Talanta 185 (2018) 344–351

Contents lists available at ScienceDirect

Talanta

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

Smart bi-metallic perovskite nanofibers as selective and reusable sensors of nano-level concentrations of non-steroidal anti-inflammatory drugs

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ARTICLE INFO

Keywords:
Nanofibers
Modified sensors
Lornoxicam
Paracetamol

ABSTRACT

A strategy for trace-level carbon-based electrochemical sensors is investigated via exploring the interesting properties of $BaNb_2O_6$ nanofibers (NFs). Utilizing adsorptive stripping square wave voltammetry (ASSWV), an electrochemical sensing platform was developed based on $BaNb_2O_6$ nanofibers-modified carbon paste electrode (CPE) for the sensitive detection of lornoxicam (LOR). Different techniques were used to characterize the fabricated $BaNb_2O_6$ perovskite NFs. The obtained data show the feasibility to electro-oxidize LOR and paracetamol (PAR) on the surface of the fabricated sensor. The amount of nanofiber and testing conditions were optimized using response surface methodology and ASSWV technique. The optimized $BaNb_2O_6$/CPE sensor exhibits low detection limit of 6.39×10^{-10} mol L^{-1}, even in the presence of the co-formulated drug paracetamol (PAR). The sensor was successfully applied for biological applications.

1. Introduction

Lornoxicam (LOR) or chlortenoxicam, chemically known as (3E)-6-chloro-3-[hydroxyl (pyridin-2-ylamino) methylene]-2-methyl-2, 3-dihydro-4H-thieno [2,3-e] [1,2] thiazin-4-one 1,1-dioxide (Scheme 1), is a non-steroidal anti-inflammatory drug (NSAID) [1]. It is a commonly used pain reliever for joint disorders, sciatica, and post-operative pain [2], as it exerts its analgesic and antipyretic activities by blocking cyclooxygenase enzyme and inhibiting the biosynthesis of prostaglandins [3]. LOR is distinguished from other oxicam derivatives by its relatively rapid onset of action, almost complete absorption from the digestive tract, and short elimination life-time (3 − 5 h), which make it highly tolerable [4].

Paracetamol (PAR), N-acetyl-p-aminophenol (Scheme 1), is also a widespread agent in pain relief medications used for headache, fever, toothache, and musculo-skeletal originated pain [5,6]. Although the general use of its normal dose is safe on public heath, long term and/or large dose therapy of PAR lead to harmful effects on vital body organs like liver, kidney and pancreas, especially when co-administered with other drugs or alcohol [7]. Therefore, the amount of PAR in pharmaceutical formulations should be strictly monitored [7,8]. Also, recent treatment trends are to utilize more than one drug in one pharmaceutical formulation, such as LOR and PAR in the same drug, making use of their synergetic effect. This makes it challenging to precisely evaluate a single component in the drug [9]. Consequently, an accurate, feasible, and fast detection of LOR, owing to its therapeutic importance, in the presence of PAR is urgently needed.

To this end, various analytical techniques have been reported for the determination of either drugs, such as high-performance liquid chromatography (HPLC) [10–12], spectrofluorimetric [13], chemiluminescence [14], and spectrophotometric [15] analyses. Despite the satisfactory sensitivity achieved by these techniques for pharmaceutical drugs, they frequently suffer from shortcomings such as tedious extraction procedures from complex formulations, high cost, time consumption, and need for professional personnel, hindering the routine analyses [16]. On the other hand, electrochemical methods have proven to be superior analytical alternatives because they are simple, rapid, inexpensive, highly sensitive, and selective, with no need to prior procedures [17–19]. Nevertheless, few studies have been reported on electrochemical determination of LOR [16,20,21], whereas vast electrochemical methods have been reported for PAR [6,22–29]. In this regard, modification of carbon paste electrode (CPE) used in the sensing platform is advantageous in order to further enhance the electro-analytical performance for LOR and PAR detection.

Recently, inorganic perovskite materials have attracted the attention of the scientific community to be utilized in various catalytic and

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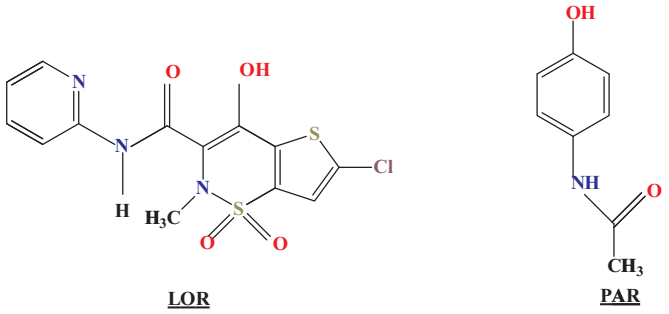
https://doi.org/10.1016/j.talanta.2018.03.104
Received 21 February 2018; Received in revised form 29 March 2018; Accepted 31 March 2018
Available online 03 April 2018



Scheme 1. Chemical structures of LOR and PAR.

electrochemical applications, such as fuel cells, gas sensing, methane combustion, and other transduction and energy conversion applications [30,31]. This is mainly attributed to their peculiar properties, such as superconductivity, ferromagnetism, ferroelectricity, high oxygen ion mobility, charge ordering, and considerable thermopower and chemical stability [31–33]. All these characteristics reveal that perovskite structures can accommodate a variety of ions [34], which would suggest a great potential for use as chemical modifiers for highly selective and sensitive detection of biomolecules. As new ferroelectric tungsten bronze materials, barium niobate ($BaNb_2O_6$) and its derivatives have recently attracted great interest, due to their excellent electrical conductivity, pyroelectric, and electro-optic properties [31,35,36]. Despite these numerous advantages, one main shortcoming of transition metal oxides is their tendency to form closely-packed aggregates on the electrode surface, which would diminish the electrochemical behavior of the sensing process [37]. Thus, electrospun perovskite nanofibers are thought to be useful, as they possess high surface area-to-volume ratio with small grain size and higher probability of charge separation, which would enhance the electrocatalytic properties of the sensor [33].

