



Ionic liquid modified carbon-ceramic electrode with structure similar to Graphene nanoplatelets: Application to Imidacloprid determination in some agricultural products



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ARTICLE INFO

Article history:

Received 27 June 2015

Received in revised form 1 May 2016

Accepted 28 June 2016

Available online 29 June 2016

Keywords:

Ionic liquid

Graphene-like nanoplatelets

Imidacloprid

Agricultural products

Carbon-ceramic electrode

ABSTRACT

1-Allyl-3-methylimidazolium tetrafluoroborate ([AMIM][BF₄]) ionic liquid modified carbon-ceramic electrode was applied for Imidacloprid electrochemical determination. Surface of the modified electrode was characterized using scanning electron microscopy (SEM), and Energy Dispersive X-ray Analysis (EDX). These analyses showed the deposition of ionic liquid on the surface of carbon-ceramic electrode caused formation of graphene-like nanoplatelets.

Based on high surface area and rich edge defects which resulting from graphene-like nanoplatelets and high ionic conductivity of ionic liquid (IL), the modified electrode exhibited electro-catalytic activity for Imidacloprid reduction. Operational parameters including IL volume, solution pH; which affect the analytical performance of modified electrode were optimized. The calibration curve for Imidacloprid was linear in the range of 5×10^{-8} – 7×10^{-6} M with the detection limit (S/N=3) of 31 nM (3.1×10^{-8} M). This modified electrode was applied for imidacloprid determination in some commercial formulation and agricultural products and the results were in good agreement with standard high-performance liquid chromatography method.

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1. Introduction

The use of pesticides in agriculture has increased dramatically and undeniably during the last few decades. Discharge of pesticides into the environment can cause their incorporation into various kinds of matrices such as soil, crops, water and this may be a serious threat to human health [1]. Imidacloprid (1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine) pesticide is the first member of the neonicotinoid family, which is available in the market since 1991 [2,3]. It acts as an agonist of acetylcholine, which can suppress the acetylcholine sterase transmission by binding to the post synaptic nicotinic receptors in the central nervous system of insect [4]. Because of the extensive application of imidacloprid in agriculture to control insect pests, such as Colorado potato beetles, aphids, termites and thrips, its residue may occur in foods, including grains, fruits and vegetables, and therefore, pose a potential hazard for consumers [5]. Therefore, developing of a fast, sensitive, accurate and easy to use method for Imidacloprid determination in agricultural products is crucial. As to now, various analytical

methods such as liquid chromatography tandem mass spectrometry [5], high-performance liquid chromatography with diode array [6], enzyme-linked immunoassay [7], fluorimetry [8], gas chromatography [9], and colorimetry [10] were reported to Imidacloprid determination in different real samples. Meanwhile, these techniques requires advanced equipment and expert persons as analyzer beside these, they are expensive and time-consuming ones. In contrast electro-analytical techniques because of their various advantages such as: low limit of detection, high analyte selectivity, compact nature, simple sample preparation procedure, cost effectiveness, adaptability to field use and minimum use of toxic organic solvents are attracted much attention in electroanalysis [2]. Therefore, because of electro-activity of Imidacloprid several electroanalytical methods have been reported for its determination in different real samples [2,4,11–16].

Carbon is a unique and very versatile element which is capable of forming different architectures at the nanoscale [17]. Graphene is a two dimensional (2-D) sheet of carbon atoms bonded by sp² bonds. This configuration provide this material with extraordinary properties, such as large surface area, theoretically 2630 m²/g for a single layer, and double that of single-walled carbon nanotubes (SWCNTs). It also shows excellent thermal ($k = 5 \times 10^3 \text{ Wm}^{-1} \text{ K}^{-1}$)

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and electrical conductivity ($\sigma = 64 \text{ mS cm}^{-1}$) [18]. Due to its unique electronic properties, rich edge defects, large surface area and strong mechanical strength; it exhibits remarkable electro-catalytic and sensing capability [19].

The history of ionic liquids goes back to 1914, when Walden reported the synthesis of ethylammonium nitrate (m.p. 12°C) [20]. Ionic liquids (ILs) are either organic salts or mixtures of salts that are fluid at room or near-room temperature. Due to the excellent physicochemical properties of room temperature ionic liquids (RTILs), such as high ionic conductivity, wide electrochemical windows, negligible vapor pressure, chemical and thermal stability, good antifouling ability, well biocompatibility, and inherent catalytic ability; they can be used as the modifier or the supporting electrolyte in electroanalysis [21–24].

Sol-gel technology the three step process of construction of materials involves the low temperature hydrolysis of a monomeric precursor of organometallic alkoxide, its condensation followed by polycondensation to yield a polymeric oxo-bridged network.

Low preparation temperatures and inorganic supports offer some advantages to this process over other methods, among which are chemical inertness, physical strength, and good surface renewability. Additional advantages come from the fact that sol-gel derived materials are porous and thus mass transport is relatively easy through pores [25]. Carbon-ceramic composite electrodes (CCEs) are comprised of a dispersion of carbon powder that is held together by sol-gel derived ceramic binder [26–28]. After the introduction of a carbon ceramic electrode on the basis of sol-gel processing, this new kind of electrode has been utilized to a great extent for electrochemical sensors [29–31].

