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Sensitively Voltammetric Determination of Vanillin with a Molecularly Imprinted Ionic Liquid Polymer-Carboxyl Single-Walled Carbon Nanotubes Composite Electrode

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A molecularly imprinted ionic liquid polymer–carboxyl single-walled carbon nanotubes composite coated glassy carbon electrode (MIP–SWNTs-COOH/GCE) was prepared. The MIP was synthesized by using vanillin (VA) as template, hydrophilic ionic liquid 1-(α -methylacrylate)-3-allylimidazolium bromide as functional monomer and ethyleneglycol dimethacrylate as crosslinker. The MIP was water-compatible and had porous structure and large surface. The ionic liquid and VA could interact through π - π and hydrogen bonds, thus the imprinted sites possessed good specific recognization ability. When it was loaded on SWNTs-COOH film, the resulting electrode exhibited highly selective and sensitive response to VA in aqueous solution. After optimizing the conditions, linear response ranges of 0.4-8 and 10-140 μ M with sensitivities of 178 μ A/ μ M cm² and 8.1 μ A/ μ M cm² were obtained. The electrode was successfully applied to the detection of VA in biscuit, soybean milk powder and vanilla tea, and the recoveries for standards added were 94–107%.

Keywords: Vanillin; Molecularly imprinted polymer; Single-walled carbon nanotubes; Ionic liquid polymer; Electrochemical sensor

1. INTRODUCTION

Vanillin (4-hydroxy-3-methoxybenzaldehyde, VA) is an additive widely used in many snacks and beverage products for its desirable flavor and aroma[1, 2]. It is also reported to have some beneficial effects such as inhibiting the oxidation of human low density lipoproteins[3] and antisickling effect[4]. However, excessive ingestion can cause headaches, nausea and vomiting, etc[5]. According to the Food and Agriculture Organization (FAO), the acceptable daily intake of VA was 10 mg kg⁻¹. In China (GB2760-2011), VA is forbidden to add into the foods for 0 - 6 months infants. Therefore, for the sake of food safety, the quantitative detection of VA is necessary.

Currently, several analytical methods including UV spectrophotometry[6], high-performance liquid chromatography (HPLC)[7-9], gas chromatography (GC)[10, 11], and capillary electrophoresis (CE)[12, 13] can be used for the determination of VA. They have advantages and disadvantages, such as high sensitivity, high selectivity, time-consuming procedures, complicated pretreatment and high cost[14]. In recent years, electrochemical method was also exploited for the detection of VA, considering its simple operation, high sensitivity and low cost[15]. For example, Silva et al. [16] used a poly (allylamine hydrochloride) stabilized gold nanopaticles modified electrode to detect VA, the linear detection range was 0.90-15 μ M and the detection limit was 55 nM. Liu et al.[17] constructed a manganese dioxide-graphene composite electrode for VA, the linear range was 0.1-45 μ M. Shang et al[15] demonstrated an AuPd nanopaticles–graphene composite modified electrode for VA detection, the detection limit was 20 nM. These electrochemical sensors were rather sensitive, but their selectivity was not enough good. To improve this shortcoming, recognition elements should be introduced.

Molecularly imprinted polymers (MIPs) are synthetic materials with highly specific recognition ability for target molecules [18]. In recent decades, they have drawn much attention [19-21]. Generally, MIPs prepared by chemical polymerization in hydrophobic medium[22, 23] show hydrophobicity, thus their performance in aqueous solutions is not so satisfactory, such as decreased recognition ability and slow kinetics. Recently, vinylimidazolium ionic liquids (ILs) were widely used as monomer for preparing MIP. They not only enhanced water-compatible ability of MIP, but also made particle scale decrease in comparison with traditional monomers. Especially, they could interact with target molecules through more ways such as electrostatic attraction, π - π and hydrogen bond. Thus, the resulting MIPs presented high selectivity and fast kinetics for target molecule recognition. For instance, Yang et al[24] used 3-hexadecyl-1-vinylimidazoliumchloride (C16VimCl) as monomer to prepare chloramphenicol imprinted polymer and then constructed a chloramphenicol sensor. It showed high selectivity and response rate; Guo et al.[25] prepared a chlorsulfuron imprinted polymer using 1vinyl-3-butylimidazoliumchloride (C3VimCl) as monomer, and the obtained MIP possessed porous structure. Also, Yuan et al.[26] synthesized proteins imprinted poly(1-vinyl-3-butylimidazolium chloride (ViBulm⁺Cl⁻)), and they presented high selectivity factors. But no MIP-based electrochemical sensor for VA has been reported.

