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Simple and Sensitive Electrochemical Sensor for Tyramine Determination Based on Overoxidized Poly(*o*-aminophenol) Film Modified Electrode

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A simple electrochemical sensing method was proposed for fast detection of tyramine in rice vinegar. *o*-Aminophenol (OAP) was electropolymerized on the surface of glassy carbon electrode (GCE) to form the poly(*o*-aminophenol) (POAP) film. Then the overoxidized poly(*o*-aminophenol) film modified GCE (OPOAP/GCE) was obtained by electrochemical treatment of POAP film in the alkaline solution. The modification method of GCE and detection conditions of tyramine were optimized. Electrochemical impedance spectroscopy and scanning electron microscopy were used to characterize the preparation process of OPOAP/GCE and binding ability of tyramine onto the OPOAP film. Furthermore, the electrochemical properties of OPOAP/GCE was investigated by square wave voltammetry. OPOAP/GCE, which was fabricated via cyclic voltammetry in 0.3 M perchloric acid solution with 0.01 M OAP and overoxidized in 0.09 M NaOH solution, showed good electrochemical response on tyramine. The oxidation current and the concentration of tyramine had good linear relationship in the ranges of 0.1-10 μM and 10-200 μM, respectively. The detection limit was 0.054 μM, based on the signal to noise ratio of 3. The recovery rates of tyramine in rice vinegar sample were from 95.6% to 117.2%. The sensor was simple, inexpensive, rapid, and suitable to detect tyramine in rice vinegar sample.

Keywords: poly(*o*-aminophenol), conducting polymer, electrochemical sensor, tyramine, rice vinegar

1. INTRODUCTION

Biogenic amines (BAs) are a kind of bioactive organic bases with low molecular weight, and widely exists in many kinds of plants, animals and food products. They are the normal physiological

components and participate in several metabolic processes of living organisms. BAs are usually produced by decarboxylation of aminoacids, which is one of the important chemical markers of bacterial corruption in food. The BAs content can be regarded as an indicator of food freshness [1,2]. Tyramine, i.e. p-hydroxyphenylethylamine, is one of the well-recognized BAs and generated by the decarboxylation of tyrosine through tyrosine decarboxylase derived from the bacteria in the food [3]. Tyramine mostly present in fermented foods [4] and beverages [5,6], meat and meat products [7], fish [8] and fish products [9,10], dairy products [11,12], etc. Normally, during the food intake process in the human gut, low amounts of BAs are metabolized to physiologically less active degradation products. While excessive intake of BAs from foods with high concentrations of tyramine may cause hypertension and migraine headaches [13,14]. Consequently, it's extremely significant to establish a sensitive and rapid detection technology for the determination of tyramine or other BAs, which will play an important role in promoting the quality of food safety and safeguarding the health of people [3,15].

In recent years, tyramine and/or other BAs have been determined by several techniques, mainly including chromatography, capillary electrophoresis and biosensors. Although chromatography such as liquid chromatography (LC) [16], gas chromatography (GC) [17] and thin-layer chromatography (TLC) [18] can offer high separation efficiency, accuracy and sensitivity, it usually requires time consuming and complex pretreatment steps, which make it difficult to achieve the rapid detection. Capillary electrophoresis (CE) [19] is famous for its low cost, simple instrument and rapid separation, but its reproducibility is poor. Biosensor [9] has advantages of high sensitivity, strong specificity and easy to miniaturization, but the source and biological activity of enzyme restrict its practical application ability [20,21]. So far, the non-biological electrochemical sensor for the detection of tyramine based on macromolecule polymerization has been seldom reported.

During the past decades, the polymer film-modified electrodes (PFMEs) had been researched increasingly [22-25]. The polymer film has wide application prospects because of its more active sites, good electrochemical performance and stability. Moreover, some simple and convenient preparation methods of PFMEs have been developed, such as dip-coating and electrochemical polymerization. Immobilising the polymer materials on the surface of electrodes can prevent interferences and electrode fouling [24]. The PFMEs have a long service life. In addition, the performance of electrodes can be regulated by bonding the various electroactive groups to the polymer film and/or controlling thickness of film by selection of experimental parameters during the electropolymerization process [23,26]. Therefore, it is remarkable to research and develop the PFMEs in life science, material science, food science and other fields.

