



Nano-perovskite carbon paste composite electrode for the simultaneous determination of dopamine, ascorbic acid and uric acid



Nada F. Atta, Shima M. Ali, Ekram H. El-Ads, A. Galal*

Chemistry Department, Faculty of Science, University of Cairo, Giza 12613, Egypt

ARTICLE INFO

Article history:

Received 4 May 2013

Received in revised form

15 September 2013

Accepted 16 September 2013

Available online 11 October 2013

Keywords:

Sensor

Nano-perovskites

Palladium-based-electrodes

Carbon paste electrode

Dopamine

ABSTRACT

A perovskite, SrPdO₃, of the type ABO₃ was used in the form of a composite with carbon paste as an electrode (CpE/SrPdO₃) for the electrochemical sensing of dopamine (DA) in biological fluids. The CpE/SrPdO₃ electrode showed a unique long term stability and low detection limit for (DA) determination. The structural characteristics of the modifier (SrPdO₃) that were prepared by a green method revealed a primary orthorhombic perovskite phase of SrPdO₃ and a secondary phase of SrPd₃O₄. The electrocatalytic activity of the CpE/SrPdO₃ electrode toward DA oxidation is relatively higher when compared to electrodeposited palladium nanoparticles modified CpE (CpE/Pd) with equivalent loading of Pd⁴⁺ salt. The prepared perovskite was characterized by XRD and SEM. Electrochemical characterization of CpE/SrPdO₃ was done using cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy. The redox behavior of DA follows a quasi reversible mechanism and two linear ranges of 7–70 μmol L⁻¹ and 90–160 μmol L⁻¹ with low detection limits of 9.3 nmol L⁻¹ and 25 nmol L⁻¹, respectively, and good correlation coefficient of 0.9981 could be determined. The electrocatalytic behavior is explained in terms of an oxygen–surface interaction between the oxygen atoms of the hydroxyl groups and the transition element in the perovskite. The protocol of DA sensing using this method was simple, sensitive and successfully applied for direct determination of DA in human urine samples with excellent recovery results. CpE/SrPdO₃ showed also high reproducibility, enhanced sensitivity, selectivity and anti-interference ability.

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1. Introduction

Perovskites prepared in the nano-scale have recently received extensive attention due to their catalytic nature when used as electrode modifiers [1–8]. Thus, perovskite-type oxides have been used in the catalytic processes like waste gas purification and combustion [9]. The high electronic conductivity, mobility of the oxide ions within the crystal, variations on the oxygen content [9], photocatalytic property, magnetic properties, electrically active structure, thermoelectric properties, dielectric property [1,10,11], thermal and chemical stability [12,13] have made the perovskite-type oxides attractive materials for their applications in electrochemical sensors, fuel cells and as catalysts in oxidation and reduction processes [9–12].

For noble metals incorporated in the perovskites structure, an interesting study by Tanaka et al. brought new insight into the behavior of Pd in perovskite structure. The study showed that Pd could reversibly move into and out of the perovskite lattice to suppress the growth of Pd particles, called self-regeneration of noble

metal [14]. Pd in perovskite is reduced under the rich condition, and the reduced Pd metal is oxidized and re-dissolved in the perovskite lattice under the lean condition [14]. Thus, Pd⁴⁺ in perovskite is reduced to Pd²⁺ and the reduced Pd metal while Pd²⁺ is oxidized to Pd⁴⁺ and is re-dissolved in the perovskite. In a different study, SrPdO₃ perovskite was prepared and proved its catalytic activity toward hydrogen evolution reaction where the presence of the modifier; SrPdO₃ increased the current due to the hydrogen evolution 100 times compared to the unmodified electrode [15].

On the other hand, perovskite-type oxides are attractive materials to be used as electrochemical sensors. Sun et al. employed La_{0.875}Ba_{0.125}FeO₃ nanocrystalline perovskite as alcohol gas sensor exhibiting excellent response, high sensitivity and good selectivity [13]. Perovskite material LaNi_{0.5}Ti_{0.5}O₃ was also employed to modify CpE in the development of non-enzymatic amperometric glucose sensor revealing high electrocatalytic activity and excellent stability for glucose determination [10], and as sensitive electrochemical sensor for amino acids exhibiting low detection limit and high sensitivity toward amino acids [16]. Moreover, it was also shown that LaNi_{0.5}Ti_{0.5}O₃/CoFe₂O₄ nanoparticles are excellent sensing materials exhibiting high electrocatalytic activity toward the oxidation of H₂O₂ [1].

* Corresponding author. Tel.: +20 0237825266; fax: +20 0235727556.
E-mail addresses: galal@sci.cu.edu.eg, galalah1@yahoo.com (A. Galal).

Dopamine (DA) is one of the most important neurotransmitters that are widely distributed in the mammalian central nervous system for message transfer [17–21]. It plays a very important role in the functioning of central nervous, renal, hormonal and cardiovascular systems. Thus, a loss of DA-containing neurons may lead to neurological disorders such as Parkinsonism and Schizophrenia [17,22–24]. Simultaneous detection of DA, ascorbic acid (AA) and uric acid (UA) is a problem of critical importance not only in the field of biomedical chemistry and neurochemistry but also for diagnostic and pathological research [18,25,26]. As reported, the concentration of AA is generally much higher than that of DA (100–1000 times) [26]. At bare electrodes, the selective determination of AA, DA and UA is impossible because their oxidation potentials are very close. Besides, stability and reproducibility cannot be achieved at bare electrodes due to the surface fouling caused by the adsorption of oxidized products of AA on electrode surface [17,21,25,26]. To overcome these problems, various modified electrodes have been constructed such as self-assembled iodine-adlayer modified palladium electrode [27], poly(3,4-ethylene dioxythiophene) modified Pt electrode in the presence of sodium dodecyl sulfate [20], Pd nanoparticles modified indium tin oxide electrode [28], Pd and Pt nanoclusters modified poly(3-methylthiophene), poly(N-methylpyrrole), and polyfuran film-coated platinum electrode [22–24], and Pd nanoparticles modified poly(3,4-ethylene dioxythiophene) electrode [29].

