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Two-electrode Sensor System for Rapid Detection of Sulfonamides by Applying the Nafion-Carboxyl Multiwalled Carbon Nanotubes Powder Microelectrode

Baoshan He[*], *Wenbo Chen*

School of Food Science and Technology, Henan University of Technology, Zhengzhou 450001, People's Republic of China
[*]E-mail: hebaoshan@126.com

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A powder microelectrode (PME), embedded with Nafion-carboxyl multiwalled carbon nanotubes (MWCNTs), was prepared for selective and sensitive determination of sulfonamides. The effects of experimental parameters on the response of electrode such as pH of buffer, scan rate were optimized. Under optimal conditions, the proposed PME can greatly improve the determination sensitivity. In a Britton-Robison (BR) buffer solution (pH 2.0), the linear response range for detection of 1.0×10^{-5} mol/L to 1.0×10^{-4} mol/L of sulfonamide ($R^2=0.984$), sulfadiazine ($R^2=0.993$), sulfamethazine ($R^2=0.987$), sulfamethoxazole ($R^2=0.982$) and the detection limits of 2.69×10^{-6} mol/L, 3.10×10^{-6} mol/L, 8.94×10^{-6} mol/L and 5.79×10^{-6} mol/L, respectively. The recoveries were in the range of 87~106% with RSD＜5% and the Nafion-MWCNTs PME performed excellent repeatability and durability. The proposed sensor was successfully applied for the determination of SAs in real samples and might offer feasibility and applicability for other determination of more complex sulfonamides compounds.

Keywords: Powder microelectrode; Nafion; Carboxyl; Multiwalled carbon nanotubes; Sulfonamides;

1. INTRODUCTION

The sulfonamides (SAs) antimicrobial family, which include a group of synthetic antibiotics, have been one of the most interesting and important studies in medicinal chemistry[1] and widely used as additive in animal feeding to prevent bacterial contamination[2, 3] and treat a series of diseases, such as diuretic[4], antibacterial[5], digestive and respiratory tracts[6]. However, excess amount of SAs can be left in animal feed, affecting human health, such as allergic reactions, damaging urinary system and even cancer. Due to the toxic effects of residues of SAs, quick systematic detecting of SAs in food is an important analytical task [7-9].

Many analytical monitoring methods of SAs in different food have been reported including gas chromatography[10-12], high performance liquid chromatography(HPLC)[13-19], liquid chromatography tandem mass spectrometry[20, 21], spectrophotometry[22] and capillary electrophoresis mass spectrometry[23, 24]. Although these methods have shown their accuracy and suitableness for SAs determination, they involve high cost of the instruments, complicated sample preparation steps and require the sophisticated laboratory personnel. Despite this drawback, electrochemical methods offer several advantages over other methods such as simplicity, low cost of instruments, facility of use, and not being time-consuming[25-29]. Numerous literatures have reported the study on determination of SAs based on glassy carbon electrodes[7-9, 30], but there are no any literatures about using powder microelectrodes (PME) to detect SAs. PME technique has been developed to study glucose, nitric oxide, and reduced glutathione[31-33].The obvious technique advantage of PME is the ratio of real surface area/apparent electrode area, which will help to enhance the electron transfer rate between surface of PME and the tested samples. Compared with conventional electrode, the diameter of a PME is much more smaller, which requires less time for establishing an electrochemical detection and reduces the voltage. Thus the potential of the counter electrode (platinum plate electrode) is stabilized and can be used as the reference electrode, simultaneously, namely simplify three-electrode system as two-electrode system. In some cases, PME technique was applied to in the determination of ultra-low concentrations of redox substances[34, 35].

Appropriate embedded materials are quite important for PME technique. Nafion, a cationic exchange polymer, has a quite high selectivity for cation through the electrostatic interaction, which is consistent with one of the characters of SAs-the cationic Nafion can be available in a dissolved form, and the surface of PME can be embedded by either dip-coating material in Nafion solution or Nafion-material compounds[36]. Due to the good electrical conductivity, high chemical stability and extremely high mechanical strength of multiwalled carbon nanotubes(MWCNTs)[37], we established a voltammetric sensor for the determination of SAs by using a manual PME embedded with compounds of Nafion and functionalized MWCNTs through the electrochemical corrosion method, the resultant Nafion-MWCNTs performed high electrochemical conductivity and the proposed sensor exhibited high sensitive response to SAs, showing adequate sensitivity and effectiveness in determination of SAs.

To the author’s knowledge, there are no previous reports about using a manual PME to detect SAs, and the purpose of this work is to establish a Nafion-MWCNTs PME technique and its application in the determination of SAs, which will illustrate the power of PME in promotion of electron transfer and the determination sensitivity, which will be crucial to the food security of chemical residues.

2. EXPERIMENTAL

2.1. Materials and Reagents

Multiwalled carbon nanotubes(MWCNTs) was purchased from Beijing Gaoke Technology Material Co., Ltd. (Beijing, China, http://www.dykjchina.com/).Four standard SAs including sulfonamide (SA), sulfamethazine (SM2), sulfadiazine (SDZ), sulfamethoxazole (SMZ) were analytical grade and purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China, http://public.company.lookchem.cn/). The pork samples were purchased from local supermarket. The Britton-Robison (BR) buffer solution was blended with 0.04 mol/L phosphate, 0.004 mol/L acetic acid and 0.04 mol/L boric acid and 0.04 mol/L sodium hydroxide. Unless stated otherwise, all other reagents used were analytical grade.

2.2. Apparatus

The experiments were performed on an electrochemical workstation CHI660E (Shanghai Chen Hua Instrument Co., Ltd, China, http://www.chinstr.com/) and two-electrode system was adopted throughout, consisting of a PME as working electrode, a platinum plate electrode (1 cm^2) as the counter electrode and reference electrode. KQ–3200E ultrasonic cleaners: Ultrasonic Instrument Co., Ltd. (Kunshan, China, http://www.ks-csyq.com/gsgj.htm); UB-7 pH meter: Sartorius Scientific Instruments Co., Ltd.(Beijing, China, http://www.sartorius-weighing.com.cn/sartorius/website/), AR124CN electronic analytical balance: Ohaus Instrument Co., Ltd.(Shanghai, China, http://www.sh17.cn/); SZ-93 automatic dual water distiller, YaRong Biochemical Instrument factory (Shanghai, China, http://www.sh17.cn/).

2.3. Preparation of embedded material

150 mg MWCNTs were dispersed with 150 mL mixed strong acid solution (the concentrated HNO_3 and H_2SO_4 volume ratio was 1:3) and vibrated ultrasonically for 24 h. Then, the functionalized MWCNTs, namely carboxyl MWCNTs, were put into a vacuum pump for suction, washed until neutral of filtrate and dried under 100^oC vacuum environment. Afterwards, 100 mg functionalized MWCNTs were dispersed into 100 μL Nafion and 900 μL phosphate buffer solution (PBS, pH 7.0) and the compounds were vibrated ultrasonically for 2 h. Then, ammonia was added into the compounds and the system was in water-bath heating for 3 h. The embedded material, Nafion-MWCNTs powder, was collected after centrifugalization, stored at the drying oven.

