Materials Science and Engineering C 72 (2017) 301–307

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

A novel electrochemical platform based on carbon nanofibers and tri-metallic nanoparticles of gold, nickel and cobalt for the quantification of ethyl paraben

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ARTICLE INFO

Article history:
Received 10 October 2016
Received in revised form 9 November 2016
Accepted 17 November 2016
Available online 24 November 2016

Keywords:
Carbon nanofibers
Ethyl paraben
Tri-metal nanoparticles
Modification
Composite material

ABSTRACT

A composite of carbon nanofibers (CNFs) and tri-metallic nanoparticles of gold, cobalt and nickel were used for the preparation of a novel voltammetric platform. The proposed voltammetric platform was utilized for quantifying ethyl paraben (EPB) in pharmaceutical and cosmetic products. The electrode layers were characterized by utilizing X-ray diffraction method (XRD) and Fourier transform infrared spectroscopy (FTIR). The electrode system, (Au-Ni-Co)NPs-CNFs/GCE, exhibited high catalytic activity and enhanced the electrochemical behaviour of EPB compared with several other electrodes. The proposed composite layer based electrode produced a well-defined oxidation peak at 0.760 V. The determination of EPB was carried out by square wave voltammetry (SWV). The electrode produced a linear plot with a concentration range from 1.0×10^{-9} to 1.0×10^{-7} M at (Au-Ni-Co)NPs-CNFs/GCE. The composite material enabled a detection limit of 3.5×10^{-10} M for EPB. Good reproducibility, high precision and excellent accuracy for EPB were obtained at (Au-Ni-Co)NPs-CNFs/GCE. The composite layer based platform was successfully applied for the quantification of EPB in pharmaceutical and cosmetic products. The sensitive quantification of EPB is of great importance for the public health care. Furthermore, data show that EPB binds to DNA via intercalation with a binding constant of $2.51\ (\pm 0.40) \times 10^4$.

1. Introduction

Parabens that are frequently used as preservatives in pharmaceuticals and cosmetics can disrupt the endocrine system of living organisms [1–5]. Thus, they may cause severe consequences on animal and human health [3–5]. In addition, paraben content has been limited by EU up to the concentration of 0.4% (w/w) for a single ester expressed as p-hydroxybenzoic acid content [6–8]. Thus, a sensitive quantification of paraben contents of products is of great importance for both human and animal interests [1,3,9,10]. Several analytical methods such as micellar electro-kinetic chromatography with electrochemical detection [11], ultra-fast liquid chromatography [12], gas chromatography [13], capillary electrophoresis [14], HPLC-mass spectrometry [15], chromatography with chemiluminescent detection [16], HPLC with electrochemical detection [17], liquid chromatography with mass spectrometry [18], gas chromatography with mass spectrometry [19], microextraction [20], UV–vis spectrophotometry [21] and electrochemical methods [2,3,5,22] were appeared in the literature for determining the paraben contents of samples. However, only a few numbers of electrochemical methods based on modified electrode were appeared in the literature for the analysis of paraben containing products [1,4,6–8,23]. Electrochemical methods at modified electrodes have presented high catalytic activity, good stability and excellent conductivity in the studies of analytes and analysis of samples [1,4,6–8,23–25]. Voltammetric techniques performed with electrodes based on carbon nanofibers (CNFs) have shown good electrical conductivity and high surface area [23,26–29]. In addition, electrodes modified with metallic nanoparticles exhibited excellent performances such as high sensitivity, good electrocatalytic activity and low detection limit [25,30,31]. Furthermore, electrodes based on nanocomposite materials have recently been reported to provide good accuracy and high precision to the electroanalysis of several analytes [30,32,33]. In addition, electrochemical methods at modified electrodes have also been successfully applied to the electroanalysis of biological, pharmaceutical and environmental samples owing to their good sensitivity and excellent selectivity [34–43].

Furthermore, it has been reported that the DNA interaction of some analytes might lead to several changes in living cells [44–47]. In addition to therapeutic applications, voltammetric methods have also been

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http://dx.doi.org/10.1016/j.msec.2016.11.080
0928-4931/

