0.20, 0.30, 0.42, 0.56, 0.72, 0.90, 1.10, 1.32, 1.56 μmol L^{-1} (a → l); (D) E_{app} = 0.55 V, c(ST) = 0.02, 0.06, 0.12, 0.20, 0.30, 0.42, 0.56, 0.72, 0.9, 1.10, 1.32, 1.56 μmol L^{-1} (a → l).

Table 1
Analytical parameters of PAMT/sCPE for AA, DA and ST determination.

Analytes	Linear equation (i/nA *vs.* c/nmol L^{-1})	Sensitivity nA (nmol L^{-1})$^{-1}$ cm^{-2}	Linear range (μmol L^{-1})	LOD (nmol L^{-1}) (S/N = 3)
AA	i = 3.06239 + 0.09399c (R = 0.9996)	1.92	0.025–1.95	1.5
DA	i = 4.44566 + 0.184246c (R = 0.9997)	3.76	0.02–1.56	0.7
ST	i = 12.3673 + 0.342946c (R = 0.9991)	7.0	0.02–1.56	0.4

same was observed with different E_{acc} (Fig. 4(B), the inset). Since no significant accumulation effect was found, the adsorption of the analytes on the surface of PAMT film is believed to be negligible. The absence of adsorption is desirable for successive sensing, not only avoiding the electrode fouling and deactivation caused by the adsorbates, but also reducing the mutual interference due to competitive adsorption of the analytes. As discussed in our previous paper [35], the electrocatalytic activity of the PAMT/sCPE is based on the accelerated charge transfer across the electrode interface, but not on the electrostatic accumulation of analytes on the film surface.

The concentration (c) effect on the DPV response was shown in Fig. 5. The increase in DA and ST concentrations enhanced their respective peak currents, without affecting significantly the peak current of AA whose concentration was held constant (Fig. 5(A)). This indicates that the oxidation reaction of AA was not interfered by the presence of the other two species. The same was also found for both DA and ST. While all the three species increased in concentration by a constant ratio (Fig. 5(B)), their corresponding peaks proportionally increased in intensity. This suggests that no competitive adsorption occurred on the nonionic PAMT film, although in pH 5.0 solution, the hydroxyl next to the carbonyl group of AA (pK_a = 4.1) is negatively charged, whereas the amine groups of DA (pK_a = 8.9) and ST (pK_a = 9.8) are positively charged. The data for the effect of scan rate on the CV peaks of the three analytes also do not show the characteristic of adsorbed species but support diffusion-controlled processes (data not shown). In addition, no interference was observed from common ions such as 1000-fold Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, PO_4^{3-}, BO_3^{3-}, SO_4^{2-} and CH_3COO^-.

3.3. Amperometric determination of AA, DA and ST at PAMT/sCPE

Amperometric responses of the PAMT/sCPE to the concentration changes of AA, DA and ST are presented in Fig. 6. The determination was made at an applied potential (E_{app}), by injecting a series of 50 μmol L^{-1} samples with different volumes to a stirred BRS (20 mL, pH 5.0). After each addition, the time required for the current signal to reach a stable plateau was less than 5 s, showing the fast response of the sensor.

Table 2
Analytical parameters of some newly reported electrodes for AA, DA and/or ST determination.