In the present work, the electrochemistry of DA is studied at the CpE/SrPdO₃ electrode that is also used as a sensor for DA determination in biological fluids. We used several surface to immobilize the SrPdO₃ including carbon paste electrode. While extensive research work is in progress using perovskite modified electrodes in the electrocatalytic production of hydrogen and oxygen gases, to the best of our knowledge, SrPdO₃ perovskite was not extensively addressed for electrochemical sensing applications. Therefore, CpE modified with SrPdO₃ was used for the first time in our work for the determination of DA in human fluids exhibiting higher electrocatalytic activity compared to bare CpE and CpE modified with Pd nanoparticles. The optimal synthesis conditions (pH, calcination time, and fuel type) of SrPdO₃ perovskite were investigated to obtain the material exhibiting the best catalytic activity toward DA sensing. The application of the proposed sensor for the simultaneous determination of DA, AA and UA proved excellent. Different parameters relevant to sensors were considered such as the reproducibility, sensitivity, selectivity, real sample analysis, long term stability as well as detection limits.

2. Experimental

2.1. Chemicals and reagents

All chemicals were used as received without further purification. Ammonium hexachloropalladate (IV) (Aldrich, 99.99%), strontium nitrate, citric acid, glycine, urea, nitric acid, ammonium hydroxide (Aldrich), graphite powder (Sigma–Aldrich, <20 μm, synthetic) and Paraffin oil (Fluka) were used as received without further purification. Dopamine (DA), uric acid (UA), ascorbic acid (AA) and potassium ferricyanide were supplied by Aldrich Chem. Co. (Milwaukee, WI, USA). Aqueous solutions were prepared using double distilled water. Phosphate buffer solution PBS (1 mol L⁻¹ K₂HPO₄ and 1 mol L⁻¹ KH₂PO₄) of pH 2–11 was used as the supporting electrolyte. pH was adjusted using 0.1 mol L⁻¹ H₃PO₄ and 0.1 mol L⁻¹ KOH.

2.2. Preparation of SrPdO₃

Stoichiometric amounts of (NH₄)₂PdCl₆ and Sr(NO₃)₂ were weighed, dissolved in distilled water, then a sufficient amount of

certain fuel (citric acid, glycine, or urea) was added. The pH of the solution was adjusted to certain value (2, 7, or 10) by nitric acid and ammonium hydroxide. The solution was heated on a hot plate to about 250 °C. The precursor complex undergoes dehydration to produce foam which then ignited giving a voluminous black fluffy powder. A ceramic nano-SrPdO₃ was obtained by calcination at 750 °C for a given time (3, 5, or 8) h [15].

2.3. Electrochemical cells and equipments

Electrochemical characterization was carried out with a standard three-electrode/one compartment glass cell. The working electrode was carbon paste electrode (CpE) (diameter: 6.3 mm). The auxiliary electrode was a large surface area platinum electrode. All the potentials in the electrochemical studies were referenced to Ag/AgCl (3.0 mol L⁻¹ NaCl) electrode. All experiments were performed at 25 °C ± 0.2 °C. The electrochemical characterization was performed using a BAS-100B electrochemical analyzer (Bioanalytical Systems, BAS, West Lafayette, USA). XRD data analysis was achieved using Proker D₈. Quanta FEG 250 instrument was used to obtain the scanning electron micrographs.

Electrochemical impedance spectroscopy (EIS) was performed using a Gamry-750 instrument and a lock-in-amplifier that are connected to a personal computer. The data analysis was provided with the instrument and applied non-linear least square fitting with Levenberg–Marquardt algorithm. All impedance experiments were recorded between 0.1 Hz and 100 kHz with an excitation signal of 10 mV amplitude. The measurements were performed under potentiostatic control at different applied potentials which were decided from the recorded cyclic voltammograms.

2.4. Electrode preparation

The carbon paste electrode (CpE) was prepared as follows: 0.125 g of reagent grade graphite powder was taken, washed with acetone and dried which was then mixed with 45 μL of paraffin oil. The carbon paste was packed into a Teflon holder that had been cut off at the end. Electrical contact to the paste was established via a thin copper rod passed through the Teflon holder. The fresh surface was obtained by polishing the electrode on a clean “weighing” paper until it showed a smooth and shiny appearance after every measurement [4].

A small amount ca. 1 ml of DMF was added to 10 mg of SrPdO₃ and sonicated until a homogeneous suspension was obtained. CpE electrode was polished well and casted with suitable volume of SrPdO₃ suspension. The electrode with SrPdO₃ was left to dry for about 2 h. The surface became ready for the electrochemical measurement.

CpE modified with Pd nanoparticles was prepared by the electrochemical deposition method [22–24].

2.5. Analysis of urine

The utilization of the proposed method in real sample analysis was also investigated by direct analysis of DA in human urine samples. Urine sample used for detection was diluted 400 times with 0.1 mol L⁻¹ PBS/pH 7.4. This dilution can actually help to reduce the matrix effect of real samples [22]. DA was dissolved in 0.1 mol L⁻¹ PBS/pH 7.40 to make a stock solution with 1 mmol L⁻¹ concentration. Standard additions were carried out from the DA stock solution in 15 mL of diluted urine.

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