As most MIPs are lack of conductivity, conductive materials should be introduced for fabricating MIPs-based electrochemical sensors. Carboxyl single-walled carbon nanotubes (SWNTs-COOH) displayed superior electronic and chemical properties. It also showed favorable electrocatalysis toward the oxidation of some molecules such as dopamine, epinephrine and ascorbic acid[27]. It is expected to be a good support for constructing MIP based sensors.

In this work, a molecularly imprinted IL polymer–SWNTs-COOH composite film modified electrode (MIP-SWNTs-COOH/GCE) was fabricated, and the voltammetric behavior of VA was studied. Various influencing factors were optimized for the detection of VA, and the application feasibility of the electrode was evaluated by determining real samples such as biscuit, soybean milk powder and vanilla tea.

2. EXPERIMENTAL

2.1 Apparatus and reagents

All electrochemical experiments were performed on a CHI660B electrochemistry workstation (Shanghai CH Instruments Co., China). A three-electrode system was used, including a modified glassy carbon electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum foil as counter electrode. Scanning electron microscopy (SEM) was performed on a Zeiss (German) with an accelerating voltage of 15 kV or 3 kV. Ultraviolet visible (UV-Vis) absorption spectra were obtained by a U-3900 spectrometer (Hitachi Co., Japan). The Fourie transform infrared (FT-IR) absorption experiments were carried out with a Nexus-670 spectrometer (Nicolet, USA). 1H NMR spectra were obtained through a Varian Mercury 400 spectrometer and the solvent used was dimethyl sulfoxide (DMSO).

Vanillin and guaiacol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The stock solution (0.0010 M) of VA was prepared with redistilled water and stored in a refrigerator. When used, it was diluted with 0.1 M phosphate buffer solution (PBS, pH = 7.0), which was prepared with NaH₂PO₄ and Na₂HPO₄. 2,2'-Azobis-(isobutyronitrile) (AIBN) was obtained from Shanghai Shisihewei Chemical Industry Limited Company (China) and employed after twice recrystallization. Ethyleneglycol dimethacrylate (EDMA) was purchased from Energy-Chemical Company (Shanghai, China), and distilled under reduced pressure to remove inhibitors. 2-(Bromomethyl) acrylic acid came from Tokyo chemical industry Co. Ltd (Japan). All other chemicals used were of analytical reagent grade. The biscuit sample, soybean milk powder sample and vanilla tea were purchased from local supermarket. The support electrolyte was 0.1 M phosphate buffer solution (pH 7.0).

2.2 Synthesis of 1-MA-3AI-Br

1-MA-3AI-Br was synthesized according to the previous report [28]. In a typical reaction, 0.50 g (3 mmol) 2-(bromomethyl) acrylic acid was slowly added to 1-allylimidazolium (0.36 g, 3.3 mmol) in 10 mL round bottom flask, and then let them react under 70 °C for 24 h, forming light yellow and viscous liquid. The resulting mixture was washed with diethyl ether. Finally, the resulting product was dried under vacuum at 60 °C overnight. It was soluble in DMF, DMSO and water. ¹HNMR (300 MHz, DMSO), δ 4.90 (d, 2H, CH₂), 5.08 (s, 2H, CH₂), 5.28 - 5.36 (m, 2H, CH₂), 6.00 (s, 1H, =CH), 6.05 (m, 1H, CC*CCH₂), 6.36 (s, 1H, =CH), 7.78 (2H, d, NC*HCHN), 9.30 (1H, s, NC*HN).

