Materials Science and Engineering C 65 (2016) 205–214

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

# Polyaniline–graphene oxide nanocomposite sensor for quantification of calcium channel blocker levamlodipine

Rajeev Jain *, Ankita Sinha, Ab Lateef Khan

School of Studies in Chemistry, Jiwaji University, Gwalior – 474011, India

ARTICLE INFO

Article history:
Received 6 November 2015
Received in revised form 4 February 2016
Accepted 31 March 2016
Available online 11 April 2016

Keywords:
Nanocomposite
Electrochemical properties
Levamlodipine (LAMP)
Polyaniline–graphene oxide modified glassy carbon electrode (PANI/GO/GCE)

ABSTRACT

A novel polyaniline–graphene oxide nanocomposite (PANI/GO/GCE) sensor has been fabricated for quantification of a calcium channel blocker drug levamlodipine (LAMP). Fabricated sensor has been characterized by electrochemical impedance spectroscopy, square wave and cyclic voltammetry, Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The developed PANI/GO/GCE sensor has excellent analytical performance towards electrocatalytic oxidation as compared to PANI/GCE, GO/GCE and bare GCE. Under optimized experimental conditions, the fabricated sensor exhibits a linear response for LAMP for its oxidation over a concentration range from 1.25 μg $mL^{-1}$ to 13.25 μg $mL^{-1}$ with correlation coefficient of 0.9950 ($r^2$), detection limit of 1.07 ng $mL^{-1}$ and quantification limit of 3.57 ng $mL^{-1}$. The sensor shows an excellent performance for detecting LAMP with reproducibility of 2.78% relative standard deviation (RSD). The proposed method has been successfully applied for LAMP determination in pharmaceutical formulation with a recovery from 99.88% to 101.75%.



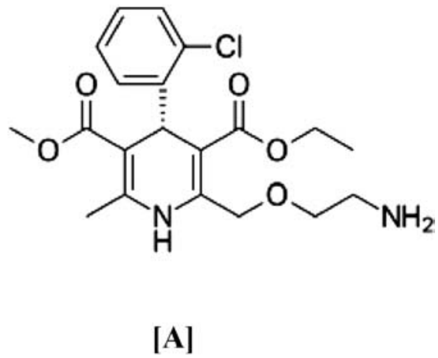
## 1. Introduction

Levamlodipine, S-(-)-2-[(2-aminoethoxy) methyl]-4-(2-chlorophenyl)-3-ethoxy-carbonyl-5-methoxycarbonyl-6-methyl-1, 4-dihydropyridine [A] is basically an S- enantiomer of amlodipine [1,2]. It is a very powerful dihydropyridine calcium channel blocker possessing vasodilation properties and used in the treatment of hypertension and angina [3].