Among the polymeric materials, polyaniline has been thoroughly researched and widely applied to fabricate modified electrodes [27,28]. And the aniline derivatives, such as *o*-aminophenol (OAP) has also become one of the most interesting research objects [29,30]. Compared with the aniline, OAP, an electroactive functional monomer, has more active groups and can be easily electropolymerized on various substrate materials to form compact poly(*o*-aminophenol) (POAP) films with hydrophilic, hydrophobic and basic functional groups, and so on. The electroactive POAP films can be formed on different electrode surface (such as gold, platinum, carbon) via electropolymerization in the acidic aqueous solution [30]. However, no electroactive films are obtained in neutral or alkaline

medium. To our knowledge, OAP is playing an important role in the development of new polymeric materials and has not been used for the determination of tyramine.

In this work, an electrochemical sensing method for tyramine determination was established by electropolymerizing OAP on the surface of glassy carbon electrode (GCE), and the resulting POAP/GCE was electrochemically treated in the alkaline solution to form overoxidized POAP film modified GCE (OPOAP/GCE). The modification method of GCE and detection condition of tyramine were optimized. Square wave voltammetry (SWV) was used to investigate the electrochemical properties (linear relationship, reproducibility and stability, etc.) of OPOAP/GCE. The results indicated that the modified electrode has wide linear range, relative low detection limit, fast response, and good reproducibility and stability. Furthermore, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) were employed to characterize the preparation process of OPOAP/GCE and binding ability of tyramine onto the OPOAP film. Finally, the sensor was applied to detect tyramine content in commercial rice vinegar samples. At the same time, the accuracy of proposed method was also investigated by high performance liquid chromatography (HPLC).

2. MATERIALS AND METHODS

2.1. Reagents and solutions

The BAs such as tyramine hydrochloride, histamine diphosphate, phenylethylamine, cadaverine hydrochloride, putrescine hydrochloride, spermine, spermidine and tryptamine were purchased from Sigma-Aldrich. *o*-Aminophenol was supplied by Sinopharm Chemistry Co. Ltd. (China). *o*-Phenylendiamine (purity≥95.0%) was obtained from Sigma-Aldrich. Pyrrole was purchased from Aladdin Chemistry Co. Ltd. (China). The 0.1 M phosphate buffer solution (PBS, pH 7.0) was prepared with Na_2HPO_4 and NaH_2PO_4. The standard solutions of BA were daily prepared by 0.1 M PBS (pH 7.0). All reagents and chemicals were of analytical reagent grade and used without further purification. All aqueous solutions were prepared with ultrapure water (resistivity, 18.2 MΩ cm) from a NW Ultra-pure Water System (Heal Force).

The commercial rice vinegar was obtained from the local market in Guangzhou (China) and used as a real sample model. The vinegar was diluted with PBS (pH 7.0), and the pH value was adjusted by NaOH before use.

2.2. Apparatus and procedures

All electrochemical experiments were performed with a CHI1030B multichannel electrochemical analyzer (CH Instruments, Shanghai Chenhua Co., China). A conventional three-electrode system was used with an Ag/AgCl (saturated KCl) electrode as the reference electrode, a platinum wire as the auxiliary electrode, and a GCE or modified GCE (3 mm in diameter) as the working electrode. All potentials given below were relative to Ag/AgCl (saturated KCl) electrode.

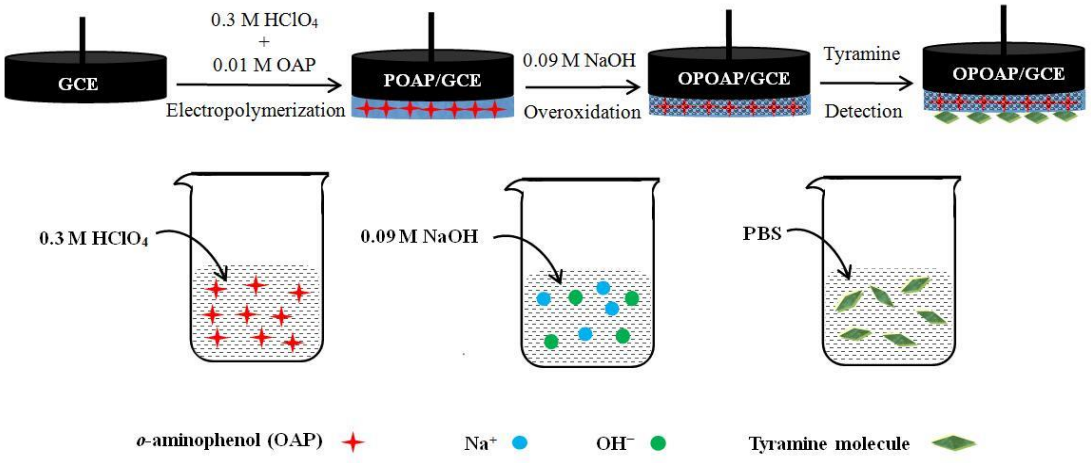
The cyclic voltammetry (CV) measurements were performed in 0.1 M PBS (pH 7.0) containing tyramine of different concentration in the potential range from 0.2 V to 1.2 V at the scan rate of 50 mV s^{-1}. The SWV experiments were carried out by scanning the potential from 0.2 V to 1.2 V with the pulse amplitude of 25 mV, frequency of 15 Hz, and a potential increment of 4 mV. The EIS measurements were carried out in a background solution of 5 mM $K_3Fe(CN)_6$ + $K_4Fe(CN)_6$ in 0.1 M KCl at a bias potential of 0.227 V in the frequency range from 0.1 Hz to 100 kHz, using an alternative voltage of 5 mV. All electrochemical measurements were referred to Ag/AgCl (saturated KCl) electrode and performed at room temperature.