2.3 Preparation of molecularly imprinted polymer

The molecularly imprinted polymer was prepared by non-covalent approach. Briefly, 76 mg (0.50 mmol) VA as template and 494 mg (2.0 mmol) as monomer were dispersed into 25 mL acetonitrile. After 1 h pre-polymerization process at room temperature, AIBN (30.0 mg, 0.18 mmol) as initiator and EDMA (1.9820 g, 10.0 mmol) as cross-linker were added to the mixture. Then it was purged with nitrogen for 30 min and sealed in nitrogen atmosphere. Next, the mixture was allowed to react in an oil bath at 60 °C for 24 h. After that, the product was collected after centrifugation for 10

min at 12000 rpm, and dried overnight. Subsequently, it was eluted by using methanol/acetic acid (9/1, V/V) until no VA was detected in the washing solution, and dried at 60 °C. The non-imprinted polymer (NIP) was synthesized in the same way except without VA.

2.4 Preparation of MIP and NIP modified electrodes

Prior to surface modification, the bare GCE was polished with slurry alumina (Φ =0.05 µm) and sonicated in water. Then 9 µL SWNTs-COOH suspension (0.50 mg mL⁻¹ in DMF) was coated on the cleaned GCE, and after the solvent evaporated under an infrared lamp, 2.5 µL MIP suspension (0.60 mg mL⁻¹ in DMSO) was dropped onto the resulting SWNTs-COOH/GCE and let to dry in the same way. Thus, a MIP–SWNTs-COOH film coated GCE electrode was constructed. Prior to measurements, the electrode was pretreated by repeating potential scan between 0.3 V and 0.9 V in a phosphate buffer solution (PBS) until obtaining a stable voltammetric curve. The NIP–SWNTs-COOH/GCE and other electrodes were prepared in the similar way.

2.5 Equilibrium adsorption experiments

The equilibrium adsorption experiments were performed as follows: 5 mg MIP (or NIP) was added to 5 mL VA solution (concentration: 0.02 mM to 0.16 mM). After stirring for 3h at room temperature, the supernatant was collected by centrifuging and determined by UV-Vis absorption spectrometry at 230 nm. The adsorption amount was calculated according to the formula: $Q = V (C_o - C_s)/m$, where V represented the volume of solution, C_o and C_s were the VA concentrations before and after adsorption, *m* was the mass of MIP (or NIP).

2.6 Electrochemical measurements

A 10 mL PBS (pH = 7.0) with proper concentration of VA was transferred to a cell, then the three-electrode system was assembled on it. After accumulation for 9 min under mildly magnetic stirring at open-circuit, cyclic voltammogram (CV) or differential pulse voltammogram (DPV) was recorded. The potential scan range was 0.3 V - 0.9 V (versus SCE). After each measurement, the electrode was eluted with methanol-acetic acid solution (V/V, 9/1) and ultrapure water to remove VA for reuse. For the study of selectivity interfering substance was introduced in the work solution (i.e. PBS + VA); after a accumulation step DPV was recorded and the peak current was comapred with that without interfering substance.

3. RESULTS AND DISCUSSION

3.1 Morphological and structural analysis

The SEM images of MIP and NIP are shown in Figure 1. As can be seen, the MIP presented porous structure, like the NIP. But the template molecule seems to have some effect on the structure since the morphology of MIP and NIP displayed some difference. The average diameter of the MIP

particles was about 0.2 μ m, much smaller than that of poly(methacrylic acid) (MAA) prepared by suspension polymerization and RAFT-MIP[19], meaning that the MIP had larger surface area and adsorption capacity. As VA molecule has one -OH, one -OCH₃ and a benzene ring, it can interact with 1-MA-3AI-Br through π - π stacking and multiple hydrogen bonds. Hence the MIP might show strong affinity to VA. In addition, 1-MA-3AI-Br possesses two groups suitable for polymerization. Consequently, the MIP was prepared more easily than by using traditional monomers, such as MAA and 4-vinylpyridine (4-VP)[28]. Figure 1 c and d display the morphology of SWNTs-COOH and MIP– SWNTs-COOH films on the surface of GCE. It can be seen that the SWNTs-COOH film is uniform and porous. The MIP is well-immobilized on the surface of SWNTs-COOH substrate, probably due to the π - π interaction and hydrogen bonds between them. It should be mentioned when the SWNTs-COOH was replaced by SWNTs, the resulting composite film was not so good, which could be ascribed to the weak interaction between SWNTs and the MIP. Therefore, SWNTs-COOH was adopted in this work.



