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An electrochemical sensor prepared by sonochemical one-pot synthesis of multi-walled carbon nanotube-supported cobalt nanoparticles for the simultaneous determination of paracetamol and dopamine

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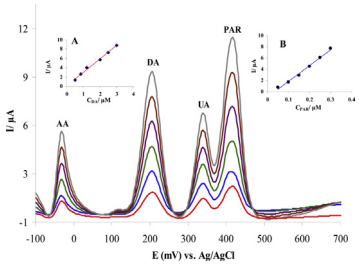
HIGHLIGHTS

- A GCE was modified with carbon nanotubes and cobalt nanoparticles.
- The composite material was obtained using an ultrasonic chemical deposition method.
- The CoNPs/MWCNT/GCE was applied for the simultaneous determination of PAR and DA.
- The presence of AA and UA did not affect the responses of PAR and DA.
- Lower detection limits were obtained using the CoNPs/MWCNT/GCE.

GRAPHICAL ABSTRACT



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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) functionalized by cobalt nanoparticles were obtained using a single step chemical deposition method in an ultrasonic bath. The composite material was characterized using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The electroactivity of the cobalt-functionalized MWCNTs was assessed in respect to the electrooxidation of paracetamol (PAR) and dopamine (DA). It was found that the carbon nanotube supported cobalt nanoparticles have significantly higher catalytic properties. The proposed electrode has been applied for the simultaneous determination of PAR and DA. The modified electrode could resolve the overlapped voltammetric waves of PAR and DA into two well-defined voltammetric peaks with peak to peak separation of about 203 mV. On the other hand, the presence of potential drug interfering compounds AA and UA did not affect the voltammetric responses of PAR and DA. The current of oxidation peaks showed a linear dependent on the concentrations of PAR and DA in the range of 5.2×10^{-9}–4.5×10^{-7} M ($R^2 = 0.9987$) and 5.0×10^{-8}–3.0×10^{-6} M ($R^2 = 0.9999$), respectively. The detection limits of 1.0×10^{-9} M and 1.5×10^{-8} M were obtained for PAR and DA, respectively. The proposed electrode showed good stability (peak current change: 4.9% with and RSD of 2.6% for PAR; 5.5% with and RSD of 3.0% for DA over 3 weeks), reproducibility (RSD 2.3% for PAR and RSD 1.5% for DA), repeatability (RSD 2.25% for PAR and RSD 2.50% for DA) and high recovery (99.7% with an RSD of 1.3% for PAR; 100.8% with an RSD of 1.8% for DA). The proposed method was successfully applied to the determination of PAR and DA in pharmaceuticals.

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1. Introduction

Electrochemical detection provides a highly sensitive approach to the analysis of a wide range of drugs [1–4]. However, this approach is sometimes restricted by limitations of selectivity due to the interference from the other redox active species which may undergo electrolysis at similar potentials to the target species in the solution [5–7]. Such an example arises in the detection of paracetamol (PAR) using carbon electrodes, since molecules such as dopamine (DA), ascorbic acid (AA) and uric acid (UA) all display redox behaviour at potentials close to those required for the oxidation of PAR. The most important method to overcome such problems is to modify the electrodes to produce a chemically modified electrode, that aims to alter the electrode kinetics of species so that the potential under which the target species undergo oxidation becomes shifted from that required to electrolyse the interfering species [8–11]. Electrochemical nanosensors based on CNTs represent a versatile alternative for the quantification of various analytes [12–15]. The performance of electrodes modified with CNTs has been found to be much superior to those of other carbon electrodes in terms of response time, increased sensitivity, resistance to surface fouling, decreased overpotentials, reuseability and limits of detection [16]. Also, metal nanoparticles can display four advantages over macroelectrodes when utilized in electroanalysis: enhancement of mass transport, catalysis, high effective surface area and control over electrode microenvironment [24–28]. Paracetamol, also known as acetaminophen is an effective pain killer used for the relief of pains associated with several parts of the body [17]. The higher dose of PAR can lead to the accumulation of toxic metabolites which may cause hepatoxicity and nephrotoxicity [18]. Thus controlling the amount of PAR in pharmaceuticals is of great importance for the general public health. A number of analytical methods have been reported for the analysis of PAR in pharmaceutical forms or biological fluids including chromatography [19], spectrophotometry [20], chemiluminescence [21], capillary electrophoresis [22], FTIR and Raman spectrometry [23] and flow injection analysis using various methods of detection [24–26]. However, these techniques are expensive and require time-consuming derivatization step and also in some cases low sensitivity and selectivity makes them unsuitable for a routine analysis. On the other hand, electrochemical techniques have several advantageous owing to their simplicity, high sensitivity and rapidness [7,16]. The development and application of electrochemical nanosensors for the detection of PAR has received considerable interest in last few decades since PAR is an electroactive compound which can be oxidized electrochemically. Most electrochemical methods rely on modifiying electrodes such as MWCNT modified pyrolytic graphite electrode [27], carbon nanoparticles modified GCE [28], SWCNT-graphene modified GCE [29], carbon nanotube modified screen printed electrode [30], SWCNT modified ceramic electrode [31], and D50wx2-GNP-modified carbon paste electrode [32]. On the other hand, dopamine (DA) is one of the most important catecholamine neurotransmitters, which mainly exists in mammalian brain tissues and fluids, and plays a very important role in the central nervous system (CNS). When present in lower concentrations it is likely to give rise to neurodegenerative diseases such as Parkinson and Alzheimer among others [33]. A number of modified electrodes have been utilized for the detection of DA such as poly(3-(5-chloro-2-hydroxyphenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid) [3], carbon paste electrode modified with carbon nanotubes and molybdenum (VI) complex [34], poly(ethylene dioxythiophene) film modified electrode [35], poly(calmagite) modified electrode [36], CNTs dispersed in polyethylenimine on GC [37], Co phthalocyanine modified MWCNTs on GC [38], graphite–polyurethane composite [39], Pd/poly(3,4-ethylenedioxythiophene) [40], SiO_2-coated graphene oxide and molecularly imprinted polymers modified electrode [41]. However, it has also been shown that low concentration of PAR significantly prevented DA neurodegeneration while high concentration of PAR did not protect DA neurons 6-hydroxydopamine-induced degeneration [42]. Therefore, the simultaneous detection of PAR and DA is of great importance for both scientific and therapeutic reasons. Various modified electrodes have been applied for the simultaneous determination of PAR and DA including, multiwalled carbon nanotubes modified electrode [43], SWCNT modified carbon – ceramic electrode [44], polypyrrole-azsophloxine modified gold electrode [45], molybdenum (VI) complex/carbon nanotubes modified carbon paste electrode [46],

