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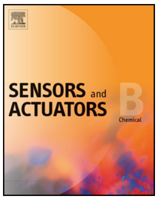

Simultaneous determination of morphine and codeine using Pt nanoparticles supported on porous silicon flour modified ionic liquid carbon paste electrode

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ABSTRACT

Pt nanoparticles supported on porous silicon (PSi) flour was synthesized by a simple in-situ redox reaction between $PtCl_6^{2-}$ and PSi, in hydrofluoric acid solution. The components and morphological properties of Pt/PSi nanocomposites were investigated by means of scanning electron microscopy, X-ray diffraction spectroscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy. Pt/PSi nanocomposite in carbon ionic liquid electrode (CILE) has synergetic effect on the oxidation of morphine and codeine. Simultaneous determination of morphine and codeine were performed using the proposed sensor by means of adsorptive striping voltammetry. Under the optimum conditions, the oxidation current responses of morphine and codeine were linear in the concentration range of 0.10–25.0 μmol L^{-1}. The detection limits of 30.0 and 20.0 nmol L^{-1} were achieved for morphine and codeine, respectively. The electrochemical sensor has high sensitivity toward the analytes with a good reproducibility (due to the high synergetic activity of Pt nanoparticles and good antifouling properties of the ionic liquid). To check the applicability of the sensor, the proposed sensor was used for the simultaneous determination of morphine and codeine in biological fluids with satisfactory results.

1. Introduction

In recent years, nano-scale materials have received a remarkable attention due to many engineering and technological applications. Although, nano-scale materials can be synthesized using various physical or chemical methods [1], but fast and facile synthesis of this materials is attractive especially if they are intended for large scale applications in science and technology. Among various nanomaterials, platinum (Pt) nanoparticles offer well-known advantages for chemical, petrochemical, pharmaceutical and electronic industries applications [2–5]. Pt nanoparticles have been widely prepared via several distinctive strategies including hydrothermal methods [6], sputtering methods [7], wet chemistry methods [8,9] and electrochemical methods [10]. However, these methods result in critical problems including a complicated and time-consuming process.

Ionic liquids (IL), also known as molten salts, are a class of materials, commonly containing a large organic cation (e.g., imidazolium, pyridinium, and pyrrolidinium etc.) and a small organic or inorganic anion (e.g., CF_3COO^-, $CF_3SO_3^-$, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, etc.), whereas some of them contain a small organic cation with large organic anion. They have recently received considerable attention in analytical chemistry due to unique chemical and physical properties including non-flammability, non-volatility, non-toxicity, and thermal stability [11–14]. In addition, the excellent electrochemical properties of ionic liquids (such as wide electrochemical windows and good conductivity) made them attractive for using in electrochemical sensors [15–17]. Moreover, one of the main drawbacks of the carbon electrodes is their contamination by the products of electrochemical reactions and the components of solutions and atmosphere (fouling effects). The ability of IL to promote electron-transfer reactions and to offer resistance to surface fouling in CILE has been documented in connection with important biomolecules [18–21].

Morphine and codeine are naturally occurring alkaloids in poppy seeds, have long been used as a drug, and are also abused [22]. As drug, morphine is used as an effective analgesic in the treatment of severe pain and codeine is widely used as a cough suppressant and moderate pain reliever too. But excessive or habitual use of these drugs causes toxic symptoms [23]. Thus,

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simple, sensitive and selective determination of morphine and codeine in biological samples is a vital of interest in control of drug abuse, clinical toxicology and forensic cases. Different analytical methods have been developed for the analysis of morphine and codeine which include GC–MS detection [24], liquid chromatography [25], electrophoresis with UV detection [26] and electrochemical detection [27]. Although these methods exhibit some merits, they are disadvantageous due to the complicated instruments required and the associated time-consuming sample pretreatment. Electrochemical techniques make a good candidate for the analysis of morphine and/or codeine due to their practicality, simplicity, low-cost, and ease of miniaturization for small-volume samples [28–31].

In our previous works we demonstrated that PSi acts as a moderate reducing agent and a porous template for fast and facile synthesis of copper nanoparticles [32,33]. In this research, as a continuation of our previous works, we developed a facile approach to synthesis Pt nanoparticles, using PSi. The Pt nanoparticles (supported on PSi, Pt/PSi) showed good chemical and electrochemical stability. Given the fact that PSi is a popular material in the fields of molecular sensing [34] due to its unique properties (biocompatibility [35] and the possibility to modulate morphology by varying the preparation conditions [36]), we have used the Pt/PSi nanocomposite as a new electrocatalyst for simultaneous determination of morphine and codeine by means of carbon ionic liquid electrode (CILE). Combination of antifouling properties of ionic liquids, biocompatibility of PSi and electrocatalytic effect of Pt nanoparticles, lead to new sensing surface for voltammetric determination of morphine and codeine with good sensitivity, acceptable selectivity and low detection limit.

2. Experimental

2.1. Chemicals and apparatus

Si powder (with mean particle size of 40 μm) and *N*-hexyl-3-methylimidazolium hexafluorophosphate were purchased from Sigma-Aldrich (Milwaukee, USA). Morphine sulfate and codeine phosphate were purchased from Temad Co, (Iran). All other chemicals used in this study, such as sodium hydroxide, nitric acid, hydrofluoric acid, potassium hexachloroplatinate, graphite and paraffin oil were of analytical grade and were purchased from Sigma-Aldrich (Milwaukee, USA). Double distilled water was used throughout the experiments. Britton–Robinson (B–R) buffer solutions were prepared by adding appropriate amounts of 0.5 mol L^{-1} NaOH solution into solutions containing a mixture of 0.1 mol L^{-1} of boric, acetic and phosphoric acids to produce buffer solutions with different pHs.