Figure 1. SEM images of the MIP (a), NIP (b), SWNTs-COOH/GCE (c), MIP-SWNTs-COOH/GCE (d).

The FT-IR spectra of 1-MA-3AI-Br, NIP and MIP were shown in Figure. S1. The spectrum of 1-MA-3AI-Br presented characteristic peaks of imidazole ring (1560 cm⁻¹ C=N, 1635cm⁻¹ C=C) and carboxy group (1705 cm⁻¹ C=C-COOH), indicating that 1-MA-3AI was synthesized successfully. The spectrum of MIP exhibited peaks at 3447 cm⁻¹, 1728 cm⁻¹ and 1161 cm⁻¹, and they could be attributed to the carbonyl O-H stretching vibration, the carbonyl C=O stretching vibration, and the C-O-C

stretching vibration, respectively. These peaks proved the existence of poly(EDMA). The characteristic peaks of the NIP were similar to those of MIP, indicating that the template molecule VA was completely extracted from the MIP.

3.2 Adsorption curves

The adsorption curves of VA on the MIP and NIP are displayed in Figure 2. It is clear that the adsorption amount of VA on the MIP changes with its concentration more rapidly, compared with that on the NIP. When VA concentration exceeds 0.14 mM, the adsorption amount of MIP reaches a platform and stays unchanged. This means that a saturated adsorption is achieved and the maximum adsorption amount of MIP is about 32 μ mol g⁻¹. By contrast, the NIP shows smaller saturated adsorption amount, about 12 μ mol g⁻¹. So it can be concluded that the adsorption efficiency is significantly enhanced through molecular imprinting. The adsorption amount also varies with adsorption time, and in this case it reaches equilibrium adsorption within 1 h.



Figure 2. Saturation rebinding curves of VA on the MIP (a) and NIP (b). Error bars represented standard deviation (SD), n = 3.

3.3 Voltammetric behavior of VA

Figure 3 exhibited the linear sweep voltammograms of VA at different electrodes. VA showed a bigger peak at the MIP and NIP coated GCEs than at the bare GCE. This was due to the enhanced adsorption ability of MIP and NIP. When SWNTs-COOH was introduced, the difference between MIP and NIP coated electrodes increased. The MIP–SWNTs-COOH/GCE showed more sensitive response to VA than NIP–SWNTs-COOH/GCE. Obviously, SWNTs-COOH played an important role in the process. Compared with SWNTs-COOH/GCE, the MIP–SWNTs-COOH/GCE exhibited slightly smaller peak current because the additional MIP film hindered the electron transfer to some extent.



Figure 3. Linear sweep voltammograms of bare GCE (a), NIP/GCE (b), MIP/GCE (c), NIP–SWNTs-COOH/GCE (d), MIP–SWNTs-COOH/GCE (e) and SWNTs-COOH/GCE (f) in 0.1 M PBS (pH 7.0) solution containing 10 μM VA. Accumulation time: 9 min; scan rate: 50 mV s⁻¹.

3.4 Optimization of parameters affecting the determination of VA

3.4.1 Effect of the amounts of SWNTs-COOH and MIP

Firstly, the effect of the amount of SWNTs-COOH was studied (Figure. S2A). As a result, when the concentration of SWNTs-COOH was fixed at 0.5 mg mL⁻¹, the peak current of VA increased with the volume of SWNTs-COOH suspension rising until it was up to 9.0 μ L, then it decreased slowly. This could be ascribed to the variation of electrode surface area and electron transfer resistance with SWNTs-COOH amount. Therefore, 9.0 μ L SWNTs-COOH suspension (0.5 mg mL⁻¹) was adopted.

The amount of MIP was also varied to investigate its impact (Figure. S2B). It could be observed that the current response increased with the amount of MIP rising, due to the increase in the number of recognition sites. However, when the concentration of MIP suspension (2.5 μ L) exceeded 0.6 mg mL⁻¹, the response signal gradually decreased, which could be ascribed to the increase of electron transfer resistance. Hence, in this case 2.5 μ L 0.6 mg mL⁻¹ MIP was a balanced point and thus was used in the following experiments.

