Electrochimica Acta 72 (2012) 179–185

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Electrochemical behaviors of roxithromycin at poly(3,4-ethylenedioxythiophene) modified gold electrode and its electrochemical determination

Long Zhang[a], Xuemin Duan[a,*], Yangping Wen[b], Jingkun Xu[b,**], Yuanyuan Yao[b], Yao Lu[a], Limin Lu[b], Ou Zhang[a]

[a] School of Pharmacy, Jiangxi Science & Technology Normal University, Nanchang 330013, PR China
[b] Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, PR China

ARTICLE INFO

Article history:
Received 17 February 2012
Received in revised form 3 April 2012
Accepted 3 April 2012
Available online 10 April 2012

Keywords:
Roxithromycin
Sensor
Voltammetric determination
Poly(3,4-ethylenedioxythiophene) modified Au electrode
Macrolide antibiotics

ABSTRACT

A simple, sensitive, and reliable method for the voltammetric determination of roxithromycin (RM) at the surface of the fabricated poly(3,4-ethylenedioxythiophene) (PEDOT) modified Au electrode has been successfully developed. The electrochemical behavior of RM at the surface of the modified electrode was investigated by cyclic voltammetry and differential pulse voltammetry. The influence of experimental parameters including PEDOT modified various solid electrodes, supporting electrolytes, nano-modified materials, buffer solutions, pH values and scan rates on the response of RM were studied. Under optimal conditions, the as-prepared modified electrode can be employed to the quantification of RM with a linear range covering from 0.08 to 20 μM, a high sensitivity of 0.9921 $\mu A\,\mu M^{-1}$, and a low detection limit of 0.0267 μM. Furthermore, the proposed modified electrode displayed high stability, good reproducibility and high sensitivity. The voltammetric determination of RM content in its capsule samples by using the as-prepared modified electrode also showed a satisfactory result with the good recovery in the range from 98.9% to 102.0%. The good result on the voltammetric determination of RM also indicated that the as-fabricated PEDOT modified Au electrode will be a good candidate for the electrochemical determination and analysis of other macrolide antibiotics.

1. Introduction

Roxithromycin (RM) is a derivative of the macrolide antibacterial erythromycin with in vitro antibacterial activity resembling that of the parent compound [1]. The semi-synthetic macrolide antibiotic has a 14-membered lactone ring with two sugars (Scheme 1). It is usually used for the treatment of respiratory tract, urinary and soft tissue infection caused by sensitive strains [2,3]. In addition, RM also exhibits increased chemical stability, strong activeness, in vivo distributes broadly, and higher concentrations of antibiotic in the serum after oral administration compared to erythromycin [1]. Many traditional methods such as spectrophotometry [4], solid-phase extraction combined with high-performance liquid chromatography–ion trap tandem mass spectrometry [5], liquid chromatography–mass spectrometry [6], near infrared reflectance spectroscopy [7], flow injection chemiluminescence procedure [8] have been widely reported for the determination of RM content. But these methods were time-consuming, expensive and complicated.

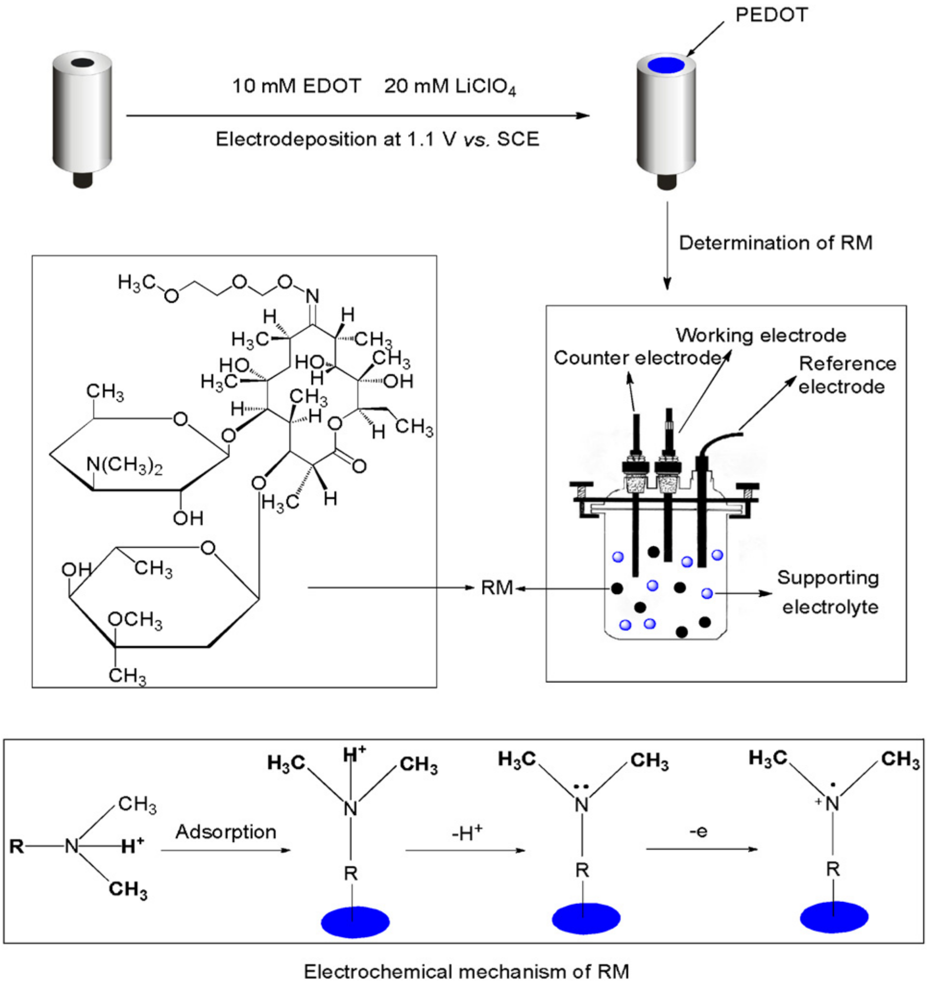
Recently, electrochemical method has been testified to be a good approach for the determination of RM using different working electrodes. For example, Nigović et al. [9–11] studied the electrochemical behavior and voltammetric determination of azithromycin, which is a macrolide antibiotic related to erythromycin, by a glassy carbon electrode (GCE). Mandić et al. [12] reported electrochemical oxidation of azithromycin and its derivatives based on GCE. Zhao et al. [13] explored the direct electron transfer and voltammetric determination of RM at a single-wall carbon nanotube modified GCE, and Avramov Ivić group investigated the electrochemical behavior of macrolide antibiotics based on gold electrode [14–20]. However, the sensing performance of solid electrode and the modified electrode for the electrochemical determination of macrolide antibiotics need to be improved.

