

Original Research Article

Electrochemical analysis of carbaryl in fruit samples on graphene oxide-ionic liquid composite modified electrode

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ABSTRACT

Graphene oxide-ionic liquid composite modified glassy carbon electrode was fabricated for the electrochemical oxidation and determination of carbaryl. The modified electrode exhibits an obvious electrocatalytic activity towards the oxidation of carbaryl. The electrochemical oxidation of carbaryl at modified electrode is a one-electron coupling with one-proton transfer process. The diffusion coefficient and standard heterogeneous rate constant are calculated to be $3.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $5.71 \times 10^{-3} \text{ cm s}^{-1}$, respectively. For the determination of carbaryl, a linear scope of 0.10–12.0 μM with a detection limit of 0.02 μM was achieved. The proposed method was applied successfully for the determination of carbaryl in fruit samples, which provided a promising tool for food safety control.

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1. Introduction

Carbaryl, 1-naphthyl methylcarbamate, is a broad-spectrum insecticide. It is extensively used on crops, lawns, trees and even on animals due to its high insecticidal activity and relatively low persistence (Garbellini et al., 2009; Nikolelis et al., 2008). However, excessive use can cause its bioaccumulation in food or water, and then lead to bioconcentration through the food chain. In humans, acute and chronic occupational exposure can lead to neurological effects, nausea, vomiting, coma, respiratory failure and death (Dong et al., 2010). Taking into account these toxic effects, sensitive and rapid determination of carbaryl is essential for the protection of environment and human health.

Many analytical methods have been employed for the determination of carbaryl including gas chromatography (Cavaliere et al., 2012), high performance liquid chromatography (Song et al., 2013), flow-injection (Sanchez-Barragan et al., 2007) and immunosensor (March et al., 2009). However, some of these methods are time-consuming and require expensive equipments

and advanced technical expertise. Electrochemical techniques have drawn the interest of researchers, due to their low cost, easy operation, fast response and high sensitivity. Electrochemical biosensors based on the inhibition of acetylcholinesterase enzyme have been developed for the detection of carbaryl (Cesarino et al., 2012; Abdolhamid, 2013; Liu et al., 2014). However, the biosensors always need considering the effects of temperature, pH, applied potential to the enzyme activity, which limiting their application in some areas. The nonenzymatic electrodes could avoid the disadvantages of enzyme-based biosensors. The electrochemical determination of carbaryl using nonenzymatic electrode modifiers such as carbon nanotube/cobalt phthalocyanine (Moraes et al., 2009), amino benzenesulfonic acid functionalized gold nanoparticles (Sun et al., 2013) and boron doped diamond electrode (Codognoto et al., 2006) have been reported. To the best of our knowledge, electrochemical oxidation and determination of carbaryl by using a graphene oxide-ionic liquid composite modified electrode has not been reported.

Recently, graphene has attracted increasing attention due to its extraordinary thermal, mechanical, electrical and electrochemical properties. Because of the large specific surface area and high electrical conductivity, it is widely used in the electrochemical fields such as electrocatalysis (Guo and Dong, 2011; Yang et al.,

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2009) and electroanalysis (Wang et al., 2011; Qiu et al., 2011; Nie et al., 2012; Han et al., 2011). Ionic liquid (IL) is a promising material adopted in the field of electrochemistry. Due to the high ionic conductivity and wide electrochemical window, it has been widely used as electrochemical solvents (Armand et al., 2009) and electrode modifiers for the fabrication of sensors (Zhou et al., 2013; Ba et al., 2012). The integration of graphene and ionic liquid could elicit synergistic effects in the electrochemical applications. Thus, graphene-ionic liquid composite could be used as a kind of robust and advanced electrode material for the determination of carbaryl.

In the present work, graphene oxide (GO)-ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate, [Bmim]PF₆) composite modified glassy carbon electrode (GO-IL/GCE), was fabricated. Electrochemical measurements were carried out to validate the electrocatalytic activity of GO-IL/GCE. Based on the obvious electrocatalytic activity of GO-IL/GCE towards the oxidation of carbaryl, a sensitive analytical method was established for the determination of carbaryl. The analytical performance of the proposed method for the determination of carbaryl in fruit samples was also evaluated.

2. Experimental

2.1. Reagents and instrumentation

Graphene oxide (purity >99%) was purchased from Beijing DK Nano technology Co., Ltd. (Beijing, China). The ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF₆), was purchased from Lanzhou Centre for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). A 1.0×10^{-3} mol L⁻¹ stock solution of carbaryl (99.8% purity, Sigma-Aldrich, Germany) was prepared with methanol. All other chemical reagents were obtained from Nanjing Chemical Reagent Company (Nanjing, China). All the solutions were prepared with double distilled water. A series of Britton-Robinson (BR) buffer solutions with different pH values were prepared by adjusting 0.04 M mixed acid solutions containing phosphoric acid, glacial acetic acid and borate with 0.20 M NaOH solution.

