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The selective detection of dopamine at a polypyrrole film doped with sulfonated β-cyclodextrins

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ABSTRACT

A highly selective dopamine sensor was fabricated by doping polypyrrole with a sulfonated β-cyclodextrin. This composite material enabled the selective sensing of dopamine in the presence of a large excess of ascorbic acid and prevented the regeneration of dopamine through the homogeneous catalytic reaction of the ascorbate anion with the dopamine-o-quinone. A single redox wave, corresponding to the oxidation of dopamine, was observed in dopamine/ascorbate mixtures, giving a truly selective dopamine sensor. The limit of detection was measured as 3.2×10^{-6} M for dopamine.

1. Introduction

Dopamine is one of the most important catecholamine neurotransmitters in the mammalian central nervous system