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Amperometric detection of acetaminophen by an electrochemical sensor based on cobalt oxide nanoparticles in a flow injection system

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ABSTRACT

This paper reports the use of a carbon ceramic electrode as a highly-porous substrate for the electrochemical formation of cobalt oxide nanoparticles. The electrocatalyst was characterized by energy dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM) and cyclic voltammetry techniques, and it was used in a homemade flow injection analysis (FIA) system for acetaminophen determination using 0.1 M KOH as the carrier solution. The rate constant (k_s) and charge transfer coefficient (α) were calculated for the electron exchange reaction of the modified film. The kinetic parameters and the mechanism of acetaminophen electrooxidation at the electrode surface were studied by cyclic voltammetry and chronoamperometry. The effects of working potential and flow rate on the performance of the FIA system were studied. Under optimized conditions, the electrode response due to the electrocatalytic oxidation of acetaminophen at 450 mV (vs. SCE) is proportional to the concentration of acetaminophen over a 5–35 μM range with an associated detection limit (S/N = 3) of 0.37 μM and a sensitivity of 0.0296 μA/μM. The relative standard deviation (RSD) was 1.6% for eight replicate measurements. The modified electrode was used to determine the acetaminophen content in tablet samples.

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1. Introduction

In recent years, there has been intense research directed to use nanoscience in a wide range of fundamental studies and technological applications. Furthermore, there is a considerable effort toward the use of nano-materials in electrochemistry due to their unique physicochemical and electrochemical properties that are not represented by the corresponding bulk forms [1]. Different types of nano-structured materials, including noble metals, oxides and composite nanoparticles, have often been used in electrochemical studies including electrocatalysts, fuel cells, photonic processes and electroanalytical techniques [2–5]. Herein, a great deal of attention has been centered on the nano-structured transition metal oxides because of their excellent activity toward the electrocatalytic oxidation or reduction of various compounds [6–11].

Recently, a part of our research activities have aimed at fabricating and characterizing modified electrodes consisting of metal oxide nanoparticles deposited on a highly-porous carbon ceramic electrode (CCE). In the present study, we describe the preparation and electrocatalytic activity of cobalt oxide nanoparticles deposited on the surface of carbon ceramic matrix. The preparation, characterization and electrochemistry of cobalt oxides have been extensively studied [12–15]. Such compounds have been employed in processes such as energy storage systems [16], electrochromic [15] and magneto-resistive devices [17] as well as heterogeneous catalysts [18].

Of the different methods for preparing cobalt oxide nanoparticles, including powder immobilization [19], chemical vapor deposition [20], sonication [21], thermal salt decomposition [22], sol–gel [23] and electrodeposition [24,25], the electrodeposition is a simple, fast and inexpensive method. The advantage of electrodeposition over chemical and physical methods is the high purity of the resultant particles, lower particle size, and short time of formation [26,27]. In electrochemical studies, not only the kind of modifying film but also the nature of electrode substrate is important. The morphologies of the modifying film and its electrocatalytic properties can be affected by the electrode substrate. Considering the interesting features of CCE, such as the renewable surface, high conductivity, stability, porosity, wide operational potential window and good mechanical properties [28,29], it was used as a substrate for the electrochemical deposition of cobalt oxide nanoparticles. Some important properties of the resulting modified electrode, including stability of redox activity, redox reaction kinetics, and electrocatalytic activity toward the oxidation of acetaminophen, were studied. The distinguished electrocatalytic features of the modified electrode were used to develop a flow injection method for determining acetaminophen content.

Acetaminophen, or paracetamol (*N*-acetyl-*p*-aminophenol), is an antipyretic and minor analgesic drug that practically has no anti-inflammatory action. It is an effective and safe analgesic agent

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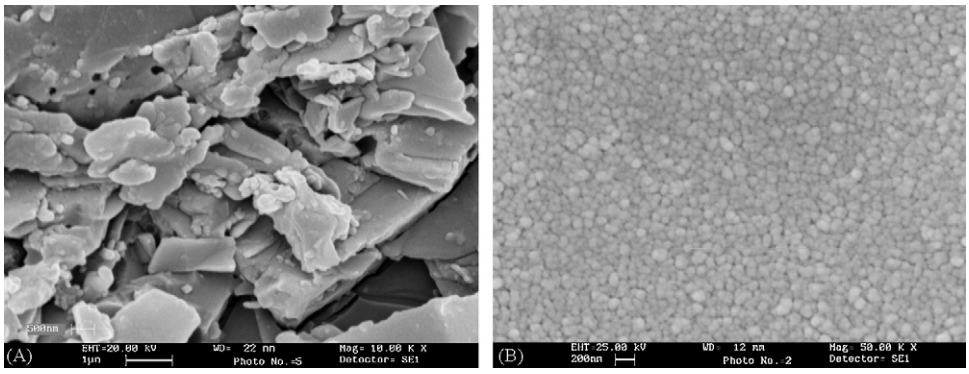

Fig. 1. SEM images of (A) bare CCE and (B) CoOx modified CCE surfaces.

used worldwide for the relief of mild to moderate pain associated with headaches, backaches, arthritis and postoperative pains. It is also used for reduction of fevers of bacterial or viral origin [30,31]. Therefore, the development of fast, sensitive and accurate methods for determining acetaminophen content are of clinical exigency. The present work was aimed at surveying the utility of cobalt oxide nanoparticles as electrocatalysts for the determination of acetaminophen content.

