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Fabrication of CdO/single wall carbon nanotubes modified ionic liquids carbon paste electrode as a high performance sensor in diphenhydramine analysis

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ABSTRACT

Diphenhydramine (DPHA) is an antihistamine that reduces the effects of natural chemical histamine in the body. DPHA is used to treat sneezing, runny nose, watery eyes, hives, skin rash, itching, and other cold or allergy symptoms. Therefore, it is important for determination of DPHA in drug samples. We describe a novel DPHA voltammetric sensor, comprising carbon-paste electrode (CPE) modified with CdO/single wall carbon nanotubes (CdO/SWCNTs) nanocomposite and 1-butyl-3-methylimidazolium hexafluoro phosphate ($[C_4mim]$-$[PF_6]$) ionic liquid as binder. CdO/SWCNTs was synthesized by direct chemical precipitation method and characterized with scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) methods. The developed voltammetric sensor displays good catalytic activity toward oxidation of DPHA, which occurs by good electrochemical conductivity of ionic liquid and nanocomposite. The suggested system detects DPHA over the range 0.05–700 μM, with a detection limit of 9.0 nM (3σ of blank). The CdO/SWCNTs/$[C_4mim]$-$[PF_6]$/CPE was successfully applied to the determination of DPHA in pharmaceutical samples.

Contents

1. Introduction

Voltammetric analysis is a high efficiency strategy for fast and sensitive determination of biological, environmental and drug compounds [1–7]. In compare to HPLC and spectroscopic methods, electrochemical

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methods have a more attention for trace level analysis due to their sensitivity, lower cost, good limit of detection and linear dynamic range, accuracy, and simplicity analysis in low time [8–15]. In between, high overvoltage and low sensitivity for drug and biological compounds at bare electrodes are important problem in trace level analysis by voltammetric sensor [16–22]. To overcome this problem, scientists suggested application of modified electrodes for the new generation of sensors [23–33]. Nanomaterials, organic ligands, metal complexes, ionic liquids, DNA and conductive polymers are usual modifiers in the modification of electrodes in electrochemical sensors [34–39]. But nanomaterials have more attention between other modifiers due high conductivity at a surface of modified electrode [40–48].

DPHA is an important and usual antihistamine that reduces the effects of natural chemical histamine in the human body. On the other hand, it can be used to treat sneezing, watery eyes, itching, hives, runny nose, skin rash, and other cold or allergy symptoms. DPHA don't give to a child younger than 2 years old. Therefore, a simple method is necessary for fast and sensitive determination of DPHA in biological and pharmaceutical samples. Owing to the wide use of DPHA, many analytical methods such as titrimetry [49], spectrophotometry [50,51], high performance liquid chromatography [52,53] and electrochemical sensors [24,54].

To best of our knowledge, there is no any report on the voltammetric determination of DPHA using modified nanostructure ionic liquid electrode and this work is first report for application of ionic liquids/nanostructure carbon paste electrode for DPHA analysis as simple and high sensitive sensor. In this work, we describe the synthesis of CdO/SWCNTs nanocomposite and its application for modification of carbon ionic liquid paste electrode. The electrochemical oxidation of DPHA at CdO/SWCNTs/[C_4mim]-[PF_6]/CPE was investigated at an optimum condition. The CdO/SWCNTs/[C_4mim]-[PF_6]/CPE is a good selective and highly sensitive sensor for the determination of DPHA in the real samples.

2. Experimental

2.1. Chemicals

Diphenhydramine hydrochloride (>98%) from Sigma and mineral oil and graphite powder (<50 μm) for the preparation of working electrode were obtained from Merck.

A main solution of diphenhydramine hydrochloride (0.01 M) was prepared by dissolving 0.297 g diphenhydramine hydrochloride in 100 buffer solution. The solution was kept in a refrigerator at 25 °C in laboratory. Phosphate buffer solutions (PBS) with different pH values were used.