To the best of our knowledge, this is the first study on the electrochemical sensing of the mixture of LOR and PAR. To achieve this, we unprecedentedly used CPE modified with electrospun barium niobate nanofibers ($BaNb_2O_6$/CPE). The modifier of $BaNb_2O_6$ was morphologically and electrochemically identified using various characterization techniques. Also, different experimental parameters, such as pH, scan rate, amount of nanofiber, and deposition time, were optimized for maximum current in adsorptive stripping square wave voltammetry (ASSWV) using response surface methodology (RSM). Finally, the developed ASSWV with the novel $BaNb_2O_6$ nanofiber-modified electrode was employed for the sensitive determination of LOR and PAR in human plasma.

2. Experimental

The Supporting information includes all the details about the used materials and reagents, instruments and experimental setup, along with the procedures followed to synthesize the $BaNb_2O_6$ nanofiber, prepare the different utilized CPEs, and spike the human plasma samples.

2.1. Recommended experimental procedure

Stock solutions of LOR and PAR (1.0×10^{-2} mol L^{-1}) were prepared in ethanol and double distilled water, respectively. The essential amount of any of these stock solutions was transferred to a 5.0 mL standard volumetric flask, in which the solution volume was completed to the mark using 4.0×10^{-2} mol L^{-1} Britton–Robinson buffer solution (pH 7.0).

Prior to voltammetric measurements, the modified electrode

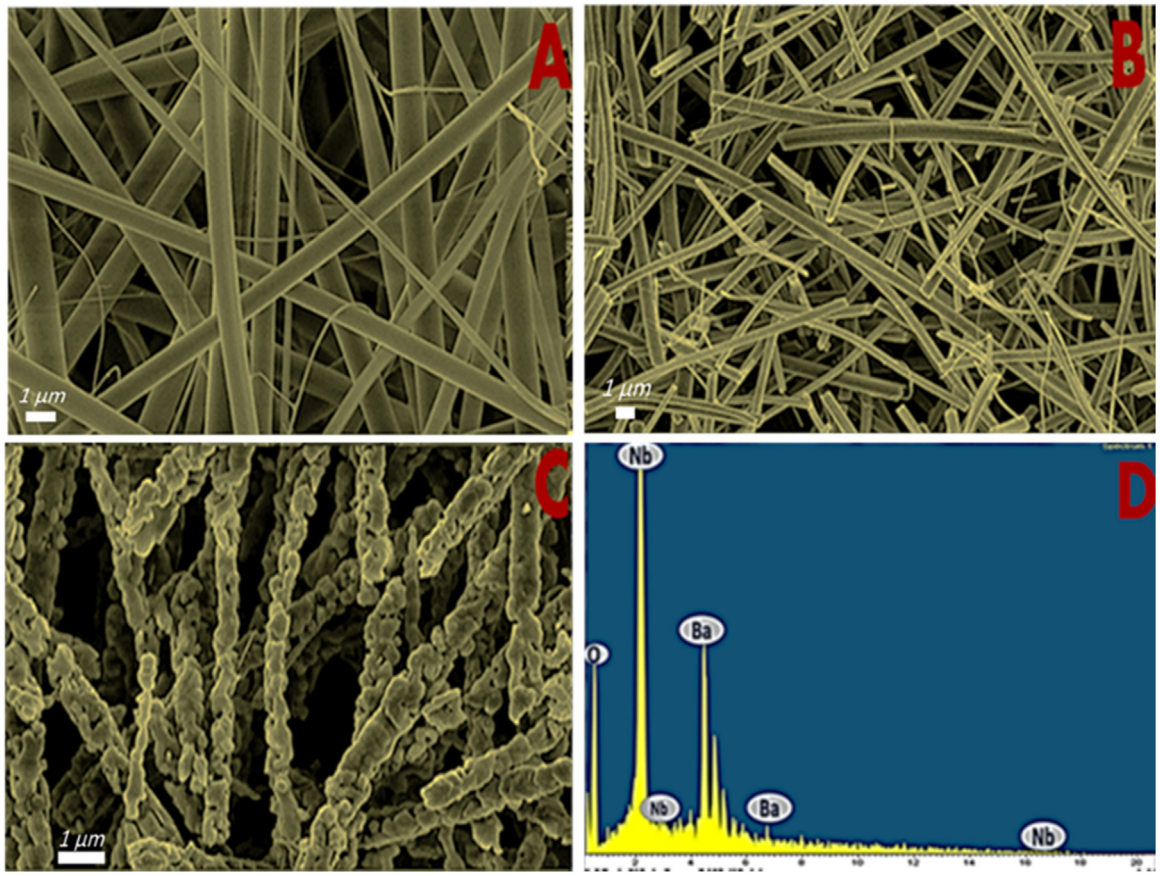


Fig. 1. SEM images of $BaNb_2O_6$ nanofibers (A) as-synthesized, (B) after calcination at 650 °C, and (C) after calcination at 950 °C; along with (D) the corresponding EDX analysis.