The pH values of solutions were measured by a STARTER-300 portable pH meter (Ohaus instruments, Shanghai Co., China). The HPLC measurements were performed by waters 2695 chromatography with waters C_{18} column (250 mm×4.6 mm, 5 μm) and ultraviolet detector (Waters, USA). SEM images were obtained by an EVO special edition scan electron microscope (Zeiss, Germany).

2.3. Preparation of the OPOAP/GCE

Prior to modification, GCE was first polished successively with 1.0 μm, 0.3 μm and 0.05 μm alumina slurry to produce a mirror like surface. Then it was sonicated thoroughly in mixture of nitric acid and water (1:1 v/v), anhydrous ethanol and ultrapure water for two minutes, respectively. The polished GCE was pretreated in 0.5 M H_2SO_4 with cyclic voltammetry in potential range from -1.0 V to 1.0 V at a scan rate of 50 mV s^{-1} until a stable voltammetric response was obtained.

The POAP/GCE was fabricated via cyclic voltammetry in (-0.5)-1.5 V for 14 cycles in 0.3 M perchloric acid solution with 0.01 M OAP. In order to remove the redundant OAP functional monomer embedded in the POAP film, POAP/GCE was cleaned with ultrasonication for one minute in anhydrous ethanol and water, respectively. Then the cleaned POAP/GCE was treated electrochemically in 0.09 M NaOH solution by cyclic scan in the potential range of (-0.15)-1.0 V at a scan rate of 50 mV s^{-1} for 16 cycles. The resulting modified electrode (OPOAP/GCE) was dried at room temperature and used for electrochemical investigations (Scheme 1).



Scheme 1. The scheme of the preparation and determination procedures of OPOAP/GCE

3. RESULTS AND DISCUSSION

3.1. Selection of detection method

The electrochemical behavior of tyramine at GCE was studied by CV and SWV, respectively (Figure 1). No peak was observed in the absence of tyramine on both CV and SWV curves (curve a), whereas CV and SWV curves of 10 μM tyramine displayed a strong peak at around 0.65 V corresponding to the oxidation of tyramine, respectively (curve c), indicating tyramine was an electroactive compound. Differing from CV response of 1.0 μM tyramine at GCE (curve b in Figure 1A), 1.0 μM tyramine at GCE showed a obvious SWV response (curves b in Figure 1B), suggesting that SWV had higher sensitivity than CV. Therefore, SWV was used in the succeeding determination of tyramine.

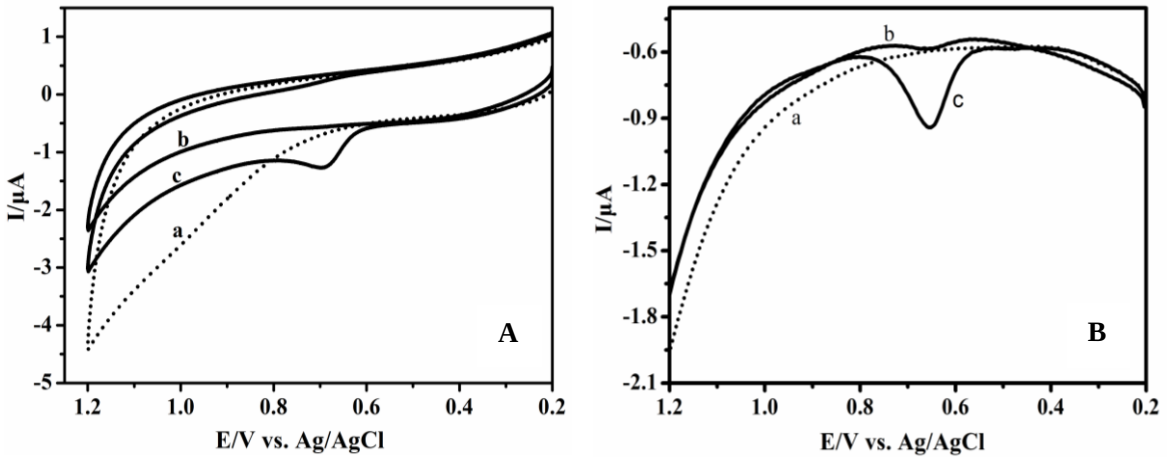


Figure 1. (A) Cyclic voltammograms and (B) square wave voltammograms on GCE for (a) 0.1 M PBS (pH 7.0), (b) 1.0 μM tyramine in 0.1 M PBS (pH 7.0), and (c) 10 μM tyramine in 0.1 M PBS (pH 7.0)