2.2. Apparatus

Voltammetric investigation (cyclic voltammetry (CVs), SWV) was performed using Metrohm potentiostat/galvanostat connected to a three-electrode cell, Metrohm Model 663 VA stand, linked with a computer (Pentium IV) and EIS was performance using Autolab potentiostat/galvanostat with FRA software. An Ag/AgCl/KCl_{sat} electrode, a platinum wire, and the CdO/SWCNTs/[C_4mim]-[PF_6]/CPE were used as the reference, auxiliary and working electrodes, respectively. Scanning electron microscopy (SEM) was used for morphological investigation. X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-Kα radiation (k = 1.54 Å).

2.3. Preparation of the electrode

After each application, a refresh surface of sensor was obtained by withdrawing some of the paste on a weighing paper. The suggestion paste electrode was prepared by mixing of 0.25 g of ([C_4mim]-[PF_6], 0.75 g of the paraffin oil, 0.1 g of cadmium oxide nanoparticle, and 0.9 g of graphite powder. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture.

2.4. CdO/SWCNTs nanocomposite

The functionalize SWCNTs/COOH was used for nanocomposite synthesis. The certain amounts of purified SWCNTs/COOH (3 g) were dispersed into distilled water solution of NaOH (0.5 M; 100 ml) by ultrasonication for 45 min. Under constant magnetic stirring, the solution of cadmium acetate (100 mL) was added drop wise to the solution of SWCNTs/COOH at 50 °C through a dropping funnel. The rate of addition of the salt solution was kept approximately at 25 ml/h. After completion of the precipitation procedure, the mixture was stirred at room temperature for 18 h, washed and filtered continually in distilled water (pH 7.0), and dried at 100 °C. The solid samples were then calcined at 450 °C for 2 h.

2.5. Real sample preparation

Then, suitable amount of each syrup dissolved in 100 mL water by ultrasonication. After good mixing, the mixture was filtered on an ordinary filter paper, 10 mL of which was subsequently transferred into a 25-mL volumetric flask and diluted to the mark with buffer solution (pH 8.5). Drug serum was used without any pretreatment for DPHA spike analysis.

3. Result and discussion

3.1. CdO/SWCNTs nanopowders characterization

CdO/SWCNTs nanopowders were analyzed by XRD method. The XRD pattern of CdO/SWCNTs nanopowder, in the 2θ range of 5–70°, is shown in Fig. 1A. The (1,1,1), (2,0,0), (2,2,0), (3,1,1) and (2,2,2) reflections are clearly seen and closely match the reference patterns for CdO (Joint Committee for Powder Diffraction Studies (JCPDS) File No. 05-0640). It clearly proves the presence of CdO nanoparticle, with a diffraction peak at ~26° from SWCNTs. The morphology of the as-grown nanostructures was characterized by SEM methods. Typical SEM micrograph of the CdO/SWCNTs nanopowder is shown in Fig. 1B. Results confirm the synthesis of CdO/SWCNTs nanopowder.

3.2. Electrochemical investigations

In the first step, we determine the active surface area using Randles–Sevcik equation in solution containing 1.0 mmol L^{-1} of $Fe(CN)_6^{-2}$/$Fe(CN)_6^{-3}$ in the 0.1 mmol L^{-1} supporting electrolyte. The obtained

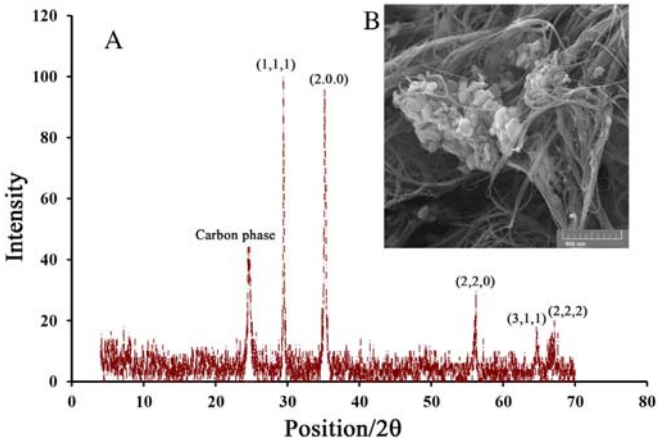

Fig. 1. (A) XRD patterns of *as*-synthesized CdO/SWCNTs/[C_4mim]-[PF_6]/CPE. (B) SEM image of CdO/SWCNTs/[C_4mim]-[PF_6]/CPE.