All electrochemical experiments were carried out on a CS350 Electrochemical Workstation (Wuhan Corrtest Instruments Co., Ltd., Wuhan, China). A conventional three-electrode cell configuration was employed for the electrochemical measurements. A modified glassy carbon electrode (disc diameter of 3.5 mm) was used as the working electrode, with saturated calomel electrode (Saturated KCl) and platinum wire for the reference and the counter electrode, respectively.

2.2. Preparing GO-IL composite and fabrication of modified electrode

3.0 mg of the graphene oxide was dispersed in 4.0 mL of [Bmim]PF₆ by ultrasonic agitation for about 1 h. Then, the suspension was centrifuged at 7000 rpm for 30 min. The GO-IL composite was finally collected by removing the supernatant. For the fabrication of modified electrode, 2.0 mg of GO-IL composite was dispersed in 2.0 mL of dimethyl formamide (DMF) forming the composite suspension. Then 10.0 μ L of the suspension was dropped on the clean GC electrode surface and then evaporating the solvent in air to prepare GO-IL/GCE.

In addition, GO was dispersed in DMF with the aid of ultrasonic agitation to prepare 1.0 mg/mL GO suspension. Then 10.0 μ L of the suspension was dropped on the clean GC electrode surface and then evaporating the solvent in air to prepare GO/GCE. The modified electrodes were stored in air at room temperature.

Prior to use, the glassy carbon electrode was carefully polished with a leather cloth containing 0.05 μ m Al₂O₃ slurry and then ordinal ultrasonically cleaned in ethanol and distilled water.

2.3. Electrochemical measurements

In a typical process, 20.0 mL electrolyte containing 10.0 mL of BR buffer (pH = 5.0), 2.0 mL of methanol, 8.0 mL of water, was transfer into a clean electrochemistry cell, and then the required volume of carbaryl stock solution was added by micropipette. Among them methanol helps to the dissolution of carbaryl in the solution. Firstly, accumulation was performed on open-circuit for 4 min with stirring. After that, the cyclic voltammetry were carried out from 0.2 to 1.0 V at scan rate of 0.1 V s⁻¹. The square wave voltammetry were carried out from 0.3 to 1.0 V with a step increment of 4 mV, amplitude of 25 mV and frequency of 15 Hz. Upon completion of each measurement, the modified electrode was placed in a blank solution and successive scan was performed until no peak came out, then the electrode was washed with water and dried in air for reuse.

2.4. Sample preparation

A 10.0 g fruit sample of grape or tomato (from local market) was cut into very small pieces and was transferred to a flask containing 20.0 mL ethanol. After vigorously shaking and ultrasonication for 40 min, the mixture was centrifuged and the supernatant was collected for analysis.

3. Results and discussion

3.1. Electrochemical behavior of carbaryl

Fig. 1 shows the cyclic voltammograms of 50.0 μ M carbaryl at bare GCE (a), GO/GCE (b) and GO-IL/GCE (c) in the 0.02 M BR buffer solution. A weak oxidation peak (E_{pa} , 0.79 V) is observed for the bare GCE, which corresponding to the oxidation of carbaryl. However, the current response of carbaryl at the GO/GCE is much higher than that of bare GCE. Moreover, the peak potential shifts to 0.7 V. This means that the GO/GCE has high electrocatalytic activity towards the oxidation of carbaryl, which may be attributed to the large specific surface area and fast electron transfer rate of GO. While the GO-IL/GCE gives a more larger and well-defined oxidation peak (E_{pa} , 0.64 V). It suggests that the presence of IL could enhance the peak current and decrease the oxidation

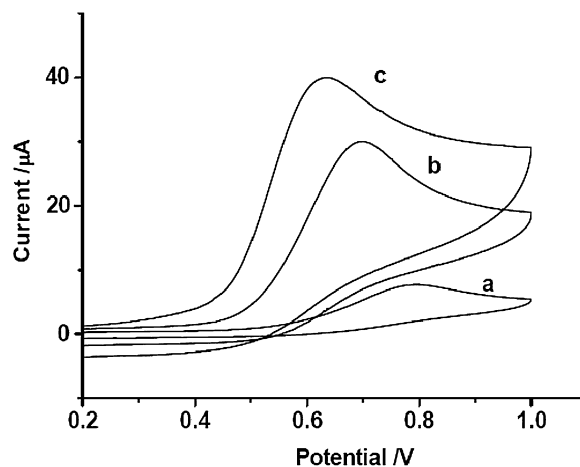


Fig. 1. Cyclic voltammograms of 50.0 μ M carbaryl at bare GCE (a), GO/GCE (b) and GO-IL/GCE (c) in 0.02 M BR buffer solution (pH = 5.0), Scan rate: 0.10 V s⁻¹.

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