In recent years, polymer nanocomposites have become an interesting area of research due to their large surface to volume ratio, excellent mechanical, optical and electrocatalytic properties and have been extensively employed for various electroanalytical sensing applications [4–17]. Polyaniline (PANI) is one of the highly conducting polymers and has attracted much attention for their use in different types of sensing applications using various electroanalytical techniques [18–30]. It is one of the most promising and unique conducting polymers having good biocompatibility, environmental stability, excellent electronic properties. Carbon based materials exhibit very fascinating and extraordinary electrochemical properties making them an appealing choice as electrode material for various electrochemical studies of different compounds [31–41]. Maleh et al. [42] have proposed a new kind of sensor based on FePt/CNTs nanocomposite/*N*-(4-hydroxyphenyl)-3,5-dinitrobenzamide modified carbon paste electrode for detection of glutathione and piroxicam simultaneously. Also they proposed, a very novel modified carbon paste electrode based on NiO/CNTs nanocomposite and (9, 10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)-4-ethylbenzene-1,2-diol for simultaneous detection of cysteamine, nicotinamide adenine dinucleotide and folic acid [43]. Mokhtari et al. [44] fabricated multiwall carbon nanotubes paste electrode and characterized by various electrochemical techniques for voltammetric quantification of morphine and diclofenac in biological and pharmaceutical samples. M. Elyasi et al. [45] developed a Pt/CNTs nanocomposite based ionic liquid modified carbon paste electrode (Pt/CNTs/ILCPE) sensor to determine Sudan I using voltammetric techniques. Also Maleh et al. [46] proposed a sensitive biosensor immobilized DNA at pencil graphite electrode modified with polypyrrole/functionalized multiwalled carbon nanotubes to detect 6-mercaptopurine. Due to the high electron transport and electrocatalytic activity, graphene based electrodes exhibit fascinating potential applications as electrochemical sensors and promote quantification of analyte at its surface with enhanced electrocatalytic performance. Nowadays, graphene based electrodes have been extensively reported for various kinds of sensing application for a variety of analytes. Recently, Akhavan et al. [47] have applied reduced graphene nanowalls for ultra sensitive detection of single nucleotide polymorphisms of DNA using differential pulse voltammetry (DPV) and efficiently developed an electrochemical biosensor for the determination of the purine and pyrimidine bases of DNA. They also succeeded in establishing a versatile $Mg^{2+}$-charged spongy graphene electrodes for sensitive detection of leukemia in blood serum using differential pulse voltammetry and compared with glassy carbon electrode [48]. Akhavan et al. [49] also applied reduced graphene oxide nanowall electrodes for highly sensitive and selective electrochemical detection of leukemia cells using DPV.

* Corresponding author.
*E-mail address:* rajeevjain54@yahoo.co.in (R. Jain).

http://dx.doi.org/10.1016/j.msec.2016.03.115




**[A].** : Structure of levamlodipine.

Graphene oxide (GO), an oxidized form of graphene is a two-dimensional nanosheet of covalently bonded carbon atoms. GO has become an interesting area of research as it exhibits very similar properties with graphene. Electrocatalytic studies on various electroactive compounds have been reported using GO as an electrode material [50,51]. The covalent oxygen functional groups in GO induce incredible mechanical strength and can interface with polymers to form GO-intercalated polymer nanocomposites [52].

The electrocatalytic activity of graphene is enhanced by conjugation with other conducting nanomaterials for electrochemical sensing of various compounds. PANI provides a uniform matrix for the immobilization of graphene oxide and hence there is an increase in the effective electrode surface area and electron transfer centers after the immobilization. Thus, conjugation of PANI with graphene oxide significantly enhance the electrocatalytic activity of the resultant electrode and due to their synergistic catalytic effect, there is an enhancement in the voltammetric response of levamlodipine (LAMP). Comparing with CNTs, graphene oxide has shown the advantages of increased conductivity, good biocompatibility, ease of production and function, and low cost source material [53–55]. Moreover, comparing with fullerene, another carbon based electrode material, it is difficult to disperse it in the polymer matrices due to its strong molecular arrangement and crystalline form. Therefore, it is difficult to prepare PANI-fullerene polymer composites [56]. Also, graphene and PANI based electrodes have much more faster electron transfer kinetics and enhanced catalytic response for electro quantification of analytes than metal nanoparticles [57,58]. Therefore, it is highly desirable to explore polyaniline–graphene oxide composite for sensing applications.

Combining the high conducting [59] and electrical properties [60,61] of these polymer nanocomposites with different types of electroanalytical techniques like square wave voltammetry, cyclic and differential pulse voltammetry, a promising sensing platform has now been developed in the area of electrochemical sensing and biosensing [57,58,62–68]. The developed method of determination of levamlodipine using voltammetry acts as an alternative to other techniques of its detection like capillary electrophoresis [69], coupled isotachophoresis-capillary zone electrophoresis with diode array detection [70], spectrophotometric and fluorescence quenching measurements [71], chemiluminescence methods [72] which require complicated extraction, sample preparation, time consuming derivatization and purification processes with expensive and sophisticated instrumentation. In the present paper, using voltammetric technique, a novel method for detection of levamlodipine at PANI/GO/GCE sensor has been developed which offers high sensitivity, accuracy, precision, fast response with relatively low cost simple instrumentation and does not require the tedius procedures like extraction and purification prior to monitoring of analytes. However, the stability of the proposed PANI/GO/GCE sensor has been studied only for 15 days as the anodic current decreases for LAMP oxidation due to deterioration of PANI/GO nanocomposite modification at glassy carbon electrode surface.