In the present work 1-Allyl-3-methylimidazolium tetrafluoroborate ionic liquid (IL) was applied for modification of carbon-ceramic electrode. The surface of modified electrode was studied by scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX), and the formation of graphene-like nanoplatelets on the electrode surface was proved. This modified electrode was applied for electrochemical determination of Imidacloprid. Based on inherent properties of formed graphene-like nanoplatelets and high ionic conductivity of ionic liquid, this modified electrode exhibited electro-catalytic behavior toward the electro-reduction of Imidacloprid; and its low level determination in real samples was done. This electrode was successfully applied for Imidacloprid determination in some commercial formulation and agricultural products and the results were in good agreement with standard high-performance liquid chromatography method.

2. Experimental

2.1. Reagents and chemicals

MethyltrimethoxySilane (MTMOS) and graphite powder were purchased from Merck and used without any further purification. Imidacloprid (content 98%) was obtained from Chem Service (United States American). Commercial formulation Soluble Concentrate (35%) was prepared from GYAH Corporation, Manufacturer of Chemical and Agricultural Products located in Karaj, Iran. 3-bromo-1-propene, kaliumtetrafluoroborate, N-methyl imidazole, acetonitrile, and ethyl acetate were purchased from Merck. 1-Allyl-3-methylimidazolium tetrafluoroborate ([AMIM][BF₄]) as room temperature ionic liquid was home-made synthesized according to literature by some alteration [32]. Briefly to a stirred solution of N-methyl imidazole (4.105 g, 50.0 mmol) in acetonitrile (40 mL) was added requisite 3-bromo-1-propene (6.653 g, 55 mmol) dropwise at 0°C . The reaction mixture was stirred for 48 h at 50°C . Removal of the solvent under reduced pressure afforded crude 1-allyl-3-methylimidazolium bromide. For anion

exchange procedure to a solution of the crude 1-allyl-3-methylimidazolium bromide, in acetone (40 mL) was added kalium tetrafluoroborate (6.56 g, 50.0 mmol). The reaction mixture was stirred for 12 h at room temperature. The resulting mixture was filtered through an aluminium oxide pad to remove the kalium salt and color. Evaporation of solvent under reduced pressure afforded the 1-allyl-3-methylimidazolium tetrafluoroborate.

The pH of solutions was adjusted to 7.0 with phosphate buffer solution (PBS). The distilled, deionized and sterilized water was used in all solution preparation.

2.2. Apparatus

Electrochemical experiments were performed using AUTOLAB PGSTAT 30 electrochemical analysis system and GPES 4.9 software package (Eco Chemie. The Netherlands). The utilized three-electrode system was composed of a modified carbon-ceramic electrode with 3 mm diameter as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. All experiments were performed at room temperature, without removing the dissolved oxygen. An electrochemical glass vessel was employed throughout the experiments. The scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX) experiments were done on a MIRA3 TESCAN made in the Czech Republic.

¹H NMR and ¹³C NMR data of 1-Allyl-3-methylimidazolium bromide [AMIM]Br and 1-Allyl-3-methylimidazolium tetrafluoroborate [AMIM]BF₄ as follows: [AMIM]Br: ¹H NMR δ 4.15 (s, 3H), 5.06 (d, $j = 6.40$, 2H), 5.45 (d, $j = 10.0$, 1H), 5.47 (d, $j = 17.20$, 1H), 6.01 (m, 1H), 7.67 (s, 1H), 7.86 (s, 1H), 10.16 (s, 1H); ¹³C NMR δ 35.36, 50.41, 120.67, 120.93, 122.52, 128.60, 135.32.

[AMIM]BF₄: ¹H NMR δ 4.10 (s, 3H), 5.12 (d, $j = 6.41$, 2H), 5.43 (d, $j = 10.0$, 1H), 5.45 (d, $j = 17.20$, 1H), 5.99 (m, 1H), 7.73 (s, 1H), 7.84 (s, 1H), 10.19 (s, 1H); ¹³C NMR δ 35.41, 50.39, 120.62, 120.90, 122.51, 128.57, 135.30.

The HPLC determinations of Imidacloprid was carried out using YOUNGLING CTS30 Product liquid chromatograph (South Korea), equipped with a UV-1650 PC SHINADZU UV-Vis detector set at 260 nm. A microsorb C18 250 mm \times 4.0 mm column with particles of 5 μm chromatographic column was used. The mobile phase consisted of a mixture of water, buffer solution (consisted of an aqueous solution of 0.1 M citrate sodium and 0.1 M hydrochloric acid by volume ratio of 40:60, pH = 3) and acetonitrile by volume ratio of 72:8:20, respectively, while the injection volume was 5 μL [33].

2.3. Preparation of modified carbon-ceramic electrode

The construction and following modification of the carbon-ceramic electrode involve two steps. First, the silica sol solution was prepared by mixing of 0.6 mL MTMOS, 0.9 mL methanol and 0.1 mL hydrochloric acid (0.1 M) and stirred for 5 min to homogeneous gel solution obtained. This ormosil was properly mixed with 300 mg graphite powder. The mixture was added into Teflon tube (with 3 mm I.D. and 3 cm length, and the length of composite in the tube was about 8 mm) and dried for 48 h at room temperature [31]. The exposed surfaces of all electrodes were polished with 800, 2000, 2500, 3000 grit polishing papers, respectively and then were rinsed thoroughly with water to yield shiny surfaces. Copper wire connected to the other end, provided the electrical contact.

In the second step, the electrode modifier solution was prepared by dissolving of 30 μL of 1-Allyl-3-methylimidazolium tetrafluoroborate ionic liquid in 0.47 mL ethanol and were sonicated for 30 min to obtain the light yellow solution. After that 10 μL of fresh prepared solution was dropped on the polished surface of the carbon-ceramic electrode and allowed to dry at room temperature for 12 h.

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