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Electrochemical oxidation and determination of dopamine in the presence of uric and ascorbic acids using a carbon nano-onion and poly(diallyldimethylammonium chloride) composite

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ABSTRACT

This is the first report of dopamine (DA) detection using a carbon nano-onion (CNO) and poly(diallyldimethylammonium chloride) (PDDA) composite. The film was deposited by a coating method on a glassy carbon electrode surface, applying a drop of solution containing the suspended CNOs and PDDA. The electrochemical properties of the composite in phosphate buffered saline (PBS) solution were examined and their ability to detect dopamine was verified. The results showed good selectivity and sensitivity for dopamine analysis. The CNOs/PDDA composite allows the determination of dopamine in a range between 5×10^{-5} and 4×10^{-3} mol L^{-1}, in the presence of ascorbic (AA) and uric (UA) acids, and simultaneous assays all three molecules in solution. The modified electrode can also be used to determine the concentration of dopamine. Results were investigated by cyclic voltammetry, differential pulse voltammetry and square wave voltammetry.

1. Introduction

Carbon-based nanomaterials, such as fullerenes, single- and multi-walled carbon nanotubes, carbon nanofibres and so forth [1,2], are currently one of the most attractive nanostructures. Unique mechanical, chemical, thermal, optical or electrical behaviour of these nanomaterials are related to their shape, size and surface area, and these provide many application possibilities. The electrical and mechanical properties of carbon nanotubes (CNTs), makes them useful in multiple nanodevices [3]. Many carbon-based nanomaterials are suitable for chemical detection because of their ability to selectively adsorb a variety of molecules on the surface [4]. Their excellent biocompatibility also makes them useful as biosensor [5], and as delivery agents [4,5].

Considerable effort is currently devoted to the preparation, characterization and applications of carbon nanocomposites. For example Jeong et al., synthesized nanocrystal quantum dot/single-walled carbon nanotube nanomaterials for photovoltaic devices [6]. Commonly used is the combination of carbon nanotubes with gold particles, which are potentially useful in electronic devices [7]. Carbon structures usually have very high capacitance, but their films are typically mechanically unstable. Therefore they have been often combined with polymer systems to enhance their mechanical stability. Graphite nanofibres with poly(vinylpyrrolidone), was reported by Hwang et al. [8], and other reports describe composites containing CNTs with conducting polymers, such as polythiophene [9] or polyaniline [10], molecular imprinted polymers [11], and chitosan [12] for sensor and biosensor construction.

Carbon nano-onions (CNOs) are spherical structures discovered by Ugarte in 1992 [13]. CNO structures consist of a hollow spherical fullerene core surrounded by concentric and curved graphene layers with increasing diameters thus constituting multilayer fullerenes. The distance between the layers is very close to the interlayer distance in bulk graphite (0.34 nm) [14]. Knowledge of nano-onion properties is still very sparse, because of their relative unavailability. Carbon nano-onions exhibit low density and large surface to volume ratio [15,16]. Therefore, CNOs have potential applications in composite materials [17], as wear-resistant materials [18], for magnetic storage media [11], as optical limiters [19], in solar cells [20] and fuel cell electrodes [21], and as field emitters [22].

Poly(diallyldimethylammonium chloride) (PDDA) is a widely used cationic polyelectrolyte, obtained by a radical polymerization [23–25]. Some of the properties of this polymer, such as water-solubility and catalytic activity with biomolecules [26], allow its use as a sensitizer [25,27,28], as an electron transfer mediator [25–27], as a flocculant [29], or as a biocatalyst agent [30]. Therefore, PDDA can be used as an interesting component in carbon composites.

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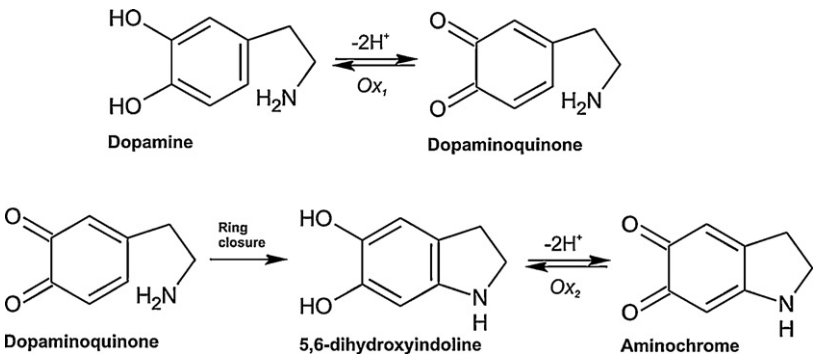

Scheme 1. Steps of electrochemical oxidation of dopamine.

