



Determination of serotonin on platinum electrode modified with carbon nanotubes/polypyrrole/silver nanoparticles nano hybrid



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ABSTRACT

A new sensor has been developed by a simple electrodeposition of multi-walled carbon nanotubes (MWCNT), polypyrrole (PPy) and colloidal silver nanoparticles on the platinum (Pt) electrode surface. The Pt/MWCNT/PPy/AgNPs electrode was applied to the detection of serotonin in plasmatic serum samples using differential pulse voltammetry (DPV). The synergistic effect of MWCNT/PPy/AgNPs nano hybrid formed yielded a LOD of $0.15 \mu\text{mol L}^{-1}$ ($26.4 \mu\text{g L}^{-1}$). Reproducibility and repeatability values of 2.2% and 1.7%, respectively, were obtained compared to the conventional procedure. The proposed electrode can be an effective material to be used in biological analysis.

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1. Introduction

There is considerable interest in developing electrochemical techniques for determination of neurotransmitters, given the vast number of publications in this regard. Serotonin (5-hydroxytryptamine) is a monoamine neurotransmitter synthesised in serotonergic neurons in the central nervous system and plays a crucial role in the emotional system together with other monoamine transmitters such as regulation of mood, sleep, emesis (vomiting), sexuality and appetite. Low levels of serotonin have been associated with several disorders, notably depression, migraine, bipolar disorder and anxiety [1,2].

Recently, the development of versatile materials to modify electrode surface has been the target of numerous research in biological and environmental analysis using electrochemical methods. In most cases, this modification increases the sensitivity, selectivity, and reproducibility compared to conventional electrodes. One of the most widely used materials as a surface modifier is the nanostructured carbon, especially carbon nanotubes (CNTs). The use of CNTs in electrochemical sensors is due to their unique properties, such as high chemical stability, good electrical conductivity, high surface–volume ratio, and high adsorption capacity [3–5]. Moreover, similar to the electrically conducting polymers [6,7], the CNTs present functional groups anchored onto them, such as hydroxyl (–OH), carboxyl (–COOH), and carbonyl (–C=O), making these materials an excellent support that can be modified with several species, including metallic nanoparticles (NPs) [8–10].

Silver nanoparticles (AgNPs) find use in many fields, and the major applications include their use as catalysts, as optical sensors, in textile engineering, in electronics, and in the medical field as a bactericidal and as a therapeutic agent [11]. When AgNPs were supported on CNTs, the CNT–AgNPs exhibited good electrocatalytic activity, remarkable antibacterial activity, and excellent surface-enhanced Raman scattering (SERS), as well as high chemical stability, excellent absorption capacity, and high selectivity [12,13].

One of the polymers most studied and applied in the development of sensors and biosensors is the polypyrrole (PPy) [14]. The use of PPy in electroanalysis is due to its suitable characteristics, such as stability at ambient conditions, high conductivity, efficient polymerisation at neutral pH, thickness controllability and a good reversibility between conducting and insulating states. In this sense, Harley et al. [15] fabricated a sensor by doping PPy with a sulfonated β -cyclodextrin to determine dopamine levels. Lu et al. [16] used a gold (Au) electrode modified with PPy/CNT/Au nanoparticles as a sensor to detect epinephrine (EP) sensitively when ascorbic acids and uric acids also exist. Another study [17] also determined EP using an overoxidised PPy/CNT composite on a glass carbon (GC) electrode.

Considering that described above, an electrochemical sensor for selective determination of serotonin using CNTs/PPy/AgNPs nano hybrid is proposed. The sensor was prepared by a simple electrodeposition of a certain ratio of multi-walled carbon nanotubes (MWCNT) and PPy on the platinum (Pt) electrode surface, followed by the electrodeposition of colloidal AgNPs. The nanocomposite formed showed excellent properties through the synergistic effects of the component materials.

