Materials Science and Engineering C 32 (2012) 1682–1689

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering C

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

MWCNTs/$Cu(OH)_2$ nanoparticles/IL nanocomposite modified glassy carbon electrode as a voltammetric sensor for determination of the non-steroidal anti-inflammatory drug diclofenac

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ARTICLE INFO

Article history:
Received 25 November 2011
Received in revised form 24 February 2012
Accepted 24 April 2012
Available online 28 April 2012

Keywords:
Nanocomposite
$Cu(OH)_2$ nanoparticles
Ionic liquid
Multiwalled carbon nanotubes
Diclofenac
Drug analysis

ABSTRACT

This paper describes the development and utilization of a new nanocomposite consisting of $Cu(OH)_2$ nanoparticles, hydrophobic ionic liquid 1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIMPF_6$) and multiwalled carbon nanotubes for glassy carbon electrode modification. The nanocomposite was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) along with energy-dispersive X-ray spectroscopy (EDX). The modified electrode was used for electrochemical characterization of diclofenac. Using differential pulse voltammetry, the prepared sensor showed good sensitivity and selectivity with low overpotential for the determination of diclofenac in the range from 0.18 to 119 μM, with a detection limit of 0.04 μM. Electrochemical studies suggested that the MWCNTs/$Cu(OH)_2$ nanoparticles/IL nanocomposite modified electrode provided a synergistic augmentation on the voltammetric behavior of electrochemical oxidation of diclofenac, which was indicated by the improvement of anodic peak current.

1. Introduction

Diclofenac, a non-steroidal anti-inflammatory drug, is one of the most commonly used pain killers, clinically largely used as sodium salt [1]. Diclofenac sodium, sodium [o-(2,6 dichloroanilino) phenyl] acetate (Scheme 1) is widely prescribed as an analgesic after surgery or injuries in acute and chronic joint inflammation and in degenerative diseases, as well as the treatment of rheumatic complaints [2,3].

Due to its extensive use, diclofenac residues can nowadays be regularly detected in surface waters throughout the world [4]. Already at realistic environmental concentration levels harmful effects to different organisms have been demonstrated [5]. There is also evidence that prolonged exposure to environmentally relevant concentrations of diclofenac leads to impairment of the general health of fish, inducing renal lesions and alteration of the gills, at the lowest observed effect concentration (LOEC) of 5 μg L^{-1} [6]. Hence, it is necessary to develop simple, sensitive and economical techniques for the quantification of diclofenac.

Various methods have been employed for the analysis of diclofenac, such as capillary zone electrophoresis [7], spectrofluorometric [8], HPTLC [9], flow-injection spectrophotometric [10], liquid chromatography [11] and HPLC [12]. Most of the methods reported are time-consuming, expensive, and need complicated preconcentration as well as derivatization. Compared with other methods, electrochemical methods are characterized by portability, simplicity, minimal cost and reasonably short analysis time. Thus, different electrochemical methods have been exploited for the determination of diclofenac [13–16]. The comparison is displayed in Table 1. The lowest electro-oxidation overpotential was achieved at proposed modified electrode along with larger diffusion coefficient, *D*.

In recent years, nanomaterials, such as carbon nanotubes (CNTs) have been widely applied to the surface modification with the aim to improve the sluggish electron transfer behavior at the bare electrodes [14].

Nanostructured transition metal hydroxides/oxides have excellent properties such as high surface area and enhanced chemical/electrochemical activities, as well.

Recent efforts have suggested that the integration of CNTs and nanostructured transition metal hydroxides/oxides could generate new kinds of nanocomposites with multifunctional properties benefitting from each kind of nanostructures [17].

Ionic liquids (ILs) belong to a special group of electrolytes consisting only of ions which are widely used as modified materials. Because of their high stability, high electrical conductivity, relatively high ionic conductivity and very low vapor pressure, ILs hold a great promise for green chemistry applications in general and for electrochemical applications in particular [18].

The aim of this work is to develop a new, simple and cheap nanocomposite with multifunctional properties benefitting from MWCNTs, $Cu(OH)_2$ nanoparticles and hydrophobic ionic liquid 1-

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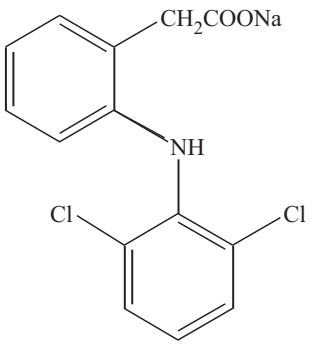
doi:10.1016/j.msec.2012.04.066



Scheme 1. The chemical structure of diclofenac sodium.

ethyl-3-methylimidazolium hexafluorophosphate ($EMIMPF_6$) with good electrocatalytic activity for the electro-oxidation of diclofenac. The nanocomposite was prepared and used as an electrode modifier to achieve electrochemical detection of diclofenac. Diffusion coefficient of diclofenac was estimated to be $3.39\times10^{-6}\,cm^2\,s^{-1}$ with the aim of proposed nanocomposite modified electrode. To the best of our knowledge, no electrochemical sensor has been reported so far with these components.

