



Analytical Methods

Electrochemical behavior and voltammetric determination of vanillin based on an acetylene black paste electrode modified with graphene–polyvinylpyrrolidone composite film



Peihong Deng^{a,*}, Zhifeng Xu^a, Rongying Zeng^{a,b}, Chunxia Ding^c

^a Department of Chemistry and Material Science, Hengyang Normal University, Hengyang 421008, PR China

^b College of Resource and Environment, Hunan Agricultural University, Changsha 410128, PR China

^c College of Science, Hunan Agricultural University, Changsha 410128, PR China

ARTICLE INFO

Article history:

Received 7 October 2014

Received in revised form 8 February 2015

Accepted 9 February 2015

Available online 14 February 2015

Keywords:

Graphene–polyvinylpyrrolidone composite film

Electrochemical sensor

Vanillin

Electrochemical behavior

Voltammetric determination

ABSTRACT

The graphene–polyvinylpyrrolidone composite film modified acetylene black paste electrode (GR–PVP/ABPE) was fabricated and used to determine vanillin. In 0.1 M H₃PO₄ solution, the oxidation peak current of vanillin increased significantly at GR–PVP/ABPE compared with bare ABPE, PVP/ABPE and GR/ABPE. The oxidation mechanism was discussed. The experimental conditions that exert influence on the voltammetric determination of vanillin, such as supporting electrolytes, pH values, accumulation potential and accumulation time, were optimized. Besides, the interference, repeatability, reproducibility and stability measurements were also evaluated. Under the optimal experimental conditions, the oxidation peak current was proportional to vanillin concentration in the range of 0.02–2.0 μM, 2.0–40 μM and 40–100 μM. The detection limit was 10 nM. This sensor was used successfully for vanillin determination in various food samples.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the major component of natural vanilla. The desirable flavor and aroma properties of vanillin have led to its widespread application in confectionery, beverage, pharmaceutical, food and perfumery industries. Vanillin is reported to have beneficial health effects such as inhibition of the oxidation of human low density lipoproteins leading to lower rates of cardiac disease mortality (Teissedre & Waterhouse, 2000) and an antisickling effect in sickle cell anaemia sufferers (Farthing et al., 1999). The source of vanilla is the bean, or pod, of a tropical Vanilla orchid. Although more than 12,000 tons of vanilla is produced each year, less than 1% of this is natural vanillin from Vanilla, the remainder is synthesized much more cheaply via chemical or biochemical processes (Walton, Mayer, & Narbad, 2003). Although synthetic vanillin is cheaper and widely produced, extensive evidence indicates that excessive ingestion of vanillin can cause headaches, nausea and vomiting, and it can also affect the function of the liver and kidney. Therefore, simple, sensitive and low-cost determination of vanillin is of great significance to people's health.

Nowadays, many analytical methods have been proposed for vanillin accurate determination in various food samples or vanilla extracts, such as high performance liquid chromatography (Farthing et al., 1999; Waliszewski, Pardo, & Ovando, 2006) gas chromatography (Pérez-Silva et al., 2006), capillary electrophoresis (Ohashi, Omae, Hashida, Sowa, & Imai, 2007), UV–vis spectrophotometry (Longares-Patrón & Cañizares-Macías, 2006) and chemiluminescence (Timotheou-Potamia & Calokerinos, 2007). With the advantages of cheap instrumentation, small sample volume and rapid analysis, the electrochemical sensor is an ideal technique for the determination of vanillin because the molecule is electrooxidisable. However, a major obstacle encountered in the detection of vanillin at bare electrode is the relatively high overpotential together with poor reproducibility resulted from a fouling effect, which causes rather poor selectivity and sensitivity (Hardcastle, Paterson, & Compton, 2001). An effective way to overcome these barriers is electrode modification. Some chemically modified electrodes have been reported (Bettazzi, Palchetti, Sisalli, & Mascini, 2006; Kong, Shen, Yu, Wang, & Chen, 2010; Luque, Luque-Pérez, Ríos, & Valcárcel, 2000; Peng, Hou, & Hu, 2012; Shang, Zhao, & Zeng, 2014; Yardım, Gülcan, & Şentürk, 2013; Zheng, Hu, Gan, Dang, & Hu, 2010). However, the performance of some electrodes was still not enough good. Thus it is important to develop new modified electrodes for vanillin detection.

* Corresponding author. Tel.: +86 13908447066.

E-mail address: dph1975@163.com (P. Deng).

Graphene (GR) has attracted enormous attention among researchers for its properties such as high thermal conductivity, high electrical conductivity and electron transfer rate (Li & Kaner, 2008). Thus GR was chosen as the electrode material in this research. However, the practical applications of GR are challenged by its irreversible agglomeration both in the drying state and in common solvents, which significantly reduces its effectiveness (Niyogi et al., 2006; Pasricha, Gupta, & Srivastava, 2009). In the present work, polyvinylpyrrolidone (PVP) was dissolved in water as the solvent to disperse GR, which can make GR dispersed more evenly, and can be better fixed on the electrode surface.

Recently, acetylene black (AB) with novel properties such as large specific surface area, strong adsorptive ability, excellent electric conductivity was developed and has been widely used in electrochemical sensors. As far as we are aware no work on the determination of vanillin by combination of the excellent properties of GR and AB has been reported previously, a novel electrochemical sensor was developed for vanillin determination using GR–PVP composite film modified acetylene black paste electrode (denoted as GR–PVP/ABPE). The electrochemical behaviors of vanillin were investigated on GR–PVP/ABPE carefully with the electrochemical parameters calculated. Finally, the fabricated sensor was applied to determine trace amounts of vanillin in food samples and the results were consistent with those obtained by HPLC. This method offers several advantages over other techniques, including being of low environmental impact, efficient, inexpensive and rapid.