Intrinsically conductive polymers (ICPs) have attracted much attention because of their potential applications in various hi-tech aspects, such as organic light emitting diodes, printed circuits, chemical/biosensors, electronic switches, rechargeable batteries, catalysts, antistatic coatings, corrosion inhibitors, electrolytic capacitors, smart windows, microwave absorbing materials, electromagnetic interference shielding, and electrostatic charge dissipation coatings [21–28]. Poly(3,4-ethylenedioxythiophene)

---

* Corresponding author. Tel.: +86 791 83802632; fax: +86 791 83805385.
** Corresponding author. Tel.: +86 791 88537967; fax: +86 791 83823320.
E-mail addresses: duanxuemin@126.com (X. Duan), xujingkun@tsinghua.org.cn (J. Xu).

0013-4686/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2012.04.019



Scheme 1. The molecular structure of RM, and the electrochemical preparation of the PEDOT modified Au electrode as well as the electrochemical determination of RM.

(PEDOT), one of the most stable ICPs, has been extensively studied due to its easy synthesis, low cost, excellent environmental stability, high charge mobility, low band gap, and high electrical conductivity as well as broad potential applications [28–35]. Moreover, PEDOT as an excellent electrode modified material or biomaterial also has attracted increasing interest because of its unique electrical properties, and has wide application in chem/biosensing devices. For example, Xu et al. [36] studied an electrochemical L-ascorbic acid biosensor based on PEDOT matrices, Cheng et al. [37] reported electrochemical determination of cysteine based on PEDOT/Au nanoparticles hybrid nanocomposites, Kilmartin et al. [38] investigated electrochemistry of sulfur dioxide, polyphenols and ascorbic acid at PEDOT modified electrodes, and Gros et al. [39] explored the mechanism occurring during the simultaneous assay of ascorbic and uric acids on the PEDOT modified gold microsensor. To the best of our knowledge, however, there has been no report on the PEDOT modified electrode for studying the electrochemical behavior and determination of macrolide antibiotics until now.

In this paper, a fast and easy method for the selective detection of RM at the PEDOT modified Au electrode has been developed. Electrochemical properties of the PEDOT/Au modified electrode for the voltammetric detection of RM were studied in detail. It was found that the electrode exhibited excellent electrocatalytic activity to the oxidation of RM. The proposed method presented a number of attractive features for the determination of RM such as high stability, good reproducibility, high sensitivity, wide linear range, and low detection limit.

2. Experimental

2.1. Chemicals

RM and 3,4-ethylenedioxythiophene (EDOT) were purchased from Aldrich. RM stock solution (5×10^{-3} M) was prepared with absolute ethanol and stored at 277–281 K. Lithium perchlorate trihydrate ($LiClO_4 \cdot 3H_2O$), disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$), and sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) were obtained from Sinopharm Chemical Reagent Co., Ltd. 0.1 M phosphate-buffered solution (PBS, pH 7.0) was prepared from 0.1 M $NaH_2PO_4 \cdot 2H_2O$ and 0.1 M $Na_2HPO_4 \cdot 12H_2O$. 1-Ethyl-3-methylimidazolium ethyl sulfate (EMIES) was obtained from Tokyo Chemical Industry Co., Ltd. All reagents were of analytical grade and used without further purification. All solutions were prepared using deionized distilled water.

2.2. Preparation of PEDOT modified electrode

Prior to the electrodeposition, the gold electrode ($\Phi = 2$ mm) was carefully polished with chamois leather containing 0.05 μm alumina slurry, and was ultrasonically cleaned with deionized distilled water, absolute ethanol and deionized distilled water each for 5 min, respectively. The gold electrode was then immersed into the mixed liquor of concentrated sulphuric acid with hydrogen peroxide in the ratio 7:3 for 20 min. Finally, the gold electrode was ultrasonically cleaned in deionized distilled water for 5 min. The modifying procedure was as follows: 0.0114 g EDOT was