2.4. Preparation of working electrode, Nafion-MWCNTs PME

The Nafion-MWCNTs PME was fabricated as the follow two steps:

The microelectrode (ME) was prepared by inserting a platinum (Pt) wire (50 μm of diameter), bonded with a copper wire, into a stretched pipette at first. Afterwards, the copper wire was sealed by epoxy resin and the protrudent Pt wire was heated under an alcohol blow lamp hermetically, making sure that the Pt wire was sealed in the pipette. After the sealing process, the tip of the pipette, sealed with the platinum wire, was successively polished metallographic abrasive paper and 1.0, 0.3, 0.05 μm graininess Al_2O_3 emulsion[38], then a ME was obtained.

The obtained ME was etched in boiling aqua regia (3 h) to form a micro cavity at its tip, with an optimal depth of 70~90 μm. After that, the etched ME was sonicated continuously by alcohol, acetone, double distilled water (each time, 10 min), and dried in vacuum oven. The micro cavity was embedded with Nafion-MWCNTs powder by grinding and pressing the etched tip on the compounds powder on the surface of a clean smooth glass. The micro cavity was supposed to be embedded with the Nafion-MWCNTs powder tightly and fully. The resultant microelectrode was Nafion-MWCNTs PME. The plan and section of Nafion-MWCNTs PME were shown in Fig. 1.

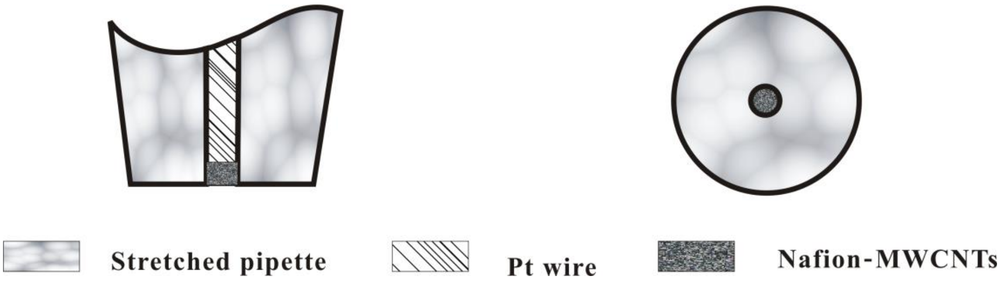


Figure 1. Plan and section images of Nafion-MWCNTs PME.

2.5. Mechanism of electrochemical determination of SAs

In the electrochemical experiment process, as an oxidation-reduction substance, SAs enriched selectively at the surface of Nafion-MWCNTs PME to form polymeride and lost electron at acertain potential, leading to the oxidation reaction. The generant signal of oxidation current was acquired and processed by electrochemical workstation. The sulfonamides content could be obtained based on the data of oxidation current. The principle of this sensor was shown in Fig. 2.

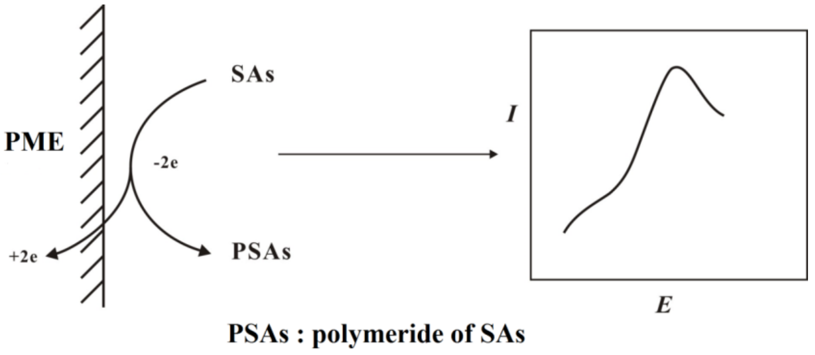


Figure 2. Schematic of SAs determination.

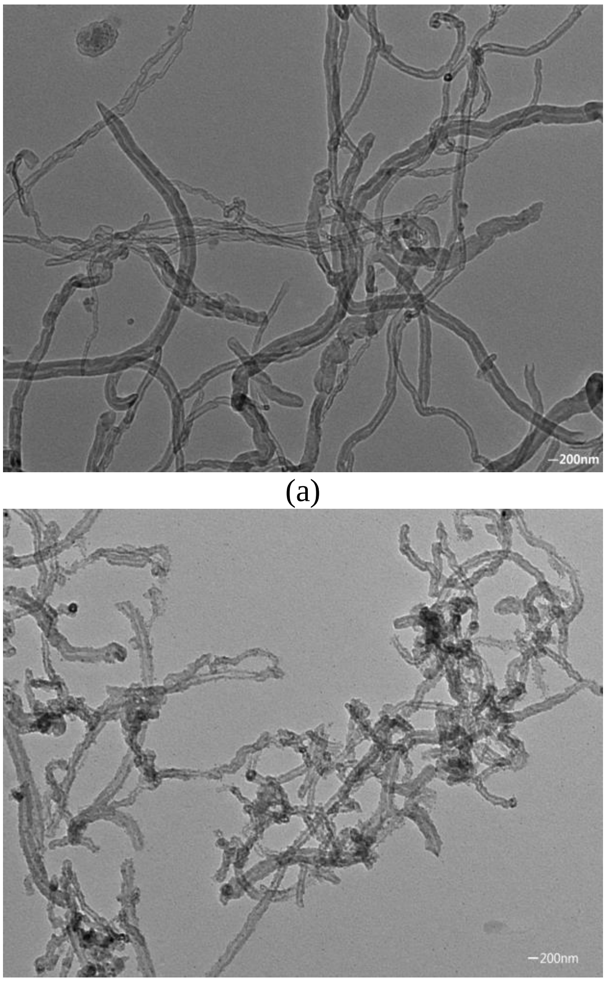
2.6. Experimental procedures

Cyclic voltammetry (CV) measurements were performed using two-electrode system, where a PME was served as working electrode, and a platinum plate electrode was used as the reference electrode and counter electrode. The two electrodes were inserted into BR buffer solution (pH2.0) containing tested concentrations of SA, SM2, SDZ, SMZ under mildly magnetic stirring. The buffer solution must be ventilated with high purity nitrogen (⩾99.999%) for 10 minutes before the experiment. The detection limit of the PME was obtained by amperometric i-t curve (i-t) measurements. CV measurements were recorded from 0.0 V to 1.2 V with the sweep rate of 100 mV/s. All experiments were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1. TEM characterization of MWCNTs

The microstructures and morphologies of MWCNTs and carboxyl MWCNTs observed by TEM were shown in Fig. 3. The length of carboxyl MWCNTs decreased to 600~5000 nm in comparison with MWCNTs (length: 2600 nm～8000 nm), and big granules were split into small granules during the carboxyl treatment, suggesting the successful formation of carboxyl MWCNTs.