Modifier/electrode substrate	Method	Linear range (μmol L^{-1})	LOD (nmol L^{-1})	Concomitant compounds
[Fe(pyterpy)$_2$](SCN)$_2$/CPE [5]	DPV	AA: 8.33–2920 DA: 2.00–740	AA: 2000 DA: 1000	AA, DA
FePCNF/CPE [6]	CV	AA: 10–120	AA: 4000	–
MWCNT-silica-AuNPs/GCE [7]	CV	AA: 1000–5000	–	DA
L-Cys-GNP/GCE [8]	CV	AA: 2–800	–	AA, UA
MWCNT-AgHCFNPs/GCE [9]	CV	AA: 4–78 DA: 2.4–130	AA: 420 DA: 140	AA, DA, UA
Ag-PLV/GCE [10]	LSV	AA: 10–1000 DA: 0.5–10	AA: 3000 DA: 80	AA, DA, UA
poly(sulfonazo III)/GCE [11]	DPV	AA: 0.5–1300 DA: 0.05–470	AA: 170 DA: 30	AA, DA, UA
poly-ACBK/GCE [12]	DPV	AA: 50–1000 DA: 1–200	AA: 10000 DA: 500	AA, DA, UA
(PDDA-[PSS-MWCNTs])$_5$/graphite [13]	AM	AA: 50–1000 DA: 50–360	AA: 500 DA: 150	AA, DA, UA
p-AMT/GCE [14]	AM	AA: 0.2–800 DA: 0.2–800	AA: 0.92 DA: 0.07	–
p-ATD/GCE [15]	DPV	AA: 30–300 DA: 5–50	AA: 2010 DA: 330	AA, DA, UA, XN
MWCNT-pDBA/GCE [16]	DPV	DA: 0.1–70	DA: 10	AA
Pd-PMT/Pt [17]	DPV	DA: 0.05–1	DA: 9	AA, UA
SP-MWCNT/GCE [18]	AdSV	DA: 0.05–1	DA: 15	AA
MWCNTs/GCE [19]	DPV	DA: 3–200	DA: 800	Acetaminophen
K_2UO_2[Fe(CN)$_6$]/Pd-Al [20]	AM	DA: 1–50	DA: 410	Aminochrom
EDTMP-ZrO_2/Au [21]	DPV	DA: 0.015–4	DA: 9	AA
EPPGE-SWCNT-Fe_2O_3 [22]	SWV	DA: 3.2–31.8	DA: 360	–
Grapheme/GCE [23]	DPV	DA: 4–100	DA: 2640	AA
GCPE [24]	DPV	ST: 0.05–0.5	ST: <50	Tryptophan
Nafion/CGSPE [25]	DPV	ST: 0.02–500	ST: 5	AA, DA, UA
ECR/GCE [26]	DPV	ST: 0.05–5	ST: 50	Norepinephrine, AA, UA
MWCNTs-IL-Gel/GCE [27]	DPV	DA: 0.1–12 ST: 0.02–7	DA: 60 ST: 8	AA

MWCNT, multiwall carbon nanotube; AuNPs, gold nanoparticles; FePCNF, ferrous pentacyanonitrosylferrate; AgHCFNPs, silver hexacyanoferrate nanoparticles; ACBK, acid chrome blue K; PDDA, poly(diallyldimethylammonium chloride); PSS, polystyrene sulfonate; PLV, poly(L-valine); EDTMP, ethylenediamine-tetramethylene phosphonic acid; EPPGE, edge-plane pyrolytic graphite electrode; SWCNT, singlewall carbon nanotube; p-ATD, poly(2-amino-1,3,4-thiadiazole); pDBA, poly(3,5-dihydroxy benzoic acid); PMT, poly(3-methylthiophene); SP, screen-printed; L-cys/GNP, L-cysteine/gold nanoparticles; CGSPE, colloidal gold screen-printed electrode; ECR, Eriochrome Cyanine R; IL, ionic liquids; GCPE, glassy carbon paste electrode; UA, uric acid; AdSV, adsorptive stripping voltammetry; AM, amperometry; LSV, linear sweep voltammetry.

Table 3
Successive determination of AA, DA and ST in pharmaceuticals using PAMT/sCPE.

Sample	Labeled (mg mL^{-1})[a]	Added (mg mL^{-1})	Found (mg mL^{-1})	Recovery (%)
AA 1	200	–	205.0	–
		193.74 (n = 5)	400.5, 403.5, 397.0, 398.4, 397.3	100.5 ± 1.5
AA 2	200	–	207.4	–
		193.74 (n = 5)	406.1, 401.8, 401.7, 401.7, 399.2	100.7 ± 1.8
AA 3	200	–	205.8	–
		193.74 (n = 5)	400.6, 400.8, 400.6, 398.3, 398.6	100.0 ± 0.7
DA 1	10	–	9.99	–
		9.482 (n = 5)	19.76, 19.56, 19.56, 19.62, 19.46	101.4 ± 1.6
DA 2	10	–	10.08	–
		9.482 (n = 5)	19.71, 19.72, 19.48, 19.56, 19.48	100.4 ± 1.2
DA 3	10	–	10.10	–
		9.482 (n = 5)	19.68, 19.68, 19.87, 19.41, 19.44	100.6 ± 2.4
	Calculated (μmol L^{-1})[b]	Added (μmol L^{-1})	Found (μmol L^{-1})	Recovery (%)
Mixture 1	AA: 0.2271 DA: 0.2110 ST: 0.2000	–	AA: 0.2200	–
		AA: 0.2200 (n = 3)	AA: 0.4402, 0.4398, 0.4402	AA: 100 ± 0.1
Mixture 2	AA: 0.2271 DA: 0.2110 ST: 0.2000	–	DA: 0.2117	–
		DA: 0.2000 (n = 3)	DA: 0.4227, 0.4117, 0.4117	DA: 102.75 ± 2.75
Mixture 3	AA: 0.2271 DA: 0.2110 ST: 0.2000	–	ST: 0.2090	–
		ST: 0.2000 (n = 3)	ST: 0.4176, 0.4118, 0.4062	ST: 101.45 ± 2.83

[a] Concentrations in the injections.
[b] Concentrations in the test buffers.