To the best of our knowledge, this is the first voltammetric study of S enantiomer levamlodipine at polyaniline/graphene oxide nanocomposite modified glassy carbon electrode. The electrochemical performance of the developed PANI/GO/GCE sensor towards levamlodipine has been compared with the results obtained at individual PANI/GCE, GO/GCE and at bare GC electrode. The fabricated sensor shows reproducible results towards levamlodipine oxidation using voltammetric techniques.

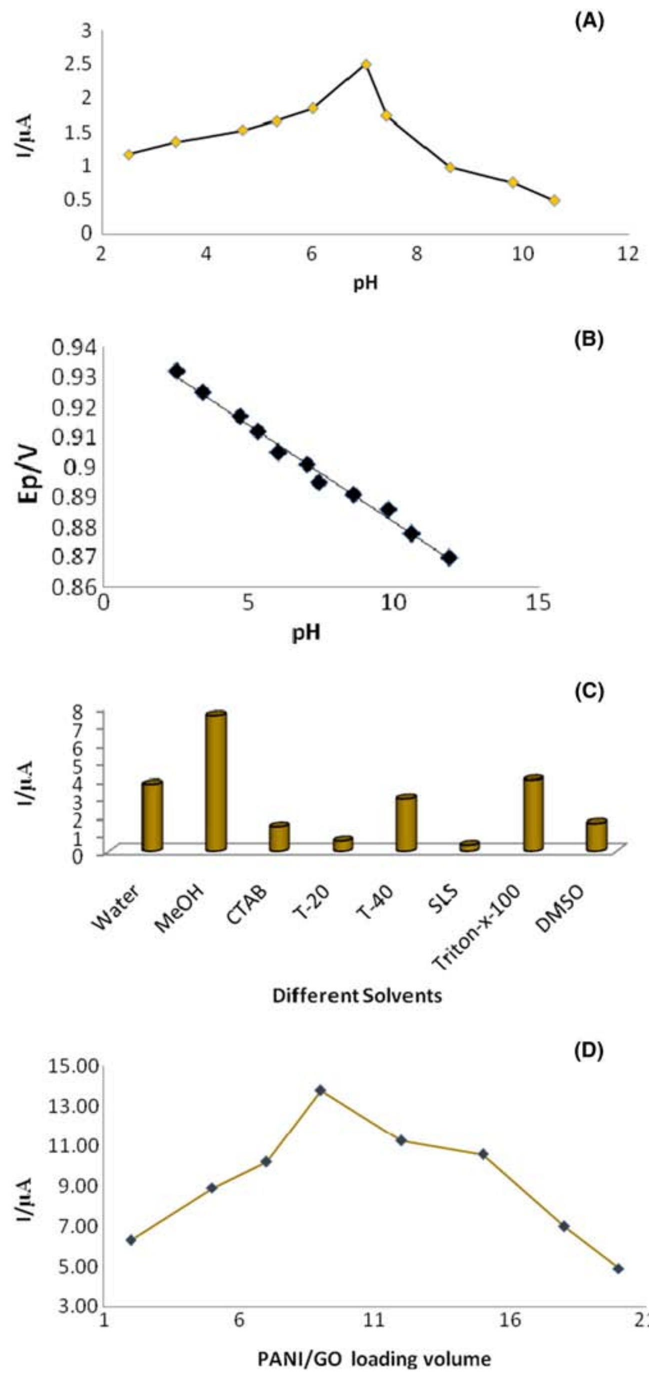



**Fig. 1.** Optimization parameters for 10 μg $mL^{-1}$ LAMP oxidation. (A) Effect of pH (pH 2.5–10.5). (B) Plot of Ep vs pH. (C) Effect of different solvents. (D) Effect of varying PANI-GO dosage.