(a)

(b)

Figure 3. TEM images of MWCNTs (a) and carboxyl MWCNTs(b).

Furthermore, due to the rougher surface and smaller size than that of MWCNTs, the carboxyl MWCNTs were beneficial for the diffusion of analytes and would provide a relative huge effective area on the PME.

The carboxyl MWCNTs were highly stable for more than 2 months without aggregation which revealed the appreciable stability of the material.

3.2. FTIR study of MWCNTs

FITR analysis was applied to confirm the difference between particles of both MWCNTs and functionalized MWCNTs as it shown in Fig. 4.

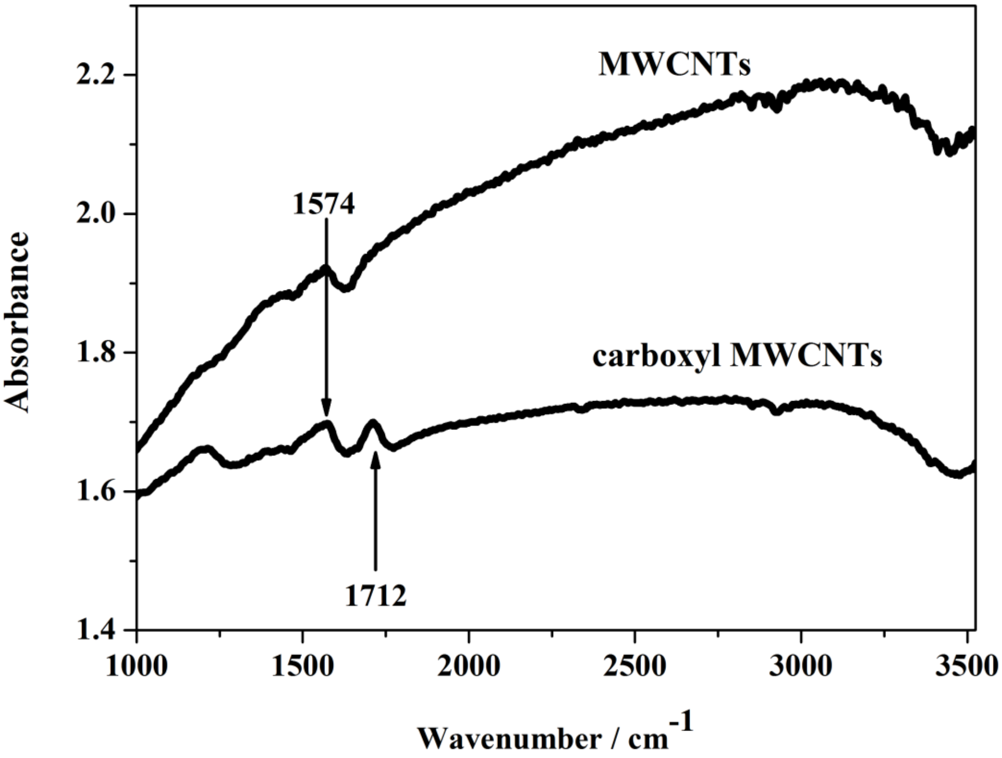
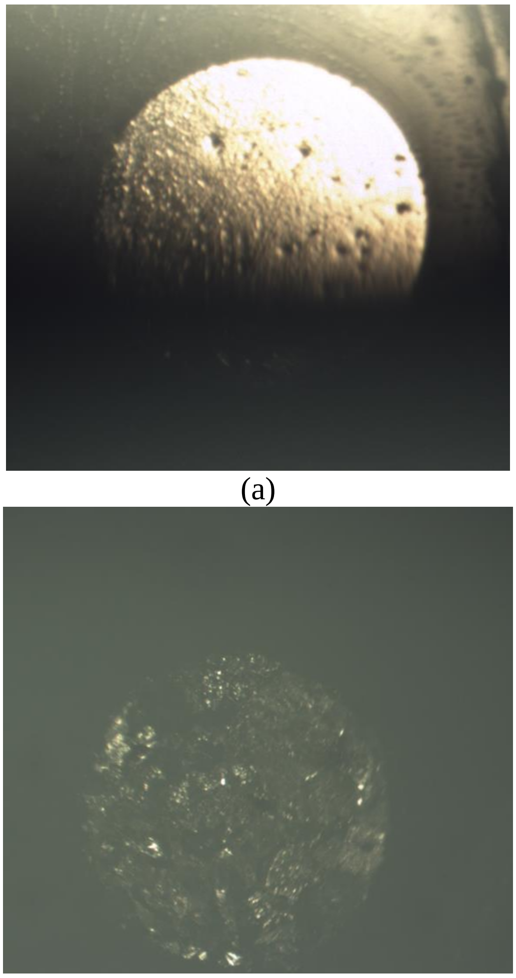


Figure 4. FTIR spectra of MWCNTs and carboxyl MWCNTs.

The FTIR spectra of pure MWCNTs displayed a peak at 1574.12 cm^{-1} due to a carbon-carbon single bond, the FTIR spectra of functionalized MWCNTs exhibited a characteristic IR peak at 1712.40 cm^{-1} corresponding to pure MWCNTs particle, this illustrated that the MWCNTs were successfully involved in the functional group of carboxyl and the peak strength got enhanced, indicating that the molecular structure of MWCNTs was interrupted to be smaller structures, that was, the functionalized MWCNTs provided more reactive sites for electrodes.

3.3. Comparison of PME before and after the embeddedness


(a)

(b)

Figure 5. Inverted metallurgic microscope images of PME(a) and embedded PME(b).

According to the images of PME (a) and embedded PME (b) from Fig. 5 obtained by inverted metallurgic microscope(×40)**,** we could see a luminous surface of Pt wire before it embedded, suggesting that nothing attached to the Pt wire. After the process of getting etched and the embeddedness of Nafion-MWCNTs powder, there were nearly no luminescent spots on the surface of Pt wire, indicating that the composite material, Nafion-MWCNTs, was embedded into the micro cavity of the PME successfully, which meant that the powder microelectrode had highly accessible bigger surface area than microelectrode.

3.4. Electrochemical behavior of SAs based on PME and ME

The purpose of this experiment was to study the electrocatalytic properties of Nafion-MWCNTs PME. CV responses of Nafion-MWCNTs PME and ME were tested in BR buffer solution (pH 2.0) with the concentration of 1.0×10^{-2} mol/L of SA and in the potential range of 0.0~1.2 V with the scan rate of 100 mV/s. The anodic oxidation of SA could occur at $-NH_2$ group, however, the reduction of $-SO_2-$ group could occur only at the higher negative potential value[39]. Therefore, only anodic peak of SA group was investigated as presented in Fig. 6. An apparent oxidation peak was obtained with the potential of 0.751 V and the current of 0.1702 μA based on ME (a), and the obtained oxidation peak current value was 1.969 μA based on the Nafion-MWCNTs PME (b), increasing more than 12 times, which fully indicated that the composites, Nafion-MWCNTs, could reduce the interfacial resistance, accelerate the electron transfer rate and improve the sensitivity of PME remarkably, this was because that the embedded material provided highly accessible surface area for the electrocatalytic reaction and increased more reactive sites of PME.

