



## Simultaneous determination of catecholamines, uric acid and ascorbic acid at physiological levels using poly(*N*-methylpyrrole)/Pd-nanoclusters sensor

Nada F. Atta \*, Maher F. El-Kady, Ahmed Galal

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

### ARTICLE INFO

#### Article history:

Received 2 October 2009

Received in revised form 17 December 2009

Accepted 6 January 2010

Available online 11 January 2010

#### Keywords:

Pd nanoclusters

Electrochemical sensor

Poly(*N*-methylpyrrole)

Catecholamine neurotransmitters

Ascorbic acid

Uric acid

### ABSTRACT

An interesting electrochemical sensor has been constructed by the electrodeposition of palladium nanoclusters (Pd<sub>nano</sub>) on poly(*N*-methylpyrrole) (PMPy) film-coated platinum (Pt) electrode. Cyclic voltammetry, electrochemical impedance spectroscopy (EIS), and scanning electron microscopy were used to characterize the properties of the modified electrode. It was demonstrated that the electroactivity of the modified electrode depends strongly on the electrosynthesis conditions of the PMPy film and Pd<sub>nano</sub>. Moreover, the modified electrode exhibits strong electrocatalytic activity toward the oxidation of a mixture of dopamine (DA), ascorbic acid (AA), and uric acid (UA) with obvious reduction of overpotentials. The simultaneous analysis of this mixture at conventional (Pt, gold [Au], and glassy carbon) electrodes usually struggles. However, three well-resolved oxidation peaks for AA, DA, and UA with large peak separations allow this modified electrode to individually or simultaneously analyze AA, DA, and UA by using differential pulse voltammetry (DPV) with good stability, sensitivity, and selectivity. This sensor is also ideal for the simultaneous analysis of AA, UA and either of epinephrine (E), norepinephrine (NE) or L-DOPA. Additionally, the sensor shows strong electrocatalytic activity towards acetaminophen (ACOP) and other organic compounds. The calibration curves for AA, DA, and UA were obtained in the ranges of 0.05 to 1 mM, 0.1 to 10 μM, and 0.5 to 20 μM, respectively. The detection limits (signal/noise [S/N] = 3) were 7 μM, 12 nM, and 27 nM for AA, DA, and UA, respectively. The practical application of the modified electrode was demonstrated by measuring the concentrations of AA, DA, and UA in injection sample, human serum, and human urine samples, respectively, with satisfactory results. The reliability and stability of the modified electrode gave a good possibility for applying the technique to routine analysis of AA, DA, and UA in clinical tests.

© 2010 Elsevier Inc. All rights reserved.

Catecholamines are a class of neurotransmitters, and their detection in the human body has been of great interest to neuroscientists. They include dopamine (DA),<sup>1</sup> epinephrine (E), and norepinephrine (NE) and play important roles in various biological, pharmacological, and physical processes [1]. They are widely distributed in the mammalian central nervous system for message transfer [2]. DA, ascorbic acid (AA), and uric acid (UA) are compounds of great biomedical interests, playing determining roles in human metabolism. DA is one of the crucial catecholamine neurotransmitters that

play an important role in the function of central nervous, renal, hormonal, and cardiovascular systems [3]. Thus, a loss of DA-containing neurons may lead to neurological disorders such as Parkinsonism and schizophrenia [4]. AA is present in both animal and plant kingdoms, is a vital vitamin in human diet, and is very popular for its antioxidant properties. It has been used for the prevention and treatment of common cold, mental illness, infertility, and cancer and in some clinical manifestations of human immunodeficiency virus (HIV) infections [5]. UA is the primary end product of purine metabolism. The extreme abnormalities of UA levels in the body are symptoms of several diseases, including gout, hyperuricemia, and Lesch–Nyan disease [6]. Therefore, simultaneous detection of DA, AA, and UA is a challenge of critical importance not only in the field of biomedical chemistry and neurochemistry but also for diagnostic and pathological research. However, the simultaneous determination of AA, DA, and UA at conventional solid electrodes (carbon and metal) usually struggles because they undergo an overlapping oxidation potential and electrode fouling takes place due to the adsorption of oxidation products [7]. Therefore, it is essential to develop simple and rapid methods for their determination in routine

\* Corresponding author. Fax: +20 0235727556.