In this study, a voltammetric nanosensor has been prepared by one-pot synthesis of multi-walled carbon nanotube-supported cobalt nanoparticles in an ultrasonic bath for the simultaneous determination of PAR and DA. The surface modification with MWCNTs and nanoparticles of cobalt served to improve peak separation from interfering compounds such as AA and UA, reduce the potential required to oxidize species and improve the detection limit.

2. Experimental

2.1. Chemical reagents

Paracetamol, dopamine, ascorbic acid and uric acid all with purity ≥99% obtained from Sigma–Aldrich Chemical Company were used as received. Cobalt (II) chloride (98% GR, ACS), disodium hydrogen phosphate, potassium dihydrogen phosphate, sodium hydroxide, hydrochloric acid with analytical grade (GR, ACS, ISO), chloroform and acetonitrile (spectroscopic grade >99.9%) were purchased from Merck Chem Co. (Darmstadt. Germany). Multi-walled carbon nanotubes (MWCNTs) of >95% purity were obtained from NanoLab, USA. All solutions were prepared using ultra pure water. Oxygen-free nitrogen was bubbled through the cell prior to each experiment. All experiments were carried out at room temperature.

2.2. Instrumentation

Electrochemical experiments were performed using an Eco-Chemie Autolab PGSTAT 12 potentiostat/galvanostat (Utrect, The Netherlands) with the electrochemical software package 4.9. A three-electrode system was used: a glassy carbon electrode as working electrode [3 mm in diameter (Bioanalytical Systems, Lafayette, USA)], a Pt wire counter electrode and a Ag/AgCl reference electrode (Metrohm, Switzerland). Prior to modification, the GCE was polished with 1 μm and 0.3 μm alumina. The electrode was then sonicated for 5 min in ethanol. All experiments were carried out at room temperature.

2.3. Preparation of solutions

A 1.0×10^{-3} M AA solution was prepared freshly by dissolving 0.1,762 g AA in 0.1 M PBS at pH 7.0 and the solution was diluted to 100 mL with 0.1 M PBS in a 100 mL volumetric flask. The solution was kept in a refrigerator at 4 °C in dark. More dilute solutions were prepared by serial dilution with 0.1 M PBS.

A 1.0×10^{-3} M DA solution was prepared freshly by dissolving 0.0190 g DA in 0.1 M PBS at pH 7.0 and the solution was diluted to 100 mL with 0.1 M PBS in a 100 mL volumetric flask. The solution was kept in a refrigerator at 4 °C in dark. More dilute solutions were prepared by serial dilution with 0.1 M PBS.

A 1.0×10^{-3} M UA solution was prepared freshly by dissolving 0.0168 g UA in 0.1 M PBS at pH 7.0 and the solution was diluted to 100 mL with 0.1 M PBS in a 100 mL volumetric flask. The solution was kept in a refrigerator at 4 °C in dark. More dilute solutions were prepared by serial dilution with 0.1 M PBS.

A 1.0×10^{-3} M PAR solution was prepared freshly by dissolving 0.0151 g PAR in 0.1 M PBS at pH 7.0 and the solution was diluted to