3.4.2 Effect of pH

As proton transfer is involved in the electrochemical reaction of VA, the solution pH does affect the peak current. Here the influence of solution pH was explored in the range of 6.0 - 8.0 (Figure. S3). As could be seen, the peak current increased with pH growing to 7.0, and then it decreased with further increasing pH. In addition, the peak potential (E_p) decreased with increasing

pH, and a good linear relationship between them was got as follows: $E_p = 0.8956 - 0.054$ pH. This indicated that the number of electron transferred was equal to the number of proton transferred in the electrochemical reaction.

3.4.3 Accumulation time

The peak current also varied with preconcentration time. As shown in Figure 4, when it was above 9 min the peak current kept almost unchanged for 0.8μ M VA, meaning that saturated rebinding of VA on the MIP–SWNTs-COOH/GCE was achieved. Therefore, 9 min was selected as the optimal accumulation time for VA determination.



Figure 4. Variation of the peak current of 0.8 μ M VA with accumulation time. Other conditions as in Fig. 3. Error bars represent SD, n = 3.

3.5 Calibration curve

Under the optimized experimental conditions, the DPVs of VA were recorded. The peak current increased with VA concentration increasing, furthermore, they showed good linear relationship (Figure 5). The linear response ranges were 4.0×10^{-7} to 8×10^{-6} M and 1.0×10^{-5} to 1.4×10^{-4} M, and the regression equations were i_p (μ A) = -5.796 + 12.58 C (μ M) (r^2 = 0.9994) and i_p (μ A) = 95.80 + 0.5767 C (μ M) (r^2 = 0.9974), with sensitivities of 178 μ A/ μ M cm² and 8.1 μ A/ μ M cm². When VA concentration was above 140 μ M, the calibration curve gradually didn't satisfy with a straight line, manifesting that saturated adsorption was gradually reached. The detection limit was 2.0×10^{-7} M (S/N = 3). Compared with other methods, this sensor offered a reasonable linear range and higher sensitivities for VA (Table 1).



Figure 5. Differential pulse voltammograms of VA at MIP–SWNTs-COOH/GCE. VA concentration (from a to n): 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0, 10, 20, 40, 60, 80, 100, 120 and 140 μ M. Inset: the calibration curves. Other conditions as in Fig. 3.

Electrodes	Linear range (µM)	Detection limit (µM)	References
AuNP-PAH/GCE	0.9-15	0.055	[16]
Graphene/GCE	0.6-48	0.056	[31]
AgNPs/GN/GCE	2-100	0.33	[32]
Arg-G/GCE	2-70	1.00	[33]
1-MA-3AI-Br-VA	0.4-8	0.2	This work
MIP-SWNTs-COOH/GCE	10-140		

Table 1. Comparison of different electrodes for VA determination.

As could be seen, the plot of peak current versus VA concentration was similar to that expected for a Langmuir adsorption isotherm (Figure. S4), $C/i_p = 1/(bI_{p,max}) + C/I_{p,max}$ [29, 30]. In this equation, i_p was the peak current based on the amount of VA attached to the MIP and *C* represented the concentration of VA in the solution, approximate to the analytical concentration. $I_{p,max}$ standed for the apparent maximum adsorption capacity and *b* was the adsorption equilibrium constant. The plot of C/i_p versus *C* yielded good linearity, with a correlation coefficient of 0.996. From the slope and intercept of the line, the maximum adsorption capacity and adsorption equilibrium constant were estimated as 162 µA and 9.72 × 10⁴ M⁻¹, respectively. Thus, the Gibbs energy change due to the adsorption was -28.454 kJ/mol, calculated according to $\Delta G^{\circ} = -RT \ln b$.

3.6 Selectivity, repeatability and stability

The selectivity of the MIP–SWNTs-COOH/GCE was evaluated by testing its electrochemical response to VA in the presence of interfering substances (Figure 6). The experimental results showed that when 1000-fold glucose, fructose or sucrose, 500-fold citric acid, 80-fold ascorbic acid, 60-fold theophylline, 10-fold salicylic acid or guaiacol was present, the change of peak current of 6.0 μ M VA was less than 7%. Therefore, the sensor had good selectivity.