Calibration plots were obtained for AA, DA and ST, respectively, from the amperometric responses to their added concentrations (see the insets). The linear equations, linear ranges, sensitivities and limits of detection (LOD) are listed in Table 1. The LODs were found to be 1.5, 0.7 and 0.4 nmol L^{-1} for AA, DA and ST (S/N = 3), respectively. Table 2 presents the analytical parameters of some newly reported modified electrodes for the determination of AA, DA and/or ST. By comparison, the PAMT modified solid carbon paste electrode used in the present work achieved more sensitive determination for all the three analytes.

The selective amperometric determination of AA can be achieved by setting E_{app} = 0.20 V, without the interference from DA and ST (Fig. 6(B)). While at E_{app} = 0.32 V, the interference from ST can be avoided for the determination of AA and DA (Fig. 6(C)). The total current from the oxidation of all three species can be measured at E_{app} = 0.55 V (Fig. 6(A)). Therefore, we can obtain three-step changes in current signal successively corresponding to the concentration of AA, DA and ST in a mixed solution, by applying potential step from 0.20 V to 0.32 V and finally to 0.55 V (see Section 3.4).

At the end of the experiment, the PAMT/sCPE was washed with twice distilled water and then cleaned by potential scanning of 30 circles between −0.4 and 1.6 V in 0.5 mol L^{-1} KCl. No Faradaic current was observed on the scan curve except for that of oxygen-evolution, indicating that the polymer film did not adsorb the analytes. The cleaned electrode was stored in an air-filled vial with a lid for the next use.

3.4. Analytical applications

The PAMT/sCPE was applied to the amperometric assay of AA in Vitamin C injection (labeled as 200 mg mL^{-1}) and DA in dopamine hydrochloride injection (labeled as 10 mg mL^{-1}), respectively, by standard addition method. The injection solutions were diluted with double distilled water by 1000 times for AA and 50 times for DA, then 20 μL of the diluted solutions or standard AA/DA solutions were successively injected into to the stirred BRS (20 mL, pH 5.0). The applied potential was 0.20 V for AA or 0.32 V for DA.

The same PAMT/sCPE was then used to determine AA, DA and ST in a mixed sample, which was 50 mL distilled water spiked with 50 μL Vitamin C injection, 1.00 mL dopamine hydrochloride injection and 10.63 mg ST. Four μL of the mixed sample was injected into the stirred BRS (20 mL, pH 5.0), then the potential was stepped from 0.20 V to 0.32 V and finally to 0.55 V at a time interval of 50 s. The resulting three steps of current response correspond to the concentrations of AA, DA and ST in the mixture, respectively. With that, the standard solutions of AA, DA and ST were severally added to the buffer solutions for the measurement of their original concentrations and recovery.

Results of the above assaying are listed in Table 3. The data indicate that AA, DA, and ST can be reliably determined from their pharmaceutical formulations, thus demonstrating the suitability of the proposed PAMT/sCPE as a sensor. The successive addition of the samples did not worsen the sensing performance, due to the good antifouling property of the nonionic polymer film.

4. Conclusions

The PAMT film-coated solid carbon paste electrode is shown to exhibit excellent performance for the oxidative sensing of AA, DA and ST. Well-defined voltammetric signals were obtained at PAMT/sCPE in the mixed samples, demonstrating good resolution to the three species. The oxidation processes occurred at PAMT/sCPE without electrostatic attraction between the ionized analytes and the nonionic polymer film, thereby reducing the fouling and deactivation of the electrode surface as well as the mutual interference among the analytes. The sensor achieved amperometric sensitivities of 1.92 nA (nmol L^{-1})$^{-1}$ cm^{-2} to AA in the linear range of 0.025–1.95 μmol L^{-1}, 3.76 nA (nmol L^{-1})$^{-1}$ cm^{-2} to DA and 7.00 nA (nmol L^{-1})$^{-1}$ cm^{-2} to ST both in the linear range of 0.02–1.56 μmol L^{-1}. The lowest detection limits were 1.5, 0.7 and 0.4 nmol L^{-1} for AA, DA and ST, respectively. The easy fabrication, high sensitivity, reproducibility and antifouling property of the nonionic polymer film make it suitable for the analytical purposes.

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