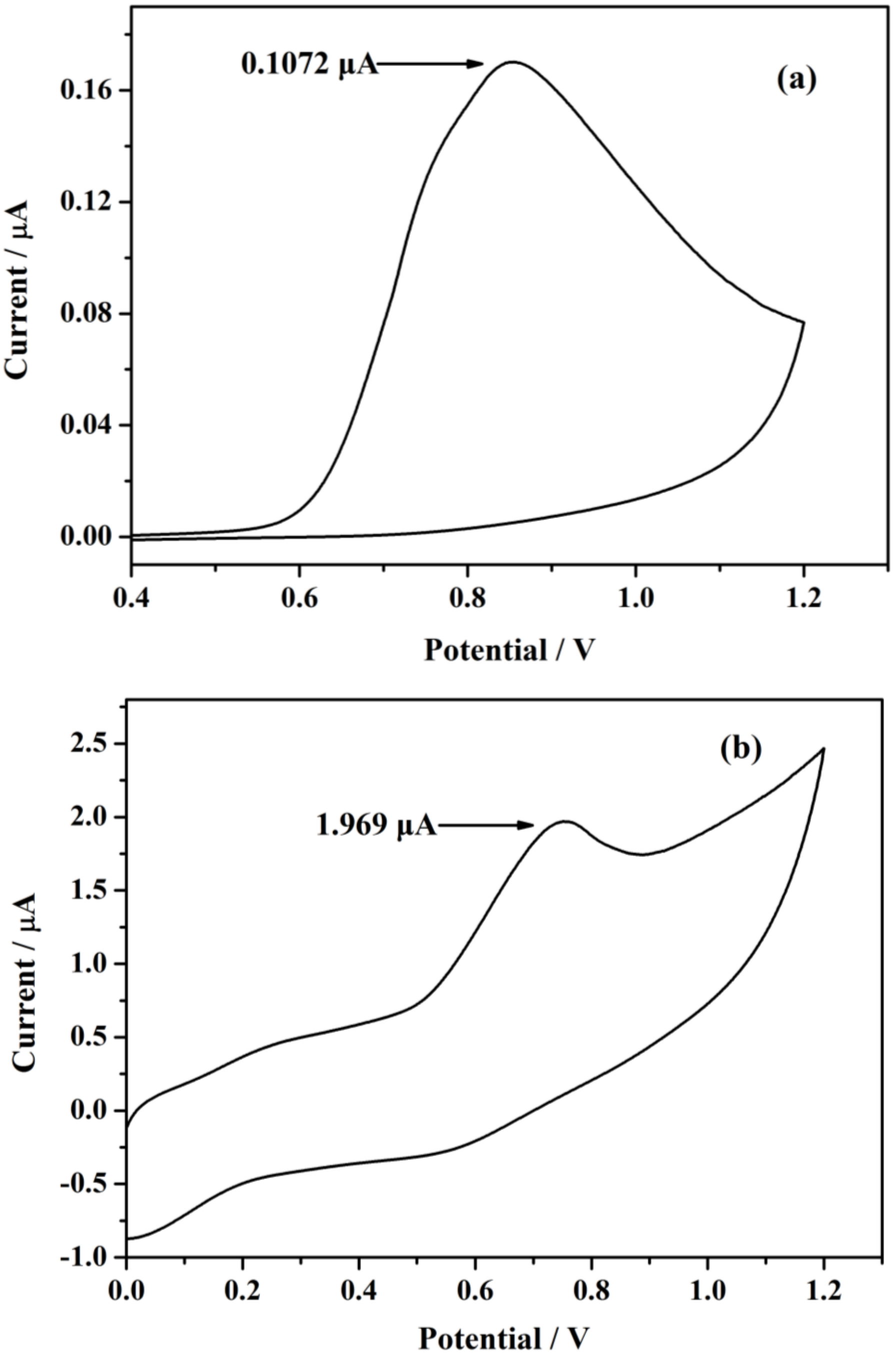


Figure 6. Cyclic voltammograms of 1.0×10^{-2} mol/L SA at ME (a) and Nafion-MWCNTs PME (b).

CVs of SDZ, SM2 and SMZ were obtained based on Nafion-MWCNTs PME in the same experimental method, and the anodic potentials of SDZ, SM2, SMZ were 0.736 V, 0.700 V, 0.786 V, respectively, which proved the good electrochemical respones of Nafion-MWCNTs PME to SAs.

3.5. Effect of pH

Using SA as an example, the influence of pH on 5.0 × 10^{-3} mol/L SA detecting was studied in the range of 1.0 to 8.0 based on CV (Fig.7).