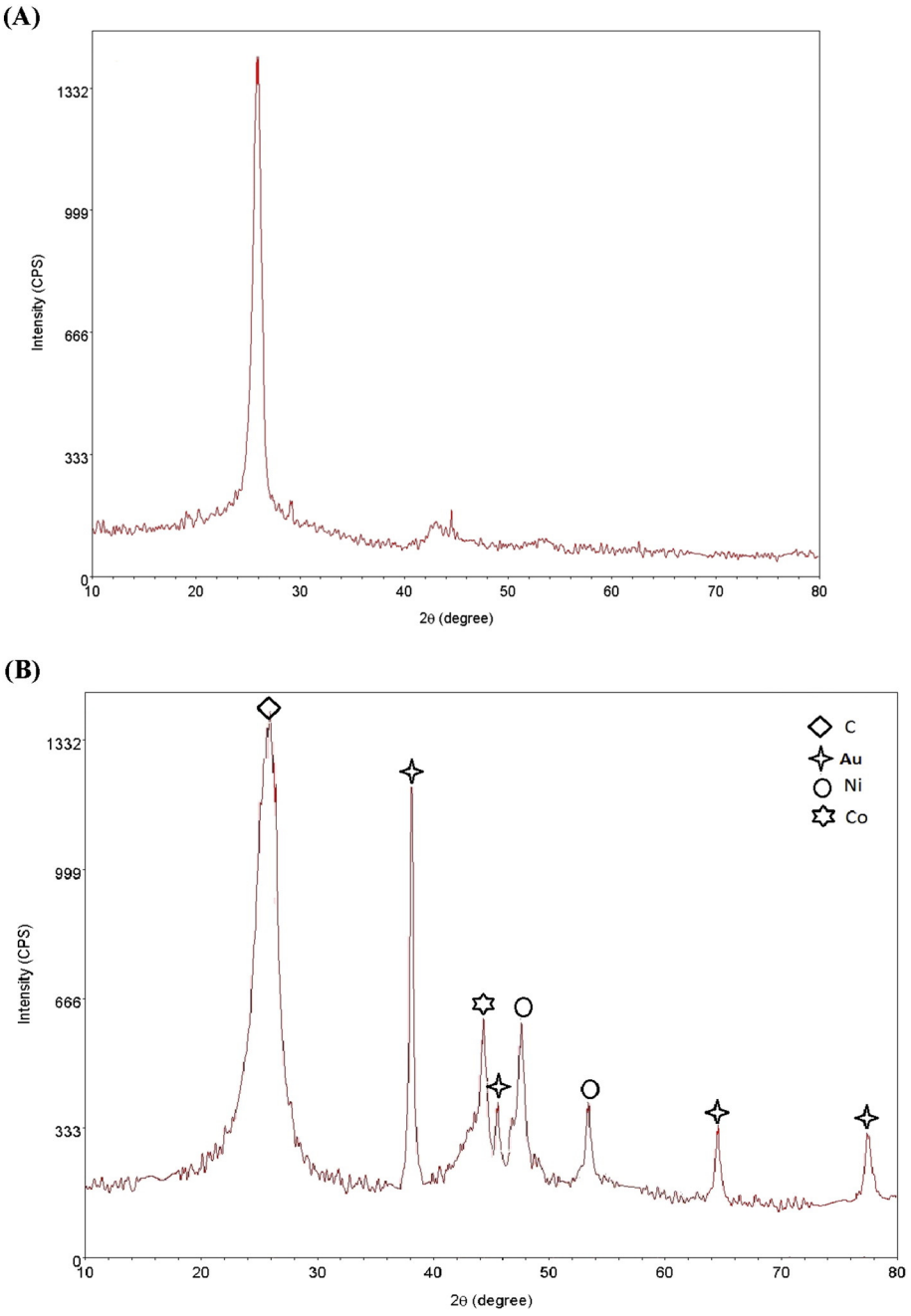

Fig. 1. XRD images of CNFs/GCE (A) and (Au-Ni-Co)NPs-CNFs/GCE (B).

useful for monitoring the interaction of electroactive analytes with DNA [24,44–47].

In this study, carbon nanofibers (CNFs), gold, nickel and cobalt nanoparticles have been used for the preparation of a novel voltammetric platform. The proposed platform, (Au-Ni-Co)NPs-CNFs/GCE, was utilized for quantifying ethyl paraben (EPB) in pharmaceutical and cosmetics products. The voltammetric platform based on (Au-Ni-Co)NPs-CNFs presented high electrocatalytic effect for the electrode reaction of EPB when compared to several other electrodes. Modifying electrodes with CNFs and nanoparticles of gold, nickel and cobalt exhibited excellent reproducibility, high accuracy and good precision for EPB. In addition, the proposed electrode, (Au-Ni-Co)NPs-CNFs/GCE, was also applied for the voltammetric studies of the binding of EPB to DNA. Data have shown that EPB was able to bind to DNA via intercalation with a binding constant of 2.51 ($\pm$0.40) $\times$ 10^4.

2. Experimental

2.1. Chemicals

Ethyl paraben (EPB), AA, DA, DNA and UA were purchased from Sigma-Aldrich Company (St Louis, USA). Cobalt(II) chloride, nickel(II) chloride, gold(III) chloride and chloroform were obtained from Merck Company (Darmstadt, Germany). Carbon nanofibers (CNFs) were purchased from US-Nano Company, USA. Solutions of EPB, AA, UA, DNA and DA were prepared with 0.1 M PBS at pH 7.0 using ultra-pure water.

2.2. Instrumentation

Voltammetry was performed by utilizing an Ecochemie Autolab potentiostat (The Netherlands). A glassy carbon electrode (GCE) was