2. Experimental

2.1. Chemicals and solutions

Graphite powder, hydrazine hydrate solution (80 wt%), polyvinylpyrrolidone and vanillin were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Acetylene black (AB, purity > 99.99%) was supplied by STREM Chemicals, USA. A standard stock solution of 1.0×10^{-3} M vanillin was prepared by dissolving vanillin in ethanol, which was preserved at 4 °C and protected from daylight when not in use. Working solutions of lower concentrations were prepared by appropriate dilution of the stock solution with 5% (v/v) ethanol aqueous solution. 0.1 M H_3PO_4 solution was used as the supporting electrolyte. All other chemicals were of analytical reagent grade and used without further purification. All solutions were prepared with doubly distilled water.

2.2. Apparatus

Cyclic voltammetry was performed on a CHI 660E electrochemical workstation (Chenhua Instrument Co., Ltd., Shanghai, China) controlled by a microcomputer with CHI660 software. Second-order derivative linear sweep voltammograms were measured on a model JP-303E polarographic analyzer (Chengdu Instrument Factory, Chengdu, China). A conventional three-electrode system was adopted. The working electrode was a GR–PVP/ABPE (diameter: 1 mm), the auxiliary and reference electrodes were a platinum wire and a saturated calomel electrode (SCE), respectively. JEOL JSM-6610LV scanning electron microscope (Jeol/Ntc., Japan) was used for the characterization of GR–PVP composite. The pH measurements were carried out on a pHs-3c exact digital pH meter (Shanghai Leichi Instrument Factory, Shanghai, China), which was calibrated with standard pH buffer solutions. High-performance liquid chromatography (HPLC) was performed on Waters model 510 system (Waters Ltd., USA) comprising a Kromasil 100-5C18 (250 mm \times 4.6 mm) column equipped with a Waters 2487

dual λ absorbance UV/Vis detector using a mobile phase consisting of aqueous acetic acid (1%, v/v)–acetonitrile (85:15, v/v) at a flow rate of 0.6 mL min^{-1} .

2.3. Preparation of GR–PVP dispersion

Graphite oxide were synthesized from natural graphite powder according to our previous reports (Deng, Xu, & Feng, 2014; Deng, Xu, & Kuang, 2013) and dispersed in water to form a 0.5 mg mL^{-1} graphene oxide (GO) dispersion by ultrasonication for 2 h. 10.0 mg of PVP was added into the 20 mL GO dispersion in a flask. After magnetic stirring for 10 min, the resulting dispersion was further treated with 20 μL of 80 wt% hydrazine hydrate solution and 80 μL of 25 wt% ammonia solution and allowed to react for 1 h at 95 °C. Finally, the color of mixture solution changed from light yellow to black at the end of the reaction, indicating the reduction of GO. The black GR–PVP suspension was stable for at least 2 months at room temperature. As a control, the pure GR suspension was prepared in the same way mentioned above but without the addition of PVP.

2.4. Fabrication of modified electrodes

The acetylene black paste electrode (ABPE) was prepared by thoroughly mixing 1.20 g acetylene black powder with 0.30 g solid paraffin in a mortar, and then the mixture was heated at 80 °C until the solid paraffin melted. The resultant paste was tightly pressed into the end cavity (1 mm in diameter) of the electrode body immediately, and the surface was polished with a piece of smooth paper until it had a shiny appearance. The electrode was subjected to cyclic potential sweeps between 0.2 and 1.2 V in 0.5 M H_2SO_4 solution until a stable cyclic voltammogram was obtained. A volume of 2 μL of the resulting GR–PVP dispersion was casted onto the surface of ABPE and dried at room temperature. For comparison, the PVP/ABPE and GR/ABPE were prepared by casting 2 μL of 0.5 mg mL^{-1} PVP and 2 μL of 0.5 mg mL^{-1} GR onto the ABPE surface respectively. In order to show the unique properties of AB, the ordinary carbon paste electrode made of graphite powder (CPE) was also prepared.

2.5. Pretreatment of the commercial food samples

Various kinds of food products such as biscuit, chocolate, candy, cake, soy milk powder, icecream, orange flavored soft drink and colo were purchased from a local supermarket. The sample solutions were prepared by the following procedure. Solid samples taken from five packages of the same brand were carefully ground to a fine powder and mixed adequately in the mortar. An accurately weighed portion of powder (about 1.0 g) was taken and dispersed in 10 mL ethanol. The mixture was sonicated for 1 h with a supersonic cleaner. After centrifugating (4000 rpm) for 10 min, 0.50 mL of the clear supernatant was diluted to 10 mL with 0.10 M H_3PO_4 for voltammetric determination. The liquid samples were transferred into beaker and degassed in an ultrasonic bath. Then 1.0 mL of the samples was pipetted into the voltammetric cell, and diluted to 10 mL with 0.10 M H_3PO_4 solution for voltammetric determination.

2.6. Experimental procedure

For voltammetric measurements, the three-electrode system was immersed in a 10-mL electrochemical cell containing an appropriate concentration of vanillin and 0.1 M H_3PO_4 solution. The solution was stirred at 500 rpm at a chosen accumulation potential throughout the selected accumulation period. Following the pre-concentration period, the stirring was stopped, and after

Download English Version:

<https://daneshyari.com/en/article/1184507>

Download Persian Version:

<https://daneshyari.com/article/1184507>

[Daneshyari.com](https://daneshyari.com)