E-mail address: [nada\\_fah1@yahoo.com](mailto:nada_fah1@yahoo.com) (N.F. Atta).

<sup>1</sup> Abbreviations used: DA, dopamine; E, epinephrine; NE, norepinephrine; AA, ascorbic acid; UA, uric acid; HIV, human immunodeficiency virus; Ppy, polypyrrole; ssDNA, single-stranded DNA; PMPy, poly(*N*-methylpyrrole); PMPy/Pd<sub>nano</sub>, PMPy modified with palladium nanoclusters; ECP, electronically conducting polymer; CV, cyclic voltammetry; Pt, platinum; DPV, differential pulse voltammetry; ACOP, acetaminophen; MPy, *N*-methylpyrrole; Bu4NPF6, tetrabutylammonium hexafluorophosphate; HPLC, high-performance liquid chromatography; EIS, electrochemical impedance spectroscopy; BE, bulk electrolysis; SEM, scanning electron microscopy; PBS, phosphate-buffered solution; Au, gold; S/N, signal/noise.

analysis without cross-interferences. Of these, electrochemical methods have received much interest because they are more selective, less expensive, and less time-consuming and can potentially be applied to a real-time determination *in vivo* [8]. There are reports of using polymer films [9], nanoparticles [10], self-assembled monolayers [11], and metal oxide [3] modified electrodes to simultaneously determine DA and AA and also in the presence of UA. All of the reported modified electrodes have their advantages and limitations.

Polypyrrole (Ppy) is one of the most extensively used conducting polymers in the design of bioanalytical sensors [12]. Versatility of this polymer is determined by a number of properties: redox activity [13], ion exchange and ion discrimination capacities [14], electrochromic effect depending on electrochemical polymerization conditions and charge/discharge processes [15], strong absorptive properties toward gases [16], proteins [17], DNA [18], catalytic activity [19], corrosion protection properties [20], and the like. Most of these properties are dependent on the synthesis procedure [21]. Ppy may be electrochemically generated and deposited on the conducting surfaces. This technique is successfully exploited for development of various types of electrochemical sensors and biosensors. In this respect, several major directions are straightforward: (i) catalytic sensors based on immobilized enzymes [22], (ii) immunosensors based on immobilized affinity exhibiting proteins [23], (iii) DNA sensors based on covalently immobilized and/or entrapped single-stranded DNA (ssDNA) [24], and (iv) affinity sensors based on molecularly imprinted polymers [25]. Nowadays, this polymer becomes one of the major tools for nanobiotechnological applications [26]. Various approaches have been considered for the synthesis of Ppy, including chemical and electrochemical methods [27]. It was reported that the catalytic activity of Ppy films depends on the synthesis conditions [21,27]. In our report, potentiostatic (controlled potential electrolysis) and potentiodynamic (cyclic voltammetry) techniques were used to synthesize poly(*N*-methylpyrrole) (PMPy) films, and their activities were tested in the electrooxidation of the compounds of study. PMPy has attracted attention as a possible alternative to PPy for technological applications in spite of its lower conductivity [28].

A step forward with respect to “simple” modification with pristine conducting polymers consists in the inclusion of metal functionalities inside the polymeric matrix to further increase the performances of the resulting composite material. In particular, inclusion of noble metal nanoparticles, whose catalytic properties are well known [20], constitutes one of the most interesting possibilities. Similar composites based on polypyrrole and polyaniline have been reported recently [29], although a precise definition of the structure and properties of the material is far from being achieved exhaustively.

