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Graphene nanoplatelets like structures formed on ionic liquid modified carbon-ceramic electrode: As a sensing platform for simultaneous determination of dopamine and acetaminophen

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ABSTRACT

Room temperature ionic liquid as 1-allyl-3-methylimidazolium tetraflouroborate ([AMIM][BF_4]) was used for surface modification of carbon-ceramic electrode. The surface of the modified electrode was characterized using scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), energy dispersive X-ray analysis (EDX), transmission electron microscopy (TEM) and Raman spectroscopy. Based on these studies we were concluded that deposition of ionic liquid on the carbon-ceramic electrode surface caused the formation of graphene nanoplatelets like structures on its surface.

This modified electrode was used for simultaneous electrochemical determination of dopamine (DA) and acetaminophen (AP). Because of effective separation of oxidation peak potentials of DA and AP on modified electrode, simultaneous determination of them was possible. Operational parameters such as amount of IL volume, solution pH, scan rate; which affected the analytical performance of modified electrode were optimized. The calibration curves for DA and AP were linear in the range of 0.1–20 μM and 0.1–20 μM with the detection limit (S/N = 3) of 68 nM and 63 nM, respectively. The high repeatability, reproducibility, and long-term life time were of modified electrode figure of merits. The present electrode was successfully applied for the determination of DA and AP in some commercial pharmaceutical samples, human blood serum, and urine samples with satisfactory results.

1. Introduction

Dopamine (3, 4-dihydroxyphenylethylamine), which was discovered in the 1950s is one of the most important catecholamine neurotransmitters in the mammalian central nervous system. Abnormalities in DA concentrations have been linked with several neurological disorders such as the debilitating ailment Parkinson's disease and the mental disorder schizophrenia [1]. DA is also believed to play a central role in Huntington's disease, a fatal genetic neurodegenerative movement disorder and has also been associated with drug addiction and attention disorders. Therefore, DA has been given tremendous consideration in biomedical investigation and there is a strong need to establish sensitive, selective and reliable methods for the direct measurement of DA [1]. Acetaminophen (*N*-acetyl-*p*-aminophenol), commonly known as paracetamol, is conventionally used as analgesic and an antipyretic medicine. AP is clinically important, though the overdoses of AP have been found to cause fatal hepatotoxicity and nephrotoxicity. The antioxidant effects of AP on neurons and its therapeutic potential in neurodegenerative diseases, particularly Alzheimer's disease have also been reported. The in vitro studies have indicated that the use of AP also protects dopaminergic neurons from the oxidative stress damage caused by acute exposure to higher levels of dopamine (DA). The prolonged dosage of AP in in vivo models has been found to reduce significantly the levels of DA [2]. Therefore, from the standpoint of clinical and pharmacological importance simultaneous determination of DA and AP in biologic fluids is necessary. Dopamine and acetaminophen contain phenolic hydroxyl group, which is electrochemically active and can be oxidized. Thus, electrochemical methods because of their good sensitivity, simplicity, good stability and low cost are the better choice for individual or simultaneous determination of DA and AP. On the other hand, in the most of bare solid electrodes the oxidation peak potentials of them overlapped seriously. With the aim of improving the selectivity, it is essential to separate the signals from each other. Therefore, various modified electrodes such as polyDAN-RB4/GC [2], Fe3O4@Au—S—Fc/GS-Chitosan/GCE [3], Ppyox/AZ/Au [4], SWCNT/CCE [5], MWCNT/GCE [6], Pyrolytic carbon (PyC) films [7], Gr-FEPA-CS/GCE [8], and ERGO/ZrO_2 [9] were applied for simultaneous determination of them.

The history of ionic liquids goes back to 1914, when Walden reported the synthesis of ethylammonium nitrate (m.p. 12 °C) [10]. Ionic liquids (ILs) are either organic salts or mixtures of salts that are fluid at room or near-room temperature. Typically ILs is composed of bulky 1, 3-dialkylimidazolium, alkylammonium, alkylphosphonium or

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alkylpyridinium organic cations and inorganic anions such as $AlCl_4^-$, BF_4^-, PF_6^-, NO_3^-, ClO_4^-, CF_3COO^-, $CF_3SO_3^-$ and CH_3COO^-. The most commonly used neutral ILs include 1-butyl-3-methylimidazolium hexaflurophospate or tetrafluroborate abbreviated as [bmim][PF_6] and [bmim][BF_4] correspondingly [11]. 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 [12–20].

Carbon is a unique and very versatile element which is capable of forming different architectures at the nanoscale [21]. Graphene is a two-dimensional (2-D) sheet of carbon atoms in a hexagonal configuration with atoms bonded by sp^2 bonds. These bonds and this electron configuration are the reasons for the extraordinary properties of graphene, which include a very large surface area, rich edge defects, a tunable band gap, room-temperature Hall effect, high mechanical strength, high elasticity and thermal conductivity [22]. Because of these properties, it exhibits remarkable electrocatalytic and sensing capability [23].