2. Experimental

2.1. Reagents and solutions

All reagents and solvents were of the highest purity available from Merck (Darmstadt, Germany) and were used without further purification. The compound diclofenac sodium ampoule was purchased from Pharmaceutical Co., Hamburg, Germany. The MWCNTs (>95%) and ionic liquid, 1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIMPF_6$, 98%), were obtained from Nanostartech and Kimia Exir chemical Co., Tehran, Iran, respectively. Paraffin was used as the pasting liquid for the nanocomposite.

Phosphate buffer solution (PBS, 0.1 M, pH 8.2) was prepared by mixing solutions of 0.1 M $Na_2HPO_4\cdot12H_2O$ and 0.1 M $NaH_2PO_4\cdot H_2O$. Aqueous solutions of diclofenac sodium were prepared fresh at the time of experiments in phosphate buffer (PBS, pH 8.2). All the solutions were prepared using double distilled water.

2.2. Apparatus

Autolab potentiostat PGSTAT 30 (Eco Chemie BV, Utrecht, the Netherlands) driven by the General Purpose Electrochemical Systems data processing software (software version 4.9) was employed for all the voltammetric measurements. A conventional three-electrode system was used, including a working modified electrode, a saturated Ag/AgCl reference electrode, and a platinum wire counter electrode. All the pH values were measured with a Metrohm pH meter (model 827, Swiss made).

A model CM10 transmission electron microscope (TEM; Philips) was used to characterize the morphology and size of the MWCNTs and $Cu(OH)_2$ nanoparticles. The morphology of MWCNTs/$Cu(OH)_2$/IL nanocomposite was investigated by TEM and scanning electron microscopy (SEM) along with energy-dispersive X-ray spectroscopy (EDX) (Electroanalyser Sama 500).

2.3. Synthesis of $Cu(OH)_2$ nanoparticles

Synthesis of $Cu(OH)_2$ nanoparticles was based on coordination homogeneous precipitation [19]. For this purpose, low-cost ammonia was chosen as the coordination agent and copper sulfate hexahydrate as Cu^{2+} source. Firstly, deep blue colored copper hexammine complex solution was formed by adding concentrated ammonia (28 wt.%) to copper sulfate hexahydrate solution (1 M) at ambient temperature. The complex solution was added into a given amount of distilled water, the reaction was carried out under magnetic stirring for 1 h at 70 °C. Finally, light blue sediments were formed. The precipitate was separated and rinsed with distilled water and ethanol three times, respectively, to remove the adsorbed ions, then dried in a vacuum oven at 80 °C for 12 h. The final product was light blue powder. As seen in TEM image (Fig. 1(c)), $Cu(OH)_2$ nanoparticles have homogeneous platelet-like structure with average diameter of 30–35 nm.

2.4. Preparation of modified electrodes

In most electrochemical studies, the nanotubes are purified and opened in concentrated acids, which could result in ions penetrating the centers of the tubes and altering their electronic properties by injecting electrons or holes into the valence or conduction bands of the tubes [20]. For this purpose, pristine MWCNTs were purified and —COOH introduced by refluxing in conc. nitric acid, filtered and washed with double distilled water until pH of filtrate became ~7 and finally dried at 40 °C for about 3 h (see Fig. 1(a) and (b)). CNTs have a strong tendency to agglomerate due to their nano size and their respective high surface energy [21] (Fig. 1(a)). After treatment with strong acid (Fig. 1(b)) and grafting of chemical functionalities on the CNT surface, such as —COOH prevented aggregation/bundling of nanotubes and the individual tubes were finely dispersed.

Glassy carbon electrode was carefully polished with alumina until a mirror finish was obtained. The electrode was rinsed thoroughly with water. The prepared electrode was dried and used immediately for modification.

The nanocomposite modified electrode was prepared by mixing 6.0 mg $Cu(OH)_2$ nanoparticles, 30.0 mg IL, 22.0 mg MWCNTs with 10 mg paraffin as the pasting liquid, thorough hand mixing in a mortar and pestle (8.8:32.4:44.1:14.7%, w/w), to get stable nanocomposite, and allowed to stand in a closed container at ambient temperature for 24 h before use. The employed IL is a solid powder at

Table 1
Comparison of the proposed electrode with other electrodes for the determination of diclofenac.

Electrode	E_{pa} (V)	Application	Dynamic range	Detection limit	Diffusion coefficient $\times10^6$ ($cm^2\,s^{-1}$)	References
$Ni(OH)_2$– nickel electrode	–	–	196 to 2650 μM	31.7 μM	0.94	[13]
SWCNTs–EPPGE	0.854	Tablet, human urine and blood samples	1×10^{-9} to 500×10^{-9} M and 25×10^{-9} to 1500×10^{-9} M	0.82×10^{-9} M and 22.5×10^{-9} M	–	[14]
MWCNTs–surfactant GCE	0.69	Tablet	1.7×10^{-7} to 2.5×10^{-6} M and 2.5×10^{-6} to 7.5×10^{-5} M	8.0×10^{-8} M	–	[15]
EPPGE	0.66	Tablet and human urine	10 to 1000 nM	6.2×10^{-9} M	–	[16]
MWCNTs/$Cu(OH)_2$ nanoparticles/IL-GCE	0.53	Ampoule, tablet, human and fish blood serum and seawater samples	0.18 to 119 μM	0.04 μM	3.39	This paper