3.2. Evaluation of the modified electrode based on different materials

In order to investigate the effect of different modified materials on electrochemical response of tyramine, three modified electrodes were fabricated by electropolymerization in 0.01 M *o*-phenylenediamine, pyrrole and OAP solution. Then the resulting three polymeric membrane electrodes were used to determine 0.5 μM, 1.0 μM and 10 μM tyramine, respectively. Compared with poly(*o*-phenylenediamine) and polypyrrole modified GCEs, POAP/GCE showed better reproducibility and higher sensitivity, which could be attributed to excellent conductivity and more active sites of POAP film. Hence, OAP was chosen as the optimized monomer to modify GCE.

3.3. Optimization of polymerization conditions

The structure and performance of POAP film could be governed by selecting the concentration of OAP and perchloric acid, the polymerization potential, and the cyclic number of voltammetric

scans. The sensitivity and reproducibility of POAP/GCE were used as main evaluation indicators. 0.005 M, 0.01 M and 0.02 M OAP solutions were prepared with 0.5 M perchloric acid solution, respectively. Then POAP/GCEs were fabricated via cyclic voltammetry in (-0.5)-1.5 V for 14 cycles and used to determine tyramine. When the concentration of tyramine was 0.1 μM, no obvious oxidation peak was observed at POAP/GCEs prepared in 0.005 M and 0.02 M OAP solutions, whereas the oxidation peak of tyramine presented at POAP/GCE fabricated in 0.01 M OAP solution. Furthermore, POAP/GCE obtained in 0.01 M OAP solution showed the better reproducibility and higher sensitivity to 10 μM (curve a in Figure 2A) and 1.0 μM (curve was not shown) tyramine. The POAP film with low polymerization degree and less active sites was prepared in 0.005 M OAP solution. Although the polymerization rate was improved in 0.02 M OAP solution, the thicker polymer film with increasing resistance was formed, which resulted in the reduction in the catalytic activity of POAP film. According to the response current of tyramine at POAP/GCE, POAP film was electropolymerized in 0.01 M OAP solution. 0.01 M OAP solutions were prepared with 0.1 M, 0.3 M and 0.5 M perchloric acid solution, respectively. Comparing the responses of tyramine at these resulting OPOAP/GCEs, it could be found that OPOAP/GCE prepared in 0.3 M perchloric acid solution displayed maximum current response. Therefore, 0.3 M perchloric acid solution was used to prepare 0.01 M OAP solution. Normally, the potential of cyclic scan should be higher than oxidation potential of polymeric monomer, so 1.5 V was considered as the high potential. Comparing the oxidation peak currents of 10 μM tyramine at OPOAP/GCEs prepared by cyclic scan in the potential range of (-0.8)-1.5 V, (-0.5)-1.5 V, 0-1.5 V, the results showed that the oxidation current value of tyramine was significantly larger at OPOAP/GCE prepared in (-0.5)-1.5 V (curve a in Figure 2B), suggesting that abundant active sites could be generated in the OPOAP film and the structure of the polymer film was more suitable for the determination of tyramine. Therefore, the OPOAP film was electropolymerized in (-0.5) -1.5 V.

