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Multi-walled carbon nanotubes modified screen-printed electrodes for cisplatin detection

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ABSTRACT

A screen printed electrode functionalized with multi-walled carbon nanotubes and factory modified with carboxyl groups (MWCNT-COOH/SPCEs) was characterized by cyclic voltammetry and differential pulse voltammetry in a NaCl (0.1 mol L^{-1}, pH 7) solution containing 800 μmol L^{-1} sodium dodecyl sulfate (SDS). The MWCNT-COOH/SDS/SPCEs sensor was tested for the detection and quantification of cisplatin. For solutions of cisplatin, the electrochemical analysis showed a linear correlation coefficient of 0.9974 to cisplatin at concentrations between 1.45×10^{-5} and 1.0×10^{-4} mol L^{-1}, a sensitivity of 4.4×10^{4} ($\pm 1.0 \times 10^{3}$) μA L mol^{-1}, and detection and quantification limits of 4.6×10^{-6} and 1.4×10^{-5} mol L^{-1}, respectively. The reproducibility of the sensor response evaluated by the analysis of three replicates, indicated a RSD of 3.91%. The excellent response of the MWCNT-COOH/SDS/SPCEs cisplatin sensor allowed it to be tested in samples of human blood serum whose levels of added cisplatin were monitored by the HPLC. The average error % (sensor/HPLC) of 3.4 indicates that the combined methodology of MWCNT-COOH modified SPCE and the addition of a surfactant such as dodecyl sulfate is a convenient alternative for the use of HPLC for cisplatin determination in biological samples. The methodology cannot be applied to non-ionizable antitumor drugs carboplatin, oxaliplatin, doxorubicin or gemcitabine.

1. Introduction

Cisplatin (cis-dichlorodiammineplatinum (II)) has been extensively used to treat cancer. The mechanism by which cisplatin enters mammalian cells is unknown, but a variety of different mechanisms have been proposed. It is believed that the drug undergoes hydrolysis because the cellular chloride ion concentration is only between 2 and 30 mmol L^{-1}. After hydrolysis, cisplatin carries a positive charge and is highly reactive, forming covalent adducts with genomic or mitochondrial DNA, RNA and proteins; therefore, detecting the hydrolysis products of cisplatin is important for monitoring the pharmacokinetics of the drug, which is known to be patient dependent [1–3]. In addition to pharmaceutical analysis related applications, detecting cisplatin is also important for environmental issues: exposure to cisplatin or other soluble platinum complexes from hospital effluents may pose a health hazard, because these poisonous substances are not biodegradable and are accumulated by the ecological system [4,5].

Conventional analytical techniques have been developed to determine cisplatin, and the most widely used method is high-performance liquid chromatography (HPLC) [6]. Inductively coupled plasma atomic emission spectrometry (ICP-AES), gas chromatography, mass spectrometry and others [7,8]. All these analytical techniques require high-cost instrumentation.

To the best of our knowledge, electrochemical detection of cisplatin have been reported in an *in vitro* study in culture media [9]; metallothionein and glutathione-s-transferase enzymes, responsible for the elimination of xenobiotic compounds, have been immobilized in electrodes for the detection [10] and quantization of the compound [11]. In addition, there has been the development of other electrochemical sensors, by the use of modified glassy carbon electrodes modified with graphene oxide/multi-walled carbon nanotubes [7] and silver deposited on a carbon paste electrode [12]. The major drawbacks of these methods are the lack of selectivity against other substances