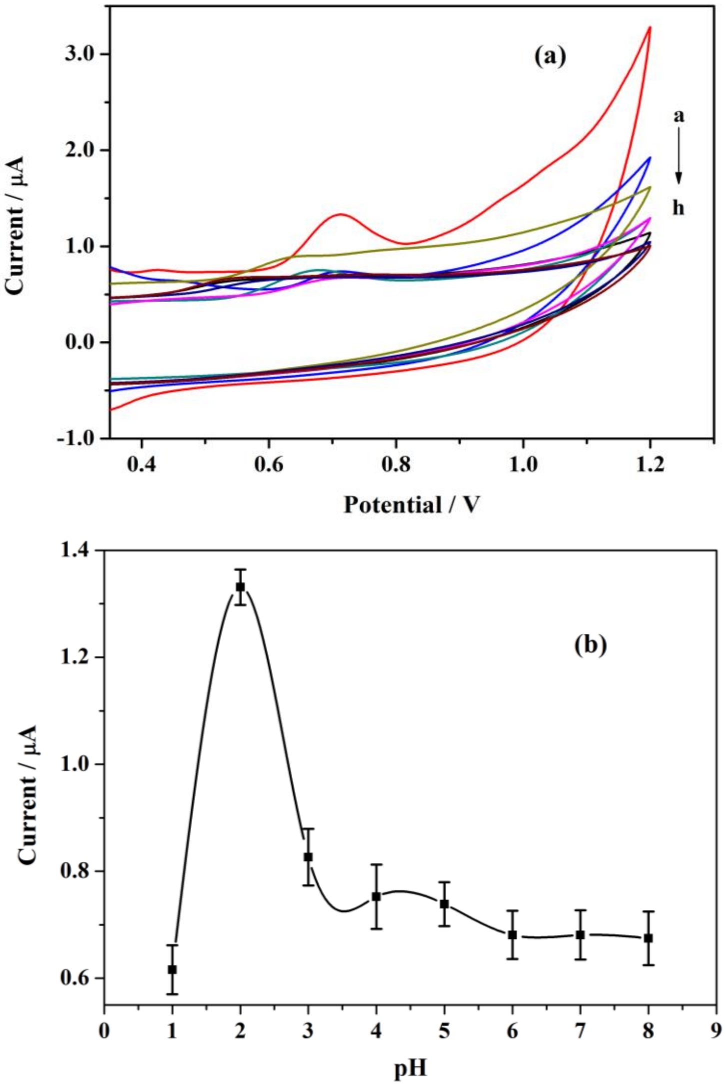
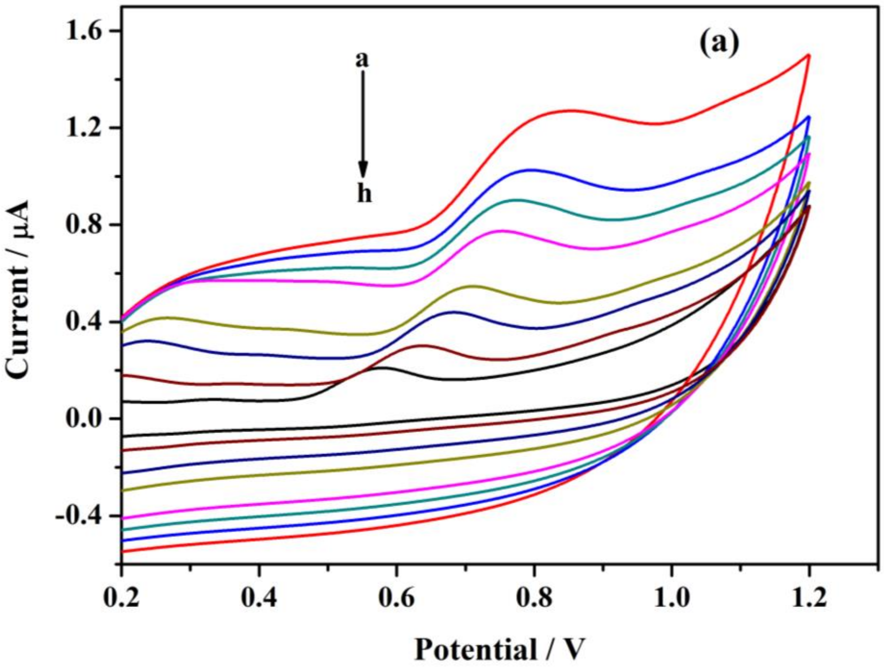


Figure 7. (a) Cyclic voltammograms of 5.0×10^{-3} mol/L SA at the Nafion-MWCNTs PME in BR solution of different pH ((curve a~h: 2, 4, 3, 1, 5, 8, 7, 6). (b) Influence of pH on the CV response.

In the tested pH range, the oxidation peak current of SA increased with the increase of pH from 1.0 to 2.0. The max electrochemical response was achieved at 2.0 and then declined when the pH value exceeded 2.0. This result might be explained that the carboxylic groups of the MWCNTs were in the neutral form that could interact with SA molecule through the hydrogen bonding at low pH environment. Under the appropriate experimental, SA had the good oxidation ability at pH 2.0. However, at the relative weak acidic experimental environment, the carboxylic groups suited on the surface of PME and the SA molecule became into anions, which hindered the hydrogen bonding and as a result, the oxidation current peak of SA declined obviously. It further demonstrated that H^+ was involved in the electrochemical reaction process[40].The effects of pH of the experimental solution containing 5.0 × 10^{-3} mol/L SDZ, SM2 and SMZ were texted with the same method, the maximum oxidation peaks were achieved at pH 2.0, which was in consistence with the result of SA. Therefore, 2.0 was selected as the admirable value of pH for the subsequent experiments.

3.6. Influence of scan rates

The influence of scan rates on the oxidation peak current of 5.0 × 10^{-3} mol/L SA was studied by CV at an optimum condition. As could be seen in Fig. 8, SA gave an irreversible cyclic voltammogram and the oxidation peak current shifted to a more positive potential with increasing scan rates as well as a concurrent increase in current. The oxidation peak currents (i_{pa}) of SA varied linearly with the square root of scan rates ($v^{1/2}$) ranging from 10 mV/s to 160 mV/s, and the linear regression equation was $i_{pa}(\mu A)=2.887\ v^{1/2}\ ((mV/s)^{1/2})-0.116$ with the correlation coefficient (R) of 0.991, indicating that the electrochemical response of SA was a diffusion-controlled process on the surface of Nafion-MWCNTs PME[46-47]. The results were in consistent with those of SDZ, SM2 and SMZ.