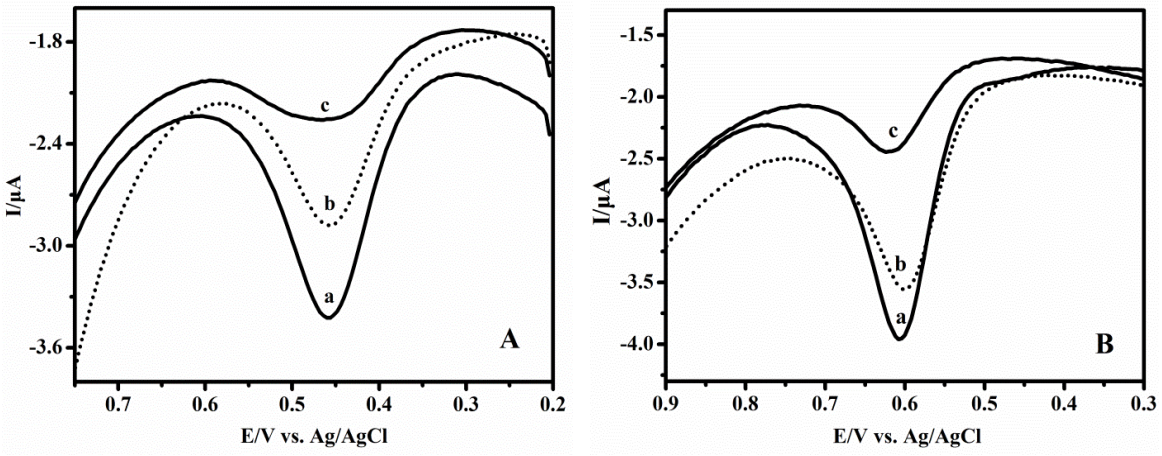


Figure 2. (A) Square wave voltammograms for 10 μM tyramine in 0.1 M PBS (pH 10.0) on POAP/GCE prepared in (a) 0.01 M (b) 0.02 M (c) 0.005 M OAP solutions. (B) Square wave voltammograms for 10 μM tyramine in 0.1 M PBS (pH 7.0) on OPOAP/GCE prepared in (a) (-0.5)-1.5 V, (b) (-0.8)-1.5 V, and (c) 0-1.5 V

As been known, the response performance of the modified electrode suffered from the thickness of polymer film, which could be easily controlled by the cyclic number of voltammetric scans during the electropolymerization [31,32]. OPOAP/GCEs were prepared by voltammetric scans of 10, 14 and 18 cycles and used to determine 10 μM tyramine, respectively. It was found that OPOAP/GCE prepared by 14 cycles showed highest response sensitivity to tyramine, which was due to the formation of thinner polymer film with poor stability for 10 cycles and the formation of thicker film with increasing resistance of electron transfer for 18 cycles. Consequently, the electropolymerization of OPOAP/GCE was carried out via voltammetric scans of 14 cycles.

3.4. Overoxidized treatment of POAP/GCE

The POAP/GCE was treated electrochemically in 0.09 M NaOH solution by cyclic scan to prepared OPOAP/GCE. In order to investigate the effect of the overoxidized treatment, POAP/GCE and OPOAP/GCE were used to determine 10 μM tyramine. Compared with POAP/GCE, the current response of tyramine was almost doubled at OPOAP/GCE. It could be attributed to the fact that the overoxidized treatment could increase the number of oxygen-containing groups in the polymer film, similarly as the cases of the overoxidized polydopamine [33] and polypyrrole films [34], which promoted tyramine molecules access to electrode surface for the oxidation-reduction reaction and further improved the response sensitivity of tyramine at OPOAP/GCE.

3.5. Optimization of test conditions

3.5.1. Accumulation time

OPOAP/GCE was immersed in 0.5 μM tyramine for 0 s, 60 s, 120 s, 180 s, 240 s and 300 s respectively, then SWV was used to evaluate the effect of accumulation time on the oxidation current of tyramine. The results showed that the response currents increased remarkably with the increase of accumulation time up to 180 s. Then the currents tended to be stable after 180 s, suggesting tyramine molecules had reached adsorption equilibrium on the surface of OPOAP/GCE when OPOAP/GCE was soaked in tyramine solution for 180 s. Therefore, 180 s was taken as the optimized accumulation time for determination of tyramine.

3.5.2. pH of supporting electrolyte

The pH of supporting electrolyte for preparing tyramine solution had an effect on the stability and existential state of tyramine, which could further influence binding way and ability between tyramine and OPOAP film. 10 μM tyramine solutions were prepared with pH 4.0, 7.0 and 10.0 PBS, respectively. Then the electrochemical responses of these tyramine solutions at OPOAP/GCE were investigated. It was found that the pH 7.0 tyramine solution showed largest oxidation current, mainly

because of good stability of tyramine in solution and strong interaction between tyramine and OPOAP film at pH 7.0. Therefore, tyramine solution was prepared with pH 7.0 PBS.

