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ORIGINAL ARTICLE

Development and application of graphite-$SiO_2/Al_2O_3/Nb_2O_5$-methylene blue (GRP-SiAlNb-MB) composite for electrochemical determination of dopamine

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Abstract In the present paper an amperometric sensor based on graphite-$SiO_2/Al_2O_3/Nb_2O_5$-methylene blue (GRP-SiAlNb-MB) composite has been successfully prepared for dopamine (DA) determination in real samples. The electrochemical behavior of DA at the GRP-SiAlNb-MB has been evaluated by employing cyclic voltammetry. The best ratio (m/m) of GRP-SiAlNb-MB composite was found to be 1:0.54. Under optimized conditions (pH 7.5 in 0.15 mol L^{-1} phosphate buffer) the amperometry method responds linearly to DA from 5.0 up to 500.0 μmol L^{-1} (r = 0.995) with limits of detection and quantification of 1.49 and 4.97 μmol L^{-1}, respectively. The developed method was successfully applied for DA determination in real samples of pharmaceutical formulations and can be used for routine quality control analysis of pharmaceutical

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formulations containing DA. The use of inorganic matrix SiAlNb was found to be very useful to adsorb MB in the composite material with further improvement of the anodic peak current of DA.

1. Introduction

The development of highly selective and stable new sensors aiming at the determination of phenolic compounds in medicinal, pharmaceutical and biotechnological samples is of paramount importance for quality control. Chemical modifications of solid electrodes have been extensively studied for this purpose since it helps to obtain various sensor configurations (Trojanowicz, 2011; Lavecchia et al., 2010; Alonso-Lomillo et al., 2010). Nonetheless, the choice of electrodic material as a substrate for the immobilization of electroactive species plays an important role in the preparation of chemically modified electrodes (CME). In this sense, graphite paste electrode has received growing attention during years owing to its properties including good adsorption properties toward the chemical modifiers, renewable surface and presence of porous surface (Kalcher et al., 2006). Methylene blue (MB) has been widely employed for electrode modification as chemical modifier playing an important electrocatalytic role (Arvand et al., 2003). However, a brief overview of literature demonstrates that the majority of electrochemical methods that makes use of MB are focused on biosensor preparation using horseradish peroxidase (HRP) as enzyme for hydrogen peroxide determination. In this case, the enzyme and MB are usually deposited onto glassy carbon or gold electrode surface (Liu et al., 2000; Lei et al., 1996; Xu et al., 2003, 2004; Qian et al., 1998; Gu and Hasebe, 2004), which makes very weak this physical immobilization, thus resulting in a loss of MB during sensor use. This shortcoming can be overcome by using inorganic matrix in the sensor preparation, such as nano-SiO_2 (Xian et al., 2006), nano-TiO_2 (Xiao et al., 2008) and SiO_2/M_xO_y mixed oxide (Zaitseva et al., 2002; Ribeiro et al., 2003), which has been very useful to strongly adsorb MB aiming at sensor preparation.

Recently, our research group has reported the outstanding features of ternary mixed oxide ($SiO_2/Al_2O_3/Nb_2O_5$) to strongly adsorb DNA in the MWCNT/$SiO_2/Al_2O_3/Nb_2O_5$/DNA composite for electrochemical determination of promethazine and amitriptyline as well as to preconcentrate metal ions (Marco et al., 2013a,b; Costa et al., 2011; Tarley et al., 2010).

Dopamine (DA), 3,4-dihydroxyphenylethylamine, is an important phenolic compound which occurs naturally as neurotransmitter in the mammalian central nervous system. The deficiency of DA can cause some serious diseases such as Parkinson, epilepsy and senile dementia in humans (Ge et al., 2009; Smith and Devlin, 1992). Nowadays, catecholamine-based pharmaceuticals are widely used in medicine. So it is extremely important to determine DA quickly, precisely and accurately for quality control.

DA can be determined by electrochemical techniques, but some difficulties still remains, since its oxidation needs a high over potential at bare electrodes and the products are often adsorbed on the electrode surface, resulting in electrode fouling and unstable analytical signal. Different electroanalytical approaches have been dedicated to the development of new modified electrodes for DA monitoring. In general the materials commonly used are based on functionalized polymers or electrochemically modified polymers such as: poly(acrylic acid) multi-walled carbon nanotubes (MWCNTs) (Liu et al., 2007), deoxyribonucleic acid (DNA)/poly(p-aminobenzensulfonic acid) bilayer (Lin et al., 2007), RNA film (Kang and Lin, 2006), functionalized single-walled carbon nanotube (SWCNT) (Zhang et al., 2007), poly(eriochrome black T) (Yao et al., 2007), functionalized thiadiazole (Kalimuthu and John, 2009), poly 3-(5-chloro-2-hydroxyphenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid (CDDA) film (Ensafi and Khayamian, 2009), poly(acid chrome blue K) (Zhang et al., 2009), mesoporous carbon/Nafion (Zheng et al., 2009), and poly(vinyl alcohol) (Li and Lin, 2006). Such approach for sensor preparation shows slight drawbacks including time-consuming to be prepared and, in some cases, low reproducibility, thus resulting in a loss of stability. Other reports concerning the DA determination by ECL (electrochemiluminescence) can be cited (Zhang et al., 2013). ECL is a sensitive technique that has been widely used for sensor preparation; however, it requires complex modification procedures on the electrode and, thus, an accuracy optimization of several variables is crucial for its success since electrochemical and chemiluminescence measurements are integrated, which requires high skills for the analyst. In this sense, graphite paste electrodes prepared from composites based on mixed oxide and chemical modifier methylene blue (MB) are considered as a suitable alternative in comparison with the film preparation aiming the development of a reliable and feasible method for routine analysis of DA in pharmaceutical samples.

Therefore, the main objective of this paper was to prepare a new graphite-$SiO_2/Al_2O_3/Nb_2O_5$-methylene blue (GRP-SiAlNb-MB) composite and employ it as an electrochemical sensor for DA determination in pharmaceutical formulation. The quickly and ease to prepare, the high stability of the MB adsorbed onto SiAlNb as well as the satisfactory sensitivity are the highlights of proposed sensor for DA determination.

2. Experimental

2.1. Chemical and reagents

Dopamine (DA) was obtained from Sigma Aldrich (St. Louis, MO, USA). Dopamine injectable samples (Dopamine Hydrochloride 5 mg mL^{-1}, Teuto®), which contain sodium chloride and sodium metabisulfite in aqueous medium, were obtained from a local hospital. A pure graphite powder (GRP), anhydrous monobasic sodium phosphate, dibasic sodium phosphate and methylene blue (MB) were purchased from Synth® (Diadema, SP, Brazil). Tris[hydroxymethyl] aminomethane (Trizma), 4-[2-hydroxyethyl] piperazine-1-

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