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2. Experimental

2.1. Apparatus and procedures

Cyclic voltammetry (CV), chronoamperometry (CA), and differential pulse voltammetry (DPV) experiments were performed using a model PGSTAT 30 Autolab electrochemical system (Eco Chemie, Utrecht, the Netherlands) equipped with GPES software (Eco Chemie Utrecht, the Netherlands). The cell was assembled with a conventional three-electrode electrochemical system: Pt modified with MWCNT/PPy/AgNPs nanohybrid as a working electrode, an Ag/AgCl/KCl (3.0 mol L⁻¹) electrode as the reference electrode and a Pt plate as the auxiliary electrode. All experiments were carried out at a 25 °C. DPV measurements were obtained over a relevant potential range, with a scan rate of 10 mV s⁻¹, pulse amplitude of 100 mV, and a step potential of 2 mV in a 0.2 mol L⁻¹ phosphate buffer solution (PBS) pH 8.0, containing 50.0 μmol L⁻¹ of serotonin standards.

The morphologies of the MWCNT/PPy and MWCNT/PPy/AgNPs nanohybrid were examined using a field-emission gun scanning electron microscope (FEG-SEM), and the images were recorded using a model FEI Inspect F50 microscope (FEI Company, Hillsboro, USA).

2.2. Chemicals and solutions

All reagents used in this study were of analytical grade and were used without further purification. Pyrrole, MWCNT (90% purity), silver nitrate and serotonin hydrochloride were purchased from Sigma-Aldrich (Germany). All solutions were prepared with Nanopure water from a Barnsted Nanopure System (Thermo Scientific, USA). 1.0 g of MWCNT was mixed with 500 mL of a 1:3 mixture of HNO₃/H₂SO₄ for 12 h, in order to promote its functionalisation. They were then filtered through a 0.45 μm Millipore Nylon filter membrane. The resulting MWCNT were continuously washed using distilled water until the pH of the filtrate was neutral, at which point the MWCNT were dried overnight in a vacuum oven at 120 °C.

2.3. Synthesis of colloidal silver nanoparticles (AgNPs)

The AgNPs were prepared from dropwise addition of 10 mL of a 1.0 mmol L⁻¹ AgNO₃ solution in 30 mL of a 2.0 mmol L⁻¹ NaBH₄ solution. The addition of silver nitrate was performed slowly (1 drop per second), under magnetic stirring and ice bath. Initially the solution is slightly yellow, but becomes bright yellow when the whole solution of AgNO₃ is added. The colloidal AgNPs is stored under refrigeration.

2.4. Preparation of the Pt/MWCNT/PPy/AgNPs electrode

Prior to modification, the Pt electrode surface was polished with 0.5 μm alumina slurries, rinsed thoroughly with double-distilled water, sonicated for 5 min in ethanol and 5 min in water, and then dried in air. 25.0 mL of 0.2 mol L⁻¹ NaCl solution containing 443 μL of pyrrole and 5.0 mg of MWCNT was sonicated for 10 min with 70% amplitude. The Pt electrode was immersed in this solution and electrocodeposition of PPy/MWCNT was performed using 10 scans of CV in the potential range of -0.2 and +0.8 V (vs. Ag/AgCl) with a scan rate of 50 mV s⁻¹. The Pt electrode containing the MWCNT/PPy film was removed from the solution and the electrodeposition of AgNPs is performed using CA at a fixed potential of -1.0 V for 420 s in 12.0 mL of a 0.1 mol L⁻¹ KCl solution containing 100.0 μmol L⁻¹ of colloidal AgNPs. After this step, the proposed Pt/MWCNT/PPy/AgNPs electrode is washed with distilled water and air dried.

2.5. Preparation of the plasmatic serum and analysis of serotonin

Samples similar to plasmatic serum were Krebs–Ringer solution and PBS. The artificial body fluid was prepared similarly as described by

Brett et al. [18]. The solution composition per litre of solution was: 6.98 g NaCl, 0.36 g KCl, 0.28 g CaCl₂, 0.15 g MgSO₄, 210 mL PBS, and pH 8.0. An aliquot of 10 mL of the plasmatic serum was spiked with 2.0 μmol L⁻¹ of serotonin. The sample analyses were performed using the standard addition method and DPV experiments were carried out directly on these samples without pre-treatment procedures.