3.6. Characterization of OPOAP/GCE

3.6.1. Electrochemical impedance spectroscopy

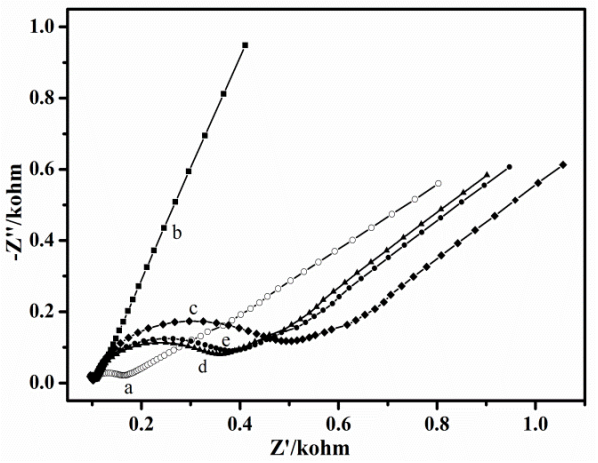


Figure 3. Nyquist plots of EIS for (a) GCE, (b) POAP/GCE, (c) OPOAP/GCE, (d) OPOAP/GCE immersed in 10 μM tyramine for 180 s, and (e) OPOAP/GCE immersed in 1.0 μM tyramine for 180 s

Electrochemical impedance spectroscopy (EIS) can be used to investigate the interface properties of modified electrode during the process of preparation and application [30,35,36]. The diameter of the semicircle in high frequency area of impedance spectra means the electron transfer resistance (R_{ct}). The stepwise preparation process and application of OPOAP/GCE were monitored by EIS (Figure 3). Compared with GCE (Figure 3a), R_{ct} of POAP/GCE (Figure 3b) decreased dramatically, indicating that POAP film had been modified on the surface of GCE, and the excellent conductivity of POAP film could facilitate the electron transfers. When POAP/GCE was electrochemically treated in the alkaline solution, R_{ct} of the resulting OPOAP/GCE (Figure 3c) increased significantly, further confirming that the overoxidized treatment could increase negative charges in the polymer film, and the strong electrostatic repulsion of OPOAP film to $[Fe(CN)_6]^{3-}$ hindered seriously the electron transfers. After soaking OPOAP/GCE in tyramine solution for 180 s, R_{ct} of the electrode decreased, moreover, tyramine solution of higher concentration caused a greater decrease in R_{ct} (Figure 3d, e), which could be attributed to the decrease of negative charges in OPOAP film due to the adsorption of tyramine in the film, and the more binding of tyramine molecules in OPOAP film from tyramine solution of higher concentration could cause a greater decrease in negative charges in the polymer film.

3.6.2. Scanning electron microscopy

The general surface morphologies of GCE, POAP/GCE, OPOAP/GCE, OPOAP/GCE with 10 μM and 1.0 μM tyramine were observed by SEM and shown in Figure 4. Comparing with GCE (Figure 4a), the surface of POAP/GCE (Figure 4b) was relatively rough and unhomogeneous, suggesting that POAP film with the redundant OAP functional monomer had formed on the surface of GCE. After overoxidized treatment, the surface roughness of the resulting OPOAP/GCE (Figure 4c) increased obviously, and cross texture surface morphology could be observed, which was likely to be the boundary or defects of polymer. After immersing OPOAP/GCE in tyramine solution, many crystalline particles arranged on these cross textures (Figure 4d, e), indicating tyramine molecules had bound onto the OPOAP film due to the surface energy or intermolecular forces.