In recent years carbon nanostructures have prompted for synthesis of many of their composites. For example, MWNTs have been used as the reinforcing element in polymer or metal matrices to fabricate new materials [31,32]. The composites of carbon structures with polymers derive properties from both components and posses effective dispersibility in a wide range of solvents [33,34], good thermal conductivity [35], thermal stability, and lower flammability [36]. The polyelectrolyte environment makes it easier to disperse CNTs in aqueous solution, as a consequence of the electrostatic repulsion between the positively charged nanotubes and subsequent PDDA adsorption on the CNTs surface [37]. Another method enhances the interaction between the components by modification of the carbon surface with negatively charged functional groups [38]. This kind of composites have been commonly used for sensing biomolecules [39–41].

Dopamine (2-(3,4-dihydroxyphenyl)ethylamine) is one of the most important neurotransmitters which plays a significant role in the central nervous, renal, cardiovascular and hormonal systems [42,43]. A deficiency of dopamine (DA) leads to such diseases as schizophrenia or Parkinson's syndrome [44,45], therefore developing a sensitive, selective and rapid method to determine DA levels is very important. There are many difficulties involved in developing a quantitative analysis of DA such as its tendency to autoxidize [46], and interfering responses from ascorbic acid (AA) [47]. Measuring DA in the presence of ascorbic and uric acids (UA) is especially significant, because they exist together with DA in high concentrations in biological samples. Therefore many reports have used electrochemical determinations of DA in the presence of AA and UA, using modified working electrode surfaces with composites [48–53]. Different composites provide good separation of the electrooxidation peaks of these analytes.

The present study shows that *small* carbon nano-onions in combination with cationic polyelectrolytes (PDDA) can be used for the electrochemical determination of dopamine in the presence of ascorbic and uric acids. Qualitative and quantitative analysis of dopamine on glassy carbon electrodes (GCE) modified with CNO/PDDA films were investigated by cyclic voltammetric (CV), differential pulse voltammetric (DPV), and square wave voltammetric (SWV) methods.

2. Materials and methods

2.1. Materials

All chemicals and solvents used were commercially available and used without further purification: poly(diallyldimethylammonium chloride) solution (PDDA, average M_w < 100,000, 35 wt.% in H_2O, Sigma–Aldrich), phosphate buffered saline (PBS, pH 7.4, Sigma–Aldrich), uric acid (minimum 99%, Sigma–Aldrich), dopamine hydrochloride (3-hydroxytyramine hydrochloride, Sigma–Aldrich), L-ascorbic acid (99+% A.C.S., Sigma–Aldrich). CNOs were obtained by annealing nanodiamond powder (5 nm average particle size) under a positive pressure of helium at 1650 °C for 1 h [54]. High resolution transmission electron microscopy images of the CNOs were reported elsewhere [55].

2.2. Apparatus

Voltammetric experiments were performed using an AUTOLAB (Utrecht, The Netherlands) computerized electrochemistry system equipped with the PGSTAT 12 potentiostat and FRA response analyser expansion cards with a three-electrode cell. The AUTOLAB system was controlled with the GPES 4.9 software from the same manufacturer.

A glassy carbon disk (GCE) with a diameter of 1.6 mm (Bioanalytical Systems Inc.) was used as the working electrode. The surface of the electrode was polished using extra fine carborundum paper (Buehler) followed by 0.3 μm alumina and 0.25 μm diamond polishing compound (Metadi II, Buehler). The electrode was then sonicated in water in order to remove traces of alumina from the carbon surface, washed with water, and dried. The counter electrode was made from platinum mesh (0.25 mm) and was cleaned by heating in a flame for approximately 30 s. A silver wire immersed in 0.1 M AgCl and separated from the working electrode by a ceramic tip (Bioanalytical Systems Inc.) served as the reference electrode.

2.3. Preparation of CNO/PDDA composites

Composites made of CNOs and PDDA were prepared according to a procedure reported elsewhere [56]. Poly(diallyldimethylammonium chloride) solutions were prepared by diluting a stock solution of PDDA with distilled water. The 3 mg mL^{-1} non-modified CNOs were dispersed by ultrasonication in PDDA solution (15 min). References were prepared in the same way as samples but without CNO addition. The CNO/PDDA composites were prepared by a coating method. 10 μL of the CNOs/PDDA suspension (mass ratio: 1:1) was deposited on a GCE surface and the solvent was evaporated under an argon stream in room temperature.

3. Results and discussion

3.1. Characterization of CNO/PDDA composites

Fig. 1 shows the SEM images of poly(diallyldimethylammonium chloride) (PDDA) and carbon nano-onion/poly(diallyldimethylammonium chloride) (CNO/PDDA) composite films on a Au gold foil. As we previously observed [56], PDDA films showed uniform structures and