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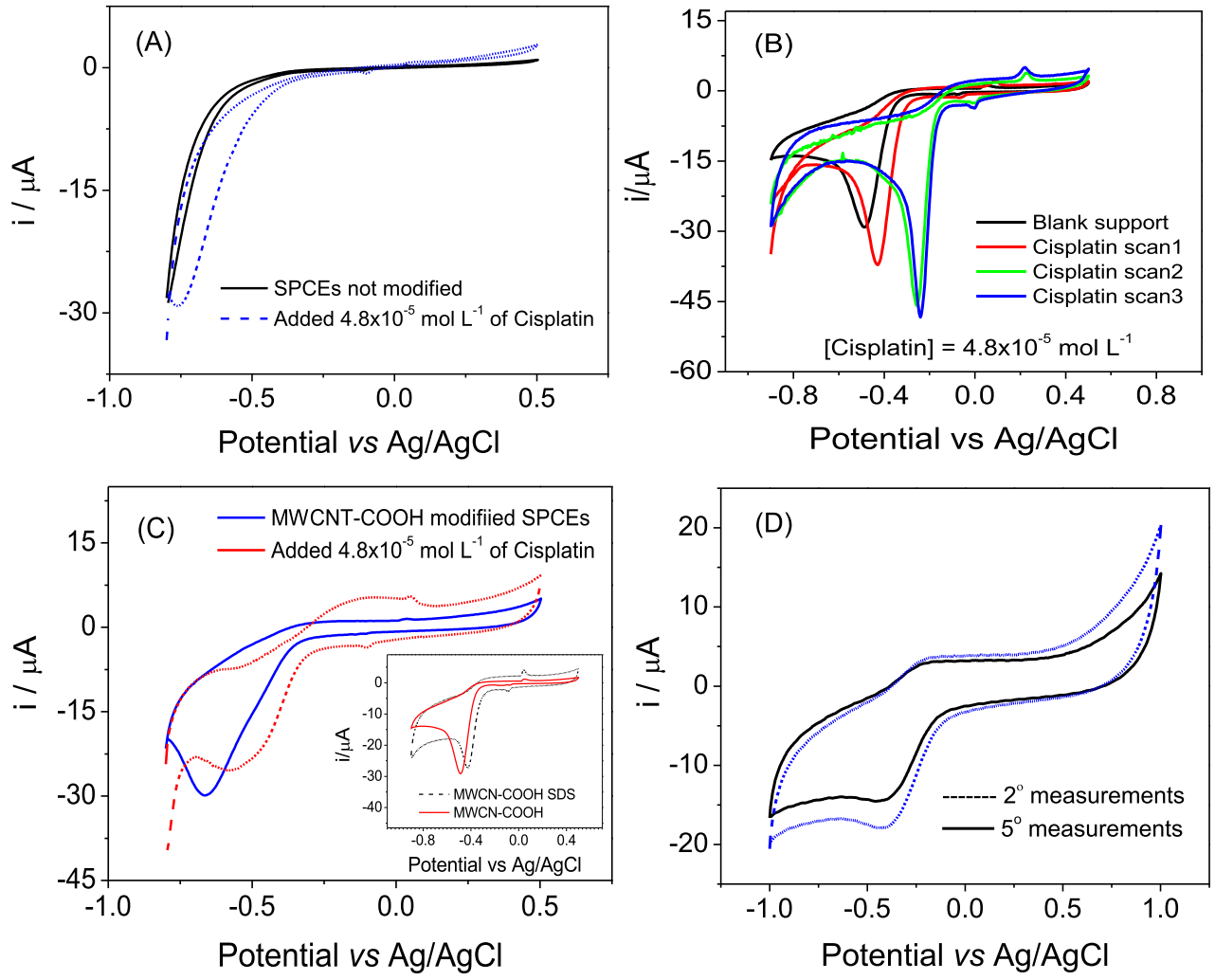

Fig. 1. Electrochemical response in cyclic voltammetry of cisplatin on screen-printed based on carbon (SPCE) sensor: (A) electrode not modified in absence of SDS; (B) electrode modified with MWCNT in absence of SDS; (C) electrode modified and in presence of SDS in the absence and presence of cisplatin (insert shows profile cyclic voltammetry of MWCNT-COOH in the absence and presence of SDS). (D) Current signal after several scans with SDS. Measurements performed in NaCl 0.1 mol L^{-1} (pH 7.0), scan rate = 20 mVs^{-1}, [Cisplatin] = 4.8×10^{-5} mol L^{-1}. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

used in chemotherapy and accumulation of the analyte on the electrode [11], and other matrix interferences. However, the increased availability of low cost modified screen printed electrodes may be a promise for the development of high-speed, miniaturized and selectivity improved electrochemical methods for drug analysis.

In the present work, an electrochemical method to detect and quantify cisplatin in human serum samples is proposed. This method is based on carboxyl-functionalized multi-walled carbon nanotube-modified screen printed electrodes in the presence of an anionic surfactant, sodium dodecyl sulfate (SDS).

2. Experimental section

2.1. Chemicals and preparation of solutions

The reagents used in this work were either analytical or HPLC grade. All aqueous solutions were prepared with deionized water (18 MΩ cm at 25 °C) obtained from a Milli-Q Direct-0.3 (Millipore) purification system. Sodium dodecyl sulphate (SDS), cisplatin, gemcitabine hydrochloride, carboplatin, oxaliplatin, doxorubicin hydrochloride, sodium chloride, NaOH were purchased from Sigma-Aldrich (St. Louis, MO, USA). Stock solutions of cisplatin (1×10^{-3} mol L^{-1}) were prepared in 0.1 mol L^{-1} NaCl by dissolving 7.4 mg of the compound in 25 mL of 0.1 mol L^{-1} NaCl. Stock solutions of sodium dodecyl sulfate were prepared by dissolving

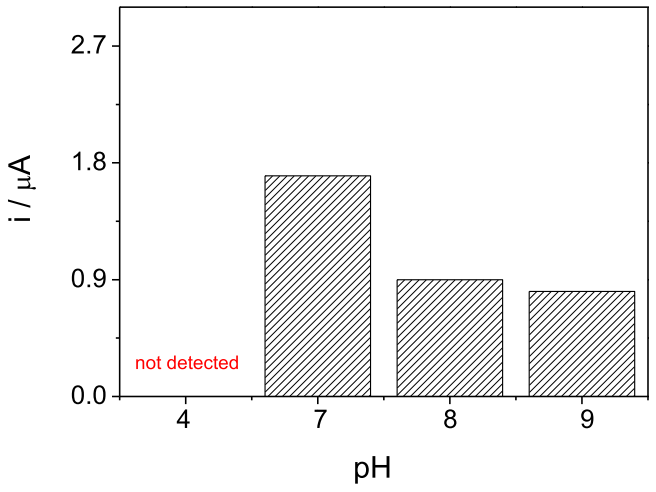

Fig. 2. Study of the influence of pH on the response *MWCNT-COOH/SDS/SPE.*