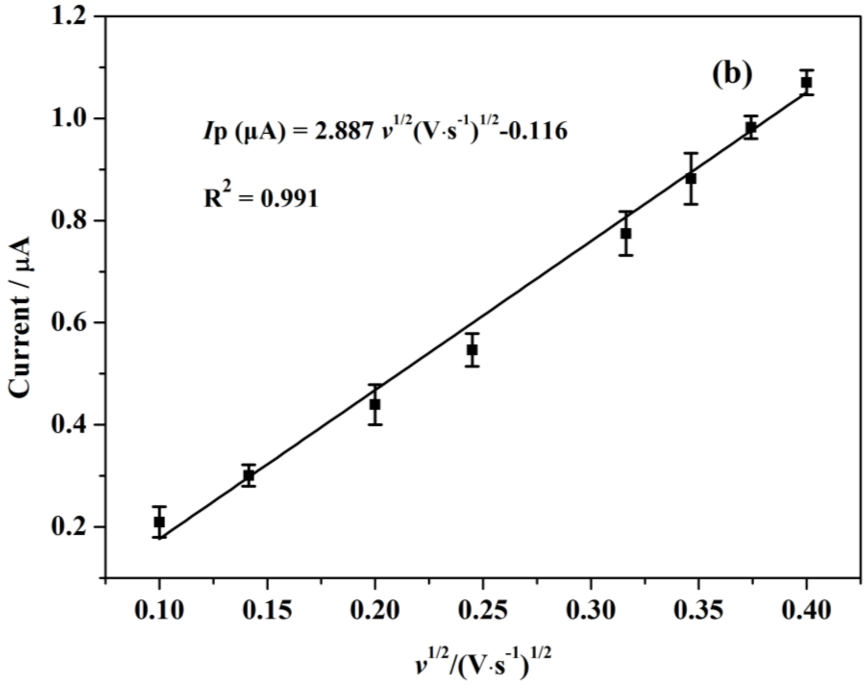


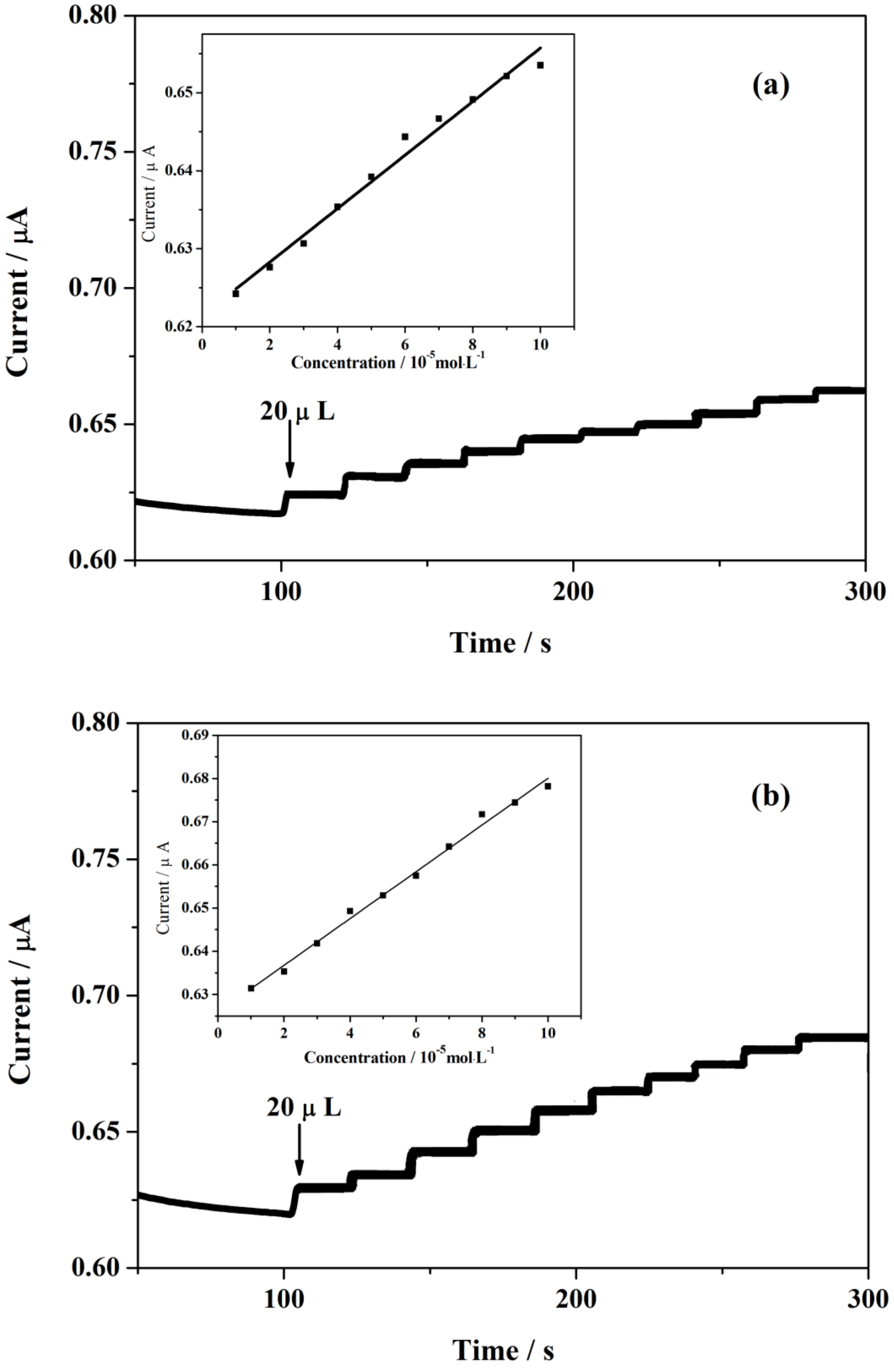
Figure 8. (a) Cyclic voltammograms of 5.0×10^{-4} mol/L SA on the Nafion-MWCNTs PME at different scan rates: (a) 160 mV/s, (b) 140 mV/s, (c) 120 mV/s, (d) 100 mV/s, (e) 60 mV/s, (f) 40 mV/s, (g) 20 mV/s, (h) 10 mV/s, (b) Plot of oxidation peak currents of SA versus the square root of scan rates.

3.7. Interference study

For studying the selectivity of Nafion-MWCNTs PME for simultaneous determination of SA, SDZ, SM2 and SMZ, several coexistent substances, as the possible interference substances, were texted under the optimum conditions with 2.0×10^{-3} mol/L SA, SDZ, SM2 and SMZ. The tolerance limit was defined as the maximum concentration of interference substance that caused an approximately ±5% relative error in the current signal for reduction of SAs[41-43]. If the detection current signal deviation was below 5%, the texted coexisting interferents were considered that they had no interference for the determination. The experimental results showed that 300-times KCl, NaCl, $MgSO_4$, 200-times glucose and sucrose did not influence the oxidation peak currents of SA, SDZ, SM2 and SMZ, markedly. The relative errors and change rates of oxidation peak currents of SA, SDZ, SMZ and SM2 varied from 0.41% to 4.86% and from 0.49% to 5.39%, no interference from these coexistent substances was observed at the potentials of SA, SDZ, SMZ and SM2, indicating that the Nafion-MWCNTs PME performed excellent selectivity for the detection of SA, SDZ, SMZ and SM2 and might be applied to the real samples analysis.

3.8. Amperometric determination of SA, SDZ, SMZ and SM2

As a sensitive electrochemical analysis method, amperometry was used for quantitive determination of the four SAs at the Nafion-MWCNTs PME. Under the optimized experimental conditions, the amperometry experiments of SA, SDZ, SM2 and SMZ were carried out in a well-stirred BR buffer solution at the applied potentials of Nafion-MWCNTs PME at 0.751 V, 0.736 V, 0.700 V and 0.786 V respectively. As could be seen in Fig. 9, the oxidation peak currents of the four SAs had an obvious increase and the currents reached stable state quickly when definite concentrations of SAs were added into BR solution, suggesting that the Nafion-MWCNTs PME had a relatively fast response for SA, SDZ, SM2 and SMZ.