Here we report the synthesis, characterization, and sensing applications of a composite material based on PMPy modified with palladium nanoclusters (PMPy/Pd<sub>nano</sub>). The aim of the development of the composite material is to improve the electrocatalytic properties of the simple polymeric electrode coating. Several procedures have been employed to prepare metal-supported nanoparticles on different carbon supports and electronically conducting polymers (ECPs) [30]; of these, electrochemical deposition is an efficient method for the preparation of metal nanoparticles. It is widely used with different strategies/methodologies such as cyclic voltammetry (CV) [31], potential step deposition [32], and double pulse [33]. Among these, potential step deposition provides a tool to fine-tune the amount of metal deposited, the number of metallic sites, and their size. Various electrochemical methods have been described for the preparation of ECP/metal nanoparticles, but the most popular approach is the deposition of metal nanoparticles onto electrodes previously coated with ECP films [34]. Moreover,

the methods of formation of the polymer film and deposition of metal nanoparticles have a strong impact on the characteristics of the polymer/metal nanoparticle composites and the possible synergistic effects between the dispersed metal nanoparticles and polymer film [10–14]. For these reasons, we explored how these factors affect the composite-modified electrode.

In the current study, PMPy/Pd<sub>nano</sub> composite-modified platinum (Pt) electrode was used for the simultaneous determination of catecholamines, UA, and AA. The electrochemical behaviors of these species at our modified electrode were investigated using CV and differential pulse voltammetry (DPV) techniques. Based on the different electrocatalytic activities of the modified electrode toward AA, DA, and UA, a sensitive and selective method for their simultaneous determination was established. The detection of AA in injection samples, UA in human urine, and DA in human serum was finally demonstrated as real sample applications. Furthermore, this work addresses the electrocatalytic properties of PMPy/Pd<sub>nano</sub> toward the oxidation of acetaminophen (ACOP), which is commercially known as paracetamol, as well as some organic compounds. ACOP is an antipyretic and analgesic drug widely used worldwide for the relief of mild to moderate pain associated with headache, backache, arthritis, and postoperative pain. Therefore, its determination is of importance as well.

## Materials and methods

### Chemicals and reagents

All chemicals were used as received without further purification except *N*-methylpyrrole (MPy, distilled under rotary evaporation prior to use). MPy, tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>), acetonitrile (high-performance liquid chromatography [HPLC] grade), hydroquinone, catechol, DA hydrochloride, E, NE, *L*-DOPA, methyl-*L*-DOPA, *p*-aminophenol, acetaminophen, AA, UA, tryptophan, cysteine, tyrosine, tyramine, serotonin hydrochloride, glucose, sulfuric acid, sodium chloride, potassium chloride, calcium chloride, and magnesium chloride were supplied by Aldrich Chemical (Milwaukee, WI, USA). Palladium(II) chloride (Schering Kaul Paum, Berlin, Germany) was also used. Aqueous solutions were prepared using doubly distilled water.

### Electrochemical cells and equipment

Electrochemical polymerization and characterization were carried out with a three-electrode/one-compartment glass cell. The working electrode was Pt disk (diameter = 1.5 mm). The auxiliary electrode was in the form of 6.0 cm Pt wire. All of the potentials in the electrochemical studies were referenced to Ag/AgCl (3.0 M NaCl) electrode. Working electrode was mechanically polished using alumina (2 μm)/water slurry until no visible scratches were observed. Prior to immersion in the cell, the electrode surface was rinsed thoroughly with distilled water and dried. Other disk electrodes were used: gold (diameter = 1.5 mm) and glassy carbon (diameter = 3 mm). All experiments were performed at 25 °C.

The electrosynthesis of the polymers and their electrochemical characterization were performed using a BAS-100B electrochemical analyzer (Bioanalytical Systems [BAS], West Lafayette, IN, USA). Electrochemical impedance spectroscopy (EIS) measurements were performed using a Gamry-750 system and a lock-in amplifier that were connected to a personal computer. The data analysis software was provided with the instrument and applied nonlinear least squares fitting with the Levenberg–Marquardt algorithm. All impedance experiments were recorded between 0.1 Hz and 100 kHz with an excitation signal of 10 mV amplitude.

Download English Version:

<https://daneshyari.com/en/article/1174777>

Download Persian Version:

<https://daneshyari.com/article/1174777>

[Daneshyari.com](https://daneshyari.com)