3. Results and discussion

3.1. Morphological characterisation of the nanohybrid

The morphologies of the PPy, MWCNT/PPy, and the MWCNT/PPy/AgNPs nanohybrid were examined by FEG-SEM analysis. Fig. 1 displays typical images of the PPy, MWCNT/PPy and MWCNT/PPy/AgNPs films assembled onto Pt electrodes. Fig. 1A characterises the electropolymerised PPy structure as compact layers of a globular shape, where each globule has an average size of 400 nm. Fig. 1B indicates that MWCNT structures were totally covered by a compact layer of PPy in a core-shell structure [14,19]. The average diameter of the MWCNT covered by a PPy layer was calculated at 750 nm, which was much larger than that of the uncovered MWCNT (80 nm). The MWCNT/PPy/AgNPs nanohybrid displayed in Fig. 1C shows that the MWCNT/PPy was modified with the colloidal AgNPs. The AgNPs were preferentially supported in the sidewalls of the MWCNT/PPy and had sizes varying from 55 to 85 nm.

3.2. Electrocatalytic oxidation of serotonin on the Pt/MWCNT/PPy/AgNPs electrode

The effect of scan rate on the electrocatalytic oxidation of serotonin at the Pt/MWCNT/PPy/AgNPs electrode was carried out in 0.2 mol L⁻¹ PBS pH 7.0 containing 100.0 μmol L⁻¹ of serotonin by cyclic voltammetry experiments, using several scan rates in a range varying from 10 to 100 mV s⁻¹, and the results obtained are presented in Fig. 2. In the voltammetric response using a scan rate of the 50 mV s⁻¹ (open circle in Fig. 2), it can be seen a well-defined oxidation peak at a potential value of +0.42 V vs. Ag/AgCl/KCl (3.0 mol L⁻¹). This peak is attributed to an irreversible oxidation of the hydroxyl group present in the aromatic ring of the serotonin forming ketone species. As can be observed in the inset of Fig. 2, there is a linear relationship between the anodic current peak and the square root of scan rate (v^{1/2}) in the range between 10 and 100 mV s⁻¹, which can be described by the equation $I_{pa} = 3.99 + 2.61 v$ (I_{pa} in μA and scan rate in mV s⁻¹, $r = 0.993$), which reflects the control of the electrochemical process by adsorbed species.

3.3. Parameters for the optimisation of the serotonin response on the Pt/MWCNT/PPy/AgNPs electrode

To maximise the DPV analytical signal, the effects of experimental parameters (electrode composition, pulse amplitude, potential step height, scan rate, pre-treatment potential and time for cleaning the electrode surface) were studied using Pt/MWCNT/PPy/AgNPs electrode in a 0.2 mol L⁻¹ PBS pH 7.0 containing 50.0 μmol L⁻¹ of serotonin. The influence of the composition of the electrode material was evaluated first. Accordingly, the colloidal AgNPs concentration on the nanohybrid electrode was optimised in the range of 37.5 to 125.0 μmol L⁻¹ in the potential interval of 0.0 to +0.6 V vs. Ag/AgCl/KCl (3.0 mol L⁻¹) as shown in Fig. 3. An increase by a factor of 2.3 was observed in the anodic peak current when the amount of colloidal AgNPs was changed from 37.5 to 100.0 μmol L⁻¹, reaching the maximum current at 100.0 μmol L⁻¹. When 125.0 μmol L⁻¹ of colloidal AgNPs was used in the nanohybrid electrode preparation the anodic peak current decreased significantly. This occurs due to the loss of the AgNPs nanostructure. This fact is attributed to the disordered formation of Ag clusters, leading to an increase in particle size. Based on these results, 100.0 μmol L⁻¹ of colloidal AgNPs was used for the nanohybrid preparation.

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