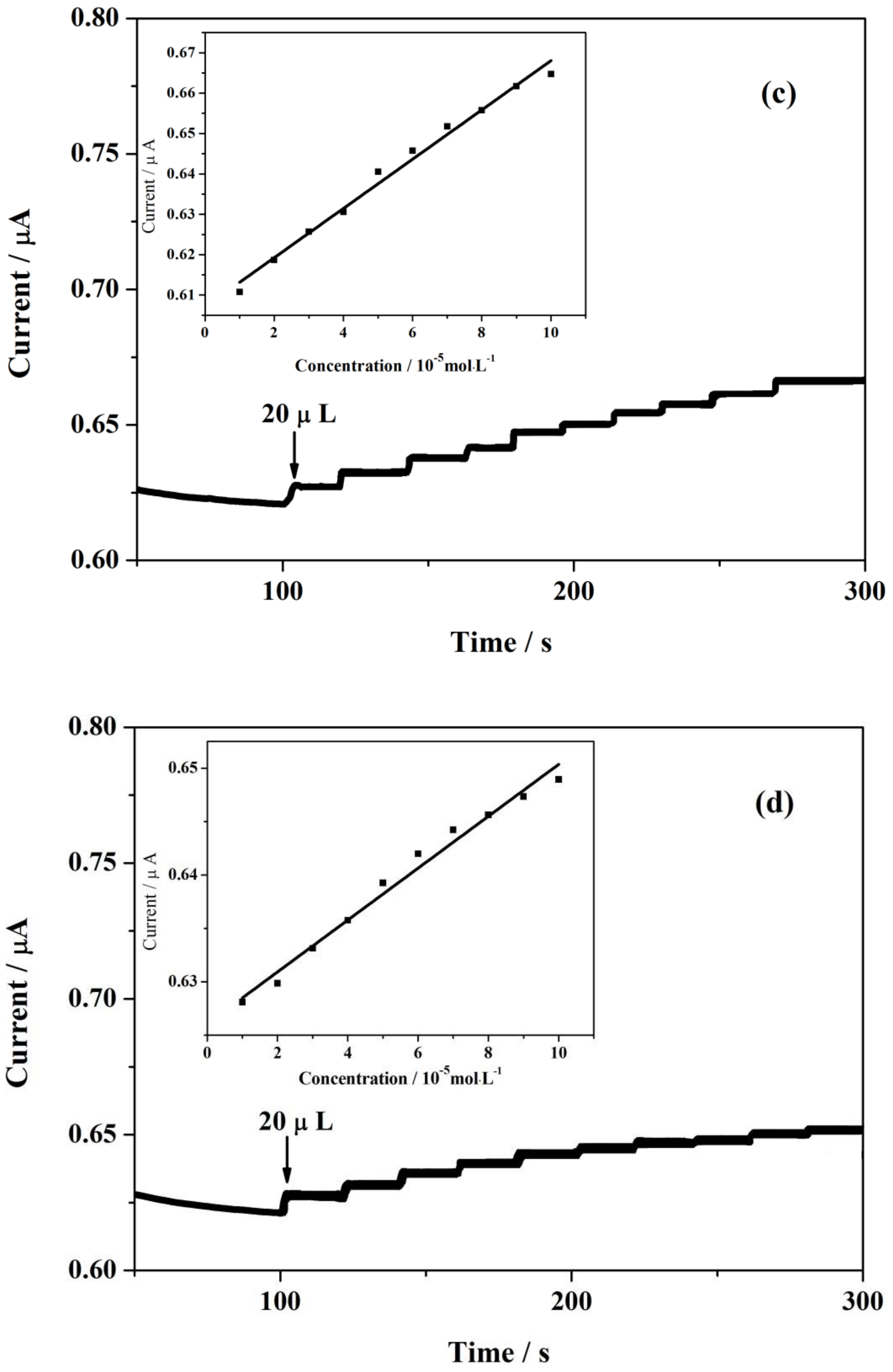


Figure 9. Amperometric curves response of Nafion-MWCNTs PME with successive addition of SA(a), SDZ(b), SMZ(c) and SM2(d). Inset shows the plot of amperometric response versus SA, SDZ, SMZ and SM2 concentration.

The Nafion-MWCNTs PME amperometric response was linear for SA concentration in the range of 1.0×10^{-5} mol/L to 1.0×10^{-4} mol/L with a slope of 0.3433 nA/μM and a correlation coefficient of R^2=0.984(n=15). The detection limit (LOD), defined as a signal-to-noise ratio=3, was 2.69×10^{-6} mol/L. The amperometric response of SDZ, SM2 and SMZ were also texted on Nafion-MWCNTs PME with the concentrations of 1.0×10^{-5}mol/L to 1.0×10^{-4} mol/L based on the same method. The regressive equations of SDZ, SM2 and SMZ were i_{pa}(μA)=5.414×$10^{-3}$$c$+0.626 ($R^2$=0.993), i_{pa}(μA)=6.102×$10^{-3}$$c$+0.607 ($R^2$=0.987) and i_{pa}(μA)=2.429×$10^{-3}$$c$+0.626 ($R^2$=0.982) with the LODs of 3.10×10^{-6} mol/L, 8.94×10^{-6} mol/L and 5.79×10^{-6} mol/L, suggesting that the Nafion-MWCNTs PME was useful for the determination of SAs with excellent sensitivity in real samples detection.

3.9. Real samples analysis

In order to evaluate the analytical applicability of Nafion-MWCNTs PME, it was also used to the determination of SA, SDZ, SM2 and SMZ in pork samples, respectively. The preparation of measuring concentrations SAs were described in detail in literature[7].

Table 1. Recovery studys of SA, SM2, SDZ and SMZ in pork samples

Analytes	Added level (10^{-5} mol/L)	Found (10^{-5} mol/L)	Mean of recovery (%)	RSD (%, n=3)
SA	3.00	2.85	98.83	3.68
	6.00	6.02	99.42	4.33
	9.00	9.15	102.50	3.62
SDZ	3.00	3.02	97.67	2.36
	6.00	6.20	104.42	2.10
	9.00	9.15	102.71	3.23
SM2	3.00	2.87	91.34	4.96
	6.00	5.87	99.92	2.63
	9.00	9.15	102.12	2.71
SMZ	3.00	2.88	96.67	2.33
	6.00	6.02	101.28	3.19
	9.00	9.45	103.44	3.58

Table 2. Comparisons of several characteristics of different methods for determination of SAs.

Detection method	Linearity range (μmol/L)	LOD (μmol/L)	Real sample	Reference
HCLP (AD[a])	0.2~400	0.044	Egg samples	Preechaworapun, A et al[14].
SWV[b] (GCE)	75~320	25.0	Veterinary and biological samples	Titus, A.M et al[44].
SWV (GCE)	62.7~340	10.9	Commercial pharmaceutical products	Braga, O. C et al[45].
Amperometry	10~100	2.69~8.94	Pork samples	This work

[a] Amperometric detector
[b] Square wave voltammetry

Standard addition method was applied to the detection and the results were shown in Table 1, the recoveries for SAs standards added were in the range of 87% to 106%. Furthermore, comparisons of several macro electrodes with some previous reports on SAs electrochemical determination were given in Table 2.

The results showed that Nafion-MWCNTs PME that we proposed exhibited a relative high electrochemical sensitivity and response for SAs. Although the LOD of this experiment was inferior to HLCP methods, it was the lowest in all electrochemical methods listed in Table 2, suggesting that the technique manual powder microelectrode was worthy of promotion and application for the complex SAs compounds in the future.

3.10. Repeatability and durability of Nafion-MWCNTs PME

The repeatability of Nafion-MWCNTs PME was investigated. The results showed that no obvious changes of oxidation peak currents of SAs were observed after six continuous assays. The durability of the sensor was also investigated and the results indicated that the Nafion-MWCNTs PME could be used successively in the system for at least 6 h. The response signal of the proposed sensor still remained up to 91.08% of its initial value, suggesting that the fabrication procedure was reliable. When not used, the sensor was stored in sealed-dry state at 4^{o}C.