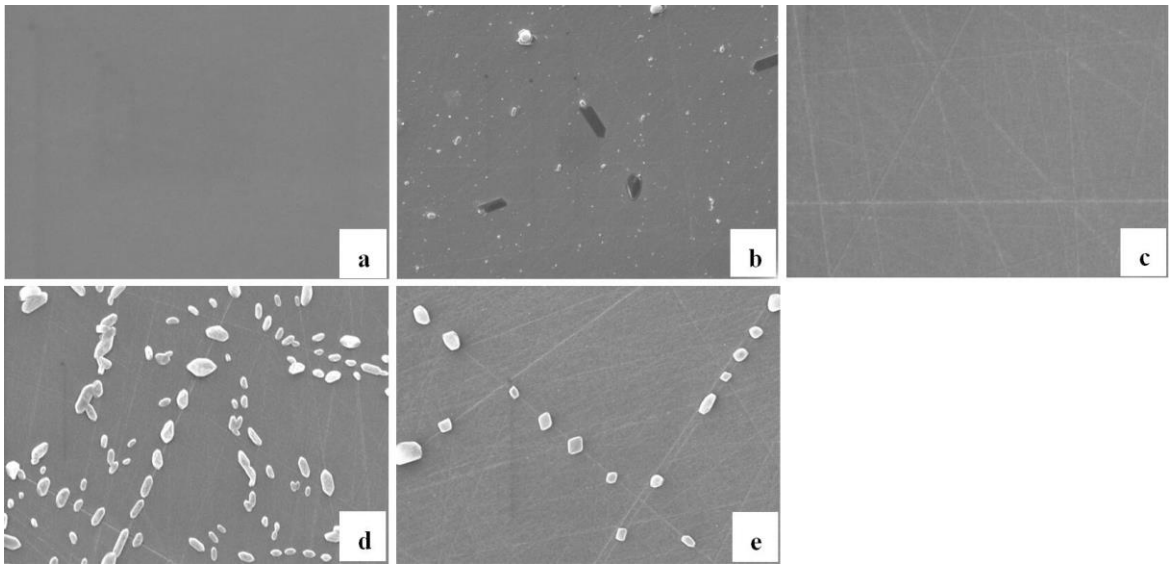


Figure 4. SEM images of (a) GCE, (b) POAP/GCE, (c) OPOAP/GCE, (d) OPOAP/GCE immersed in 10 μM tyramine for 180 s, and (e) OPOAP/GCE immersed in 1.0 μM tyramine for 180 s

3.7. Analytical performance of OPOAP/GCE

3.7.1. Reproducibility and stability

To investigate the reproducibility of the OPOAP/GCE, six OPOAP/GCEs were prepared and used to detect 10 μM tyramine solution by SWV under the optimized conditions. The relative standard deviation (RSD) of the six peak current values was 2.6%, suggesting that the OPOAP/GCE had good fabrication reproducibility. Furthermore, the repeatability of OPOAP/GCE was also examined by performing ten measurements of 10 μM tyramine solution with the same OPOAP/GCE. After determining every time, the electrode was washed with ultrapure water. The RSD of 6.5% was obtained, indicating that the OPOAP/GCE was expected to be used repeatedly.

The stability of the OPOAP/GCE was checked by monitoring the peak current response of 1.0 μM tyramine at regular intervals (one day) for a period of ten days. The peak current showed a RSD of

6.1%. Additionally, when the OPOAP/GCE was stored under the dry, dark and room temperature conditions, the initial current value of 92.5% could be retained for 1.0 μM tyramine after eight days, suggesting that the OPOAP/GCE had acceptable stability.

3.7.2. Interference studies

It is well known that there are other common seven BAs (histamine, phenethylamine, cadaverine, putrescine, spermine, spermidine, tryptamine) in food or food products. Therefore, to evaluate the selectivity of OPOAP/GCE to tyramine, the electrochemical responses of the seven BAs of 1.0 μM and 10 μM were investigated by SWV and compared with peak current of 1.0 μM tyramine, respectively. The results exhibited that these solutions of BAs except for 10 μM tryptamine had no electrochemical response around 0.65 V, suggesting that the other common BAs other than tryptamine did not significantly interfere with the determination of 1.0 μM tyramine. Generally, the OPOAP/GCE had an excellent selectivity to tyramine.

3.7.3. Calibration curves

The calibration curves were obtained for the determination of tyramine, using the sensor prepared under the optimum conditions previously described. The apparent growth of oxidation current was observed in the calibration curves (Figure 5). The inset of Figure 5 showed that the oxidation peak current increased linearly as the increase of concentration of tyramine. The current response (-*I*, μA) produced by the OPOAP/GCE was linearly related to the tyramine concentration (*C*, μM) in both lower concentration regions (0.1-10 μM) and higher concentration regions (10-200 μM). The corresponding linear regression equations were $-I = 0.1875C - 0.0129$ ($r = 0.999$, $n = 5$) and $-I = 0.0205C + 1.8675$ ($r = 0.994$, $n = 5$).

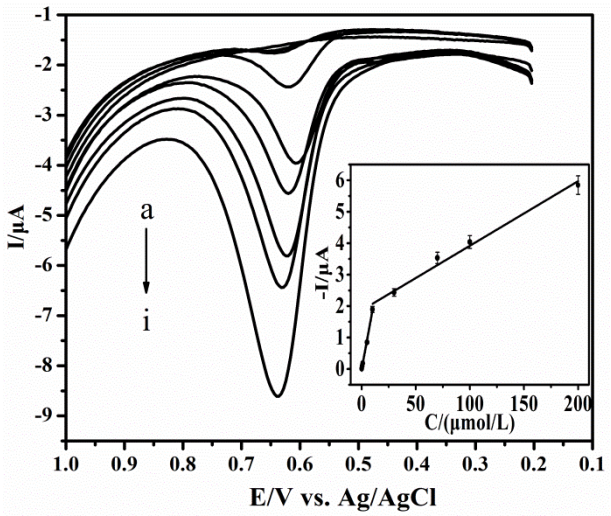


Figure 5. Square wave voltammograms of tyramine solutions with different concentrations (a→i) 0.1, 0.5, 1, 5, 10, 30, 70, 100, 200 μM. Inset: calibration curve of the oxidation current on OPOAP/GCE vs. the concentrations of tyramine.