Figure 6. Influence of coexistent substances on the electrochemical response of MIP–SWNTs-COOH/GCE to VA. Solution composition: (a) 6.0 μ M VA + 0.1 M PBS (pH 7.0), (b) a + 10-fold guaiacol, (c) a + 60-fold theophylline, (d) a + 10-fold salicylic acid, (e) a + 500-fold citric acid, (f) a + 80-fold ascorbic acid, (g) a + 1000-fold D-fructose, (h) a + 1000-fold sucrose. Other conditions as in Figure 3.

The repeatability was examined by detecting a 6.0 μ M VA solution with above modified electrode, and the relative standard deviation (RSD) of peak current was 3.2% (n = 5). After used successively for 30 assays the current response of the sensor still maintained 94% of its initial value. Meanwhile, five MIP–SWNTs-COOH/GCEs were prepared in the same way and a 6.0 μ M VA solution was determined. As a result, the RSD of peak current was 5.6% (n = 5). After a five-day storage in a refrigerator, the MIP–SWNTs-COOH/GCE retained 95% of its initial current response for 6.0 μ M VA solution; after a two-week storage it still retained 88% of its initial current response. These reflected the good repeatability and stability of MIP– SWNTs-COOH/GCE.

3.7. Real sample analysis

The electrode was applied to the detection of VA in practical samples, including biscuit, soybean milk powder and vanilla tea. Prior to determination, the biscuit and the soybean milk powder were grinded into powder in a mortar with a pestle, and then about 0.50 g powder was taken and dispersed in 10 mL ethanol. The mixture was sonicated for 1 h. After centrifugated (12000 rpm) for 10

min, 1 mL of the supernatant was diluted to 10 mL with 0.1 M PBS (pH 7.0) for determination. As for vanilla tea sample, 0.6 g was extracted with 200 mL hot water for 1 h. Afterwards, the mixture was centrifugated (12000 rpm) for 15 min. The remaining solid was dissolved in 300 mL PBS (0.1 M, pH 7.0) for determination. The contents of VA in these samples were calculated and they were 22.9 μ g g⁻¹ (for biscuit), 125 μ g g⁻¹ (for soybean milk powder) and 70 μ g g⁻¹ (for vanilla tea), respectively. The recoveries for standards added were 94–107% (Table 2), indicating that the method was reliable.

Samples	vanillin	vanillin	RSD	Recovery
	added	found	(%,n=3)	(%)
	(µM)	(µM)		
biscuit	0	0.75	3.5	-
	4.00	4.98	3.1	106
	6.00	6.47	2.6	95
	8.00	8.72	2.8	99
soybean milk	0	4.12	4.5	-
powder	4.00	8.38	3.8	107
	6.00	9.80	3.6	95
	8.00	11.6	2.7	94
vanilla	0	0.93	3.8	-
tea	4.00	4.99	2.7	102
	6.00	6.73	3.0	97
	8.00	9.19	3.4	103

Table 2. Measurement results of VA in sample solutions.

4. CONCLUSIONS

A novel molecularly imprinted ionic liquid polymer–SWNTs-COOH film coated glassy carbon electrode was fabricated for VA sensing. The MIP was water-compatible and it had large surface and high recognition capacity to hydrophilic VA. The SWNTs-COOH provided conductive substrate and it could cooperate with MIP. Thus the resulting modified electrode exhibited good selectivity, high sensitivity towards VA. The sensor could be applied to the detection of VA in real samples.

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Supplementary Information



Figure S1. FT-IR spectra of 1-MA-3AI-Br, MIP and NIP.



Figure S2. Effects of the amounts of SWNTs-COOH (A) and MIP (B). Concentration of SWNTs-COOH suspension: 0.5 mg mL⁻¹; volume of MIP suspension: 2.5 μL. Accumulation time: 9 min; scan rate: 50 mV s⁻¹.



Figure S3. Effect of pH on the oxidation peak current and peak potential of 6 μ M VA. Other conditions as in Fig. 3. Inset: peak potential vs pH plot. Error bars represent SD, n = 3.



Figure S4. The plot of C/i_p versus C of VA at a MIP–SWNTs-COOH/GCE, corresponding to Fig. 6.

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