4. CONCLUSIONS

Direct electrochemical determinations of SA, SDZ, SM2 and SMZ were first achieved by using a powder microelectrode (PME) embedded with Nafion-MWCNTs in the present work. The resultant sensor exhibited high catalytic activity and electrochemical conductivity for SAs detection with low detection of limit, excellent repeatability and durability. Moreover, the fabrication of a PME was convenient, fast and simple, and compared to conventional macro electrodes, PME approach could be a significant savings, which was favorable for its huge potential application for rapid detection on the spot.

ACKNOWLEDGMENTS
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References

1. C. D. Souza, O.C. Braga, I. C. Vieira, A.Spinelli, *Sensors and Actuators B: Chemical*, 135(2008)

66-73.
2. S. Y. Won, C. H. Lee, H. S. Chang, S. O. Kim, S. H. Lee, D. S. Kim, *Food Control*, 22(2011) 1101-1107.
3. S. Borras, R. Companyo, J. Guiteras, *J Agric Food Chem*, 59(2011) 5240-5247.
4. J. Leitans, A. Sprudza, M. Tanc, I. Vozny, R. Zalubovskis, K. Tars, *Bioorganic & medicinal chemistry*, 21(2013) 5130-5138.
5. S. M. Ghoreishi, A. Khoobi, M. Behpour, S. Masoum, *Electrochimica Acta*, 130(2014) 271-278.
6. G. Z. Fang, J. X. He, S. Wang, *Journal of chromatography*, A 1127(2006) 12-17.
7. B. S. He, W. B. Chen, *International Journal of Electrochemical Science*, 10 (2015) 4335-4345.
8. A. M. Bueno, A. M. Contento, Á. Ríos, *Analytical Methods*, 5(2013) 6821.
9. X. P. Hong, Y. Zhu, Y. Z. Zhang, *Journal of Zhejiang University. Science*,13(2012) 503-510.
10. B. R. Valerie, *Journal of Chromatography B*, 723 (1999) 127-137.
11. U. Koesukwiwat, S. Jayanta, N. Leepipatpiboon, *Journal of chromatography*, A 1140 (2007) 147-156.
12. N. Assassi, A. Tazerouti, J. P. Canselier, *Journal of Chromatography*, A 1071(2005) 71-80.
13. K. Kishida, *Food Chemistry*, 101(2007) 281-285.
14. A. Preechaworapun, S. Chuanuwatanakul, Y. Einaga, K. Grudpan, S. Motomizu, O. Chailapakul, *Talanta*, 68(2006) 1726-1731.
15. J. J. Soto-Chinchilla, L. Gamiz-Gracia, A. M. Garcia-Campana, K. Imai, L. E. Garcia-Ayuso, *Journal of chromatography*, A 1095(2005) 60-67.
16. H. H. Chung, J. B. Lee, Y. H. Chung, K. G. Lee, *Food Chemistry*, 113(2009) 297-301.
17. A. V. Pereira, Q. B. Cass, *Journal of chromatography. B, Analytical technologies in the biomedical and life sciences*, 826 (2005) 139-146.
18. K. E. Maudens, G. F. Zhang, W. E. Lambert, *Journal of Chromatography*, A 1047(2004) 85-92.
19. N. Furusawa, *Analytica Chimica Acta*, 481(2003) 255-259.
20. N. H. David, A. N. Maureen, D. Dan, P. Lynda, R. Herbert, H. T. Michael, *Journal of Chromatography B*, 774(2002) 39-52.
21. T. S. Thompson, D. K. Noot, *Analytica Chimica Acta*, 551(2005) 168-176.
22. P. J. Sven, C. Margareta, J. Ulf, N. Gun, J*ournal of Pharmaceutical & Biomedical Analysis*, 13(1995) 415-417.
23. S. Lamba, S.K. Sanghi, A. Asthana, M. Shelke, *Analytica Chimica Acta*, 552(2005) 110-115.
24. M. R. S. Fuh, S. Y. Chu, *Analytica Chimica Acta*, 499(2003) 215-221.
25. V. K. Gupta, R. Jain, K. Radhapyari, N. Jadon, S. Agarwal, *Analytical biochemistry*, 408(2011) 179-196.
26. V. K. Gupta, R. Jain, S. Agarwal, R. Mishra, A. Dwivedi, *Analytical biochemistry*, 410(2011) 266-271.
27. R. Jain, V. K. Gupta, N. Jadon, K. Radhapyari, *Journal of Electroanalytical Chemistry*, 648 (2010) 20-27.
28. R. N. Goyal, V. K. Gupta, S. Chatterjee, *Biosensors & bioelectronics*, 24(2009) 3562-3568.
29. R. N. Goyal, V. K. Gupta, S. Chatterjee, *Biosensors & bioelectronics*, 24 (2009)1649-1654.
30. A. Guzman-Vazquezde Prada, A. J. Reviejo, J. M. Pingarron, *Journal of pharmaceutical and biomedical analysis*, 40(2006) 281-286.
31. M.A. McRipley, R.A. Linsenmeier, Journal of Electroanalytical Chemistry, 414(1996) 235-246.
32. Z. Guo, J. Chen, H. Liu, C. Cha, *Anal Chim Acta*, 607(2008) 30-36.
33. J. Chen, Z. He, H. Liu, C. Cha, *Journal of Electroanalytical Chemistry*, 588(2006) 324-330.
34. C. S. Cha, J. Chen, P.F. Liu, *Biosensors and Bioelectronics*,13(1998) 87-94.
35. J. Chen, C. S. Cha, *Journal of Electroanalytical Chemistry*, 463 (1999) 93-99.
36. S. Daniele, C. Bragato, M. A. Baldo, *Journal of Electroanalytical Chemistry*, 471(1999) 48-54.
37. S. Shahrokhian, E. Asadian, *Electrochimica Acta*, 55(2010) 666-672.
38. T. Łuczak, *Electrochimica Acta*, 54(2009) 5863-5870.

39. N. Thammasoontaree, P. Rattanarat, N. Ruecha, W. Siangproh, N. Rodthongkum, O. Chailapakul, Talanta, 123(2014) 115-121.
40. S. Sadeghi, T. Garmroodi, *Journal of Electroanalytical Chemistry*, 727 (2014) 171-178.
41. Q. Zhou, L. Yang, G. Wang, Y. Yang, *Biosensors & bioelectronics*, 49(2013) 25-31.
42. Y. Wang, C. Bi, *Journal of Molecular Liquids*, 177(2013) 26-31.
43. S. Sadeghi, A. Motaharian, A. Z. Moghaddam, *Sensors and Actuators B: Chemical*, 168(2012) 336-344.
44. A. M. Titus, N. Catherine, *Talanta*, 58(2002) 605-610.
45. C. B. Otoniel, C. Iolana, C. V. Iolanda, S. Almir, *Journal of the Brazilian Chemical Society*, 21 (2010) 813-820.
46. *S. A. Kumar, H. W. Cheng, S. M. Chen, Reactive & Functional Polymer*, 69(2009)364-370.
47. G. Li, S. L. Yang, L. B. Qu, R. Yang, J. J. Li, *J Solid State Electrochem*, 15(2011) 161-166.