2. Experimental

2.1. Chemicals and reagents

Methyltrimethoxysilane (MTMOS) was obtained from Fluka. Potassium nitrate, acetic acid, methanol, high purity graphite powder, acetaminophen and $Co(NO_3)_2$ were obtained from Merck. Acetaminophen tablets were purchased from a local pharmacy (made in Hakim and Shafa pharmaceutical Co., Thehran, Iran). Buffer solutions (0.1 M) were prepared from Na_3PO_4, Na_2HPO_4, NaH_2PO_4, CH_3COOH, KOH and HCl for the pH range 4–13. All solutions were prepared with distilled water.

2.2. Instrumentation

An AUTOLAB PGSTAT-100 potentiostat/galvanostat, equipped with a USB electrochemical interface and driven by GPES software, was used for electrochemical experiments. A conventional three-electrode cell was used at room temperature. The modified carbon ceramic electrode (3.9 mm diameter) was used as the working electrode. A silver|silver chloride electrode (Ag|AgCl, KCl 3 M) and a platinum wire were used as reference and auxiliary electrodes, respectively.

The scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses were carried out using a scanning electron microscope (LEO 440i, Oxford) equipped with an EDX microanalyzer. Amperometric flow injection measurements were performed using a homemade single-channel FIA system.

2.3. Modified electrode preparation

The modified electrode was prepared by the following steps: first, 0.3 mL of MTMOS was mixed with 0.45 mL of methanol and then 10 μL of 11 M HCl was added as a catalyst. The mixture was magnetically stirred for approximately 3 min until a clear and homogeneous solution resulted. Then, 0.3 g of graphite powder was added, and the solution was shaken for an additional 1 min. The homogenized mixture was packed firmly into a Teflon tube (with 3.9 mm i.d. and 10 mm length) and dried for at least 24 h at room temperature. Afterward, the dried carbon ceramic electrode (CCE) is pulled out of the tube and a copper wire was inserted to create an electric contact. The electrode surface was polished with emery paper (grade 1500) and rinsed with distilled water. To form cobalt oxide nanoparticles at the electrode surface, the electrode was immersed in an aqueous solution of 20 mM $Co(NO_3)_2$ at pH = 7 (modifying solution). The modification was performed by cycling the electrode potential between −0.3 and 0.9 V vs. SCE at scan rate of 50 mV s^{-1} for 50 consecutive cycles.

3. Results and discussion

3.1. Physicochemical characterizations of the modified electrode

Fig. 1A shows a SEM image of a bare carbon ceramic surface immediately after polishing with emery paper (grade 1500). The surface is dense, scaly and has a high porosity. After modification of the carbon ceramic surface, cobalt oxide nanoparticles were formed uniformly with an average size of approximately 70 nm (Fig. 1B).

EDX measurements were performed to identify the elemental composition of the electrocatalyst. The corresponding results are shown in Fig. 2. The peaks appearing at 7 and 7.5 keV are related to Co. We can also observe one silica peak at 1.7 keV that overlaps severely with the gold peak. This peak was attributed to available silica in the carbon ceramic matrix.

3.2. Electrochemical behavior of the modified electrode

The electrodeposition of cobalt oxide particles at the CC electrode surface by consecutive cyclic voltammetry (CV) in the preparation solution is shown in Fig. 3. The continuous growth of peak heights is due to the formation of catalyst layers. After preparation, the electrochemical behavior of the modified electrode was characterized by CV. The inset in Fig. 3 shows a typical

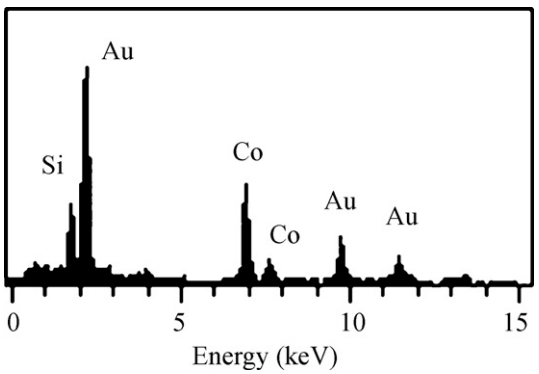

Fig. 2. EDX spectra of CoOx modified CCE surface.

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