Sol-gel technology the three step process of construction of materials involves the low temperature hydrolysis of a monomeric precursor of organometalic 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 [24]. Carbon- ceramic composite electrodes (CCEs) are comprised of a dispersion of carbon powder that is held together by sol-gel derived ceramic binder [25,26]. 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 [27–29]. However; bare carbon-ceramic electrodes have some drawbacks such as low detection sensitivity and poor resolution to specific analytes such as mixtures of DA and AP, therefore their modification is necessary.

In the present work, carbon-ceramic electrode was modified with 1-Allyl-3-methylimidazolium tetraflouroborate ionic liquid (IL). Characterization experiments on modified electrode surface were revealed the formation of graphene nanoplatelets like structures on its surface. This modified electrode was applied for simultaneous electrochemical determination of dopamine and acetaminophen. The modified electrode displayed electro-catalytic behavior toward the oxidation of DA and AP; and selectivity of the modified electrode was improved for the simultaneous and low level determination of them. The modified electrode was successfully used for the simultaneous determination of DA and AP in some pharmaceutical products, human blood serum, and urine samples.

2. Experimental

2.1. Reagents and chemicals

Methyltrimethoxy Silane (MTMOS) and graphite fine powder (with the particle size of <45 μm) were purchased from Merck and used without any further purification. Dopamine, acetaminophen, uric acid, 3-Bromo-1-propene, Kalium tetraflouroborate, *N*-methyl imidazole, acetonitrile, and ethyl acetate were purchased from Merck. Graphene nanoplatelets purchased from Xiamen knano graphene technology Co. Ltd. Dopamine hydrochloride was purchased from hospital drug store and was of USP quality. The AP tablets (500 mg) were obtained from a local market. The human blood serum and urine samples were obtained from Drug Applied Research Center, Tabriz University of Medical Sciences-Iran. 1-Allyl-3-methylimidazolium tetraflouroborate ([AMIM][BF_4]) as room temperature ionic liquid was synthesized according to our previous work [30].

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 an MIRA3 TESCAN made in the Czech Republic.

The XRD patterns of all electrode surfaces were recorded on an X-ray diffractometer (D500 Siemens) using Cu Ka ($k = 1.54$ Å) radiation source (30–40 kV and 40–50 mA) in the range of $2\theta = 4$–70°.

The TEM images of modified electrode surface were taken by transmission electron microscopy (TEM, Leo 906, Zeiss, Germany). Raman spectrum of graphene like nanoplatelets structures was recorded using an Almega Thermo Nicolet Dispersive Raman Spectrometer (USA) with a 532 nm laser.

2.3. Preparation of modified carbon-ceramic electrode

First the silica sol solution was prepared by mixing 0.6 mL of MTMOS, 0.9 mL methanol and 0.1 mL hydrochloric acid (0.1 M) and stirred for 5 min to homogeneous sol solution resulted. This ormosil was mixed well with 300 mg graphite powder. The mixture was added to teflon tube (with 3 mm id and 3 cm length, and the length of the paste in the tube was about 8 mm) and dried for 48 h at room temperature [29]. The surface of all electrodes was removed by mechanical polishing with 800, 2000, 2500, and 3000 grit polishing papers, respectively. The electrodes were rinsed thoroughly with water to yield shiny surfaces. Copper wire contacted to the other end, provided the electrical contact.

The electrode modifier solution was prepared by mixing 50 μL of 1-Allyl-3-methylimidazolium tetraflouroborate ionic liquid, 0.45 mL ethanol. Then they were stirred 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.

2.4. Real samples preparation

The real sample analysis of DA and AP were carried out in dopamine hydrochloride injection (200 mg/5 mL), acetaminophen tablet (500 mg), human blood serum, and urine samples. An accurate injection sample volume equivalent to about 5 mg of DA and 5 mg of powdered AP tablet was transferred to a two separate 50 mL flask and adjusted to volume with doubly distilled water. A 0.10 mL portion of the DA and AP solution was subjected to differential pulse voltammetry (DPV) measurements as described in Section 3.5. A 1.0 mL human blood serum sample was deproteinized by adding 2.0 mL of acetonitrile. After centrifugation at 12,000 rpm for 20 min, the supernatant was transferred into another centrifuge tube and dried with a N_2 stream. The residue was dissolved in 1.0 mL of water and stored in refrigerator until analytical measurements. Dopamine and acetaminophen was spiked in 10 times diluted human blood serum by DPV method. The urine samples of healthy persons before and after 4 h of the oral