The occurrence of the two linear ranges might be ascribed to the changes in the binding mode [37] of tyramine in OPOAP film and the dynamics rule of the electrochemical process with the increasing concentration of tyramine. Moreover, the possible fouling of oxidation product of tyramine to the electrode surface might also result in the decrease in slope at higher concentration [38]. The detection limit (DL) was 0.054 μM at a signal to noise ratio of 3 in this work, which was apparently lower than those reported in the previous literatures [19,23,35,39-41], and very close to 0.057 μM of multiwalled carbon nanotube-gold nanoparticle composites and molecularly imprinted polymer system [42]. Although the lower DL of 0.01 and 0.018 μM were reported based on HPLC-fluorescence detection [43] and flow-injection analysis/fast-scan cyclic voltammetry [44], respectively, the simple work procedure, low cost, good reproducibility and selectivity make the present method in this work be sufficient to detect tyramine in real samples and field fast analysis. The comparison of the different determination methods for tyramine was shown in Table 1.

Table 1. Comparison of the different determination methods for tyramine.

Analytical system	Analytical method	Linear range(μM)	Detection limit (μM)	References
CZE[a] with capacitively coupled contactless conductivity detection	CZE	3.6-729	0.83	[19]
Tyrosinase/polypyrrole doped with phosphate ions/Pt	Amperometry	4-80	0.57	[23]
Quercetin/fMWNT[b]/GCE	DPV[c]	0.7-75	0.647	[35]
fMWNT/GCE	DPV	1-85	0.8	[39]
Pea seedling amine oxidase/MnO_2/screen printed carbon electrode	FIA[d]	10-100	3	[40]
Poly(3-methylthiophene)/Pt	DPV	4.4-14000	1.32	[41]
MWNT-gold nanoparticle/chitosan/ molecularly imprinted polymer/GCE	Amperometry	0.1-10	0.057	[42]
HPLC[e]-FLD[f] based on one-step fluorescence labeling and UA-DLLME[h]	HPLC-FLD	—[g]	0.01	[43]
FIA and fast-scan cyclic voltammetry at carbon-fiber microelectrodes	FIA	0.1-5	0.018	[44]
OPOAP/GCE	SWV	0.1-200	0.054	This work

[a] CZE, capillary zone electrophoresis. [b] fMWCNT, functionalized multi-wall carbon nanotube. [c] DPV, differential pulse voltammetry. [d] FIA, flow injection analysis. [e] HPLC, high-performance liquid chromatography. [f] FLD, fluorescence detection. [g] No data. [h] UA-DLLME, ultrasound-assisted dispersive liquid–liquid microextraction.

3.8. Sample analysis

A kind of commercial rice vinegar was selected as a model sample to demonstrate the practical application of the proposed OPOAP/GCE for the determination of tyramine. Before measurements, the rice vinegar was diluted 50 times with 0.1 M PBS (pH 7.0), then pH of the diluted sample was adjusted to 7.0 with sodium hydroxide to obtain test solution. After the OPOAP/GCE was immersed in the test solution for 180 s, SWV was used to determine tyramine. The obvious peak current response was found at the peak position of tyramine. The tyramine concentration in the test solution was obtained to be 0.36 μM, which could be transferred into tyramine content of 2.5 mg L^{-1} in the commercial rice vinegar. Furthermore, the spiked recovery study was carried out to evaluate accuracy of this method. The recoveries of 0.5 μM and 150 μM tyramine were from 102.4% to 114.8%, and the RSD values were 7.0% and 1.8%, respectively, indicating the suitability and practicability of the proposed method to quantify tyramine in rice vinegar samples. It was also suggested that the proposed detection method has higher accuracy and precision.

In order to further investigate the reliability of the proposed method, the concentration of tyramine in rice vinegar was also determined by HPLC according to the national standard (GB/T 5009.208-2008) of the People's Republic of China. The concentration value of 2.68 mg L^{-1} was very close to the result obtained from the OPOAP/GCE, indicating the proposed method was suitable for the accurate and reliable determination of tyramine in rice vinegar.

4. CONCLUSIONS

In this work, an electrochemical sensor, based on the electropolymerization of OAP and overoxidized treatment of POAP film, had been developed and successfully applied to the determination of tyramine in commercial rice vinegar. The proposed sensor showed to be promising for tyramine determination with many desirable properties, including high sensitivity, good reproducibility, simple preparation and lower detection limit. Moreover, excellent selectivity and fast response appeared to be further distinctive features of the method. Most importantly, this sensor presented such a good application ability to determine tyramine in real sample.

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