The morphology of the nanocomposites was carried out with a Hitachi S4160field emission scanning electron microscope (FE-SEM, Tokyo, Japan) at an accelerating voltage of 20 kV. An X-ray photoelectron spectrometer (XPS), Model XR3 E2-(VG Microtech) with twin anode X-ray source was used for the XPS analysis. The EDS spectra of the nanocomposites were recorded using a Philips XLS instrument (The Netherlands) in ambient condition. Powder X-ray diffraction (XRD) of the nanocomposite was performed on a Bruker D_8/Advance X-ray diffractometer with Cu-*K*α radiation ($\lambda = 1.5418$ Å). Electrochemical experiments were carried out using a computer controlled Autolab (PGSTAT 302 N, Eco-Chemie, The Netherlands) with NOVA 1.10 software. A conventional three-electrode system was employed incorporating a working modified electrode, a saturated Ag/AgCl reference electrode and a Pt wire counter-electrode. The pH measurements were performed using a Metrohm 827 pH/ion meter (Switzerland) equipped with a combined glass electrode.

2.2. Synthesis of the nanocomposite

PSi was synthesized according to our previous work [32]. Briefly, about 1.0 g of Si-powder was dispersed in 100 mL of etching solution that consisted of HF, HNO_3, and H_2O with molar ratios of 4.0, 1.0 and 30.0, respectively. After mild stirring for about 10 min, the initial metallic color of the silicon powder was converted into brown, which indicates that PSi has been formed.

The Pt/PSi nanocomposite was synthesized by a simple redox reaction between hexachloroplatinate ions and PSi, in an aqueous solution of HF, without using any reducing agent. For this purpose, 0.50 g of PSi was transferred into a beaker containing 100 mL of 0.1 mol L^{-1} HF solution. Then, 5 mL of 0.10 mol L^{-1} potassium hexachloroplatinate was added to the mixture, drop by drop with vigorous stirring.

The corresponding half reactions for the galvanic loading of Pt nanoparticles on the PSi surface are as follow:

$$SiF_6{}^{2-} + 4e^- \rightarrow Si^0{}_{(s)} + 6F^- E^0{}_{SiF6}{}^{2-}/{}_{Si}{}^0 = -1.20\text{vs.NHE} \quad (1)$$

$$PtCl_6{}^{2-} + 4e^- \rightarrow Pt^0{}_{(s)} E^0{}_{Pt}{}^{4+}/{}_{Pt}{}^0 = +1.42\text{vs.NHE} \quad (2)$$

Finally, the obtained nanocomposite was separated from the mixture by filtration, and washed several times with distilled water and dried at room temperature overnight.

2.3. Electrode preparation

Several electrodes with different percent of the IL (*N*-hexyl-3-methylimidazolium hexafluorophosphate) and Pt/PSi nanocomposites were prepared and examined for simultaneous determination of morphine and codeine. The results showed that an electrode, which contains 10.0 w/w% IL and 5.0 w/w% Pt/PSi nanocomposites has good sensitivity for simultaneous determination of morphine and codeine. So Pt/PSi–CILE was prepared by mixing of 100 mg (10.0 w/w%) IL, 300 mg (30.0 w/w%) of liquid paraffin, 50 mg (5.0 w/w%) of Pt/PSi nanocomposite and 550 mg (55.0 w/w%) of graphite powder. Then, the mixture was mixed well in an agate mortar and ground into a uniform paste. A portion of the resulting paste was packed firmly into the end of an insulin syringe (i.d.: 2.0 mm). The electric contact was established via a stainless steel handle. The procedure for the fabrication of CILE was similar to that of Pt/PSi–CILE, except addition of Pt/PSi nanocomposite. The bare carbon paste electrode (CPE) was fabricated by hand mixing of graphite powder and paraffin oil with 60/40 (w/w) graphite/liquid paraffin. The surface of the prepared electrodes were wiped and smoothed with weighing paper.

2.4. General procedure and real sample preparation

Blood serum and urine samples were obtained from healthy volunteers. Urine samples were stored in a refrigerator (at 4° C) after collection. 10 mL of the sample was centrifuged for 10 min at 2000 rpm. The supernatant was filtered using a 0.45 μm pore size filter and then diluted five times with the B–R buffer (pH 6.0). The solution was transferred into the electrochemical cell to be analyzed without any further pretreatment.

In order to precipitate proteins in the blood serum samples, 1.0 mL of the sample was treated with 20 μL perchloric acid ($HClO_4$, 20% v/v). Then, the mixture was vortexed for a further 45 s and then centrifuged at 6000 rpm for 7 min. The separated solution was diluted five times with B–R buffer (pH 6.0) and transferred into the electrochemical cell to be analyzed without further pretreatment. Standard addition method was used for the determination of morphine and codeine in blood serum and urine samples.

The blank (I_b) and analytical signal (I_a) were recorded in 0.1 mol L^{-1} of B–R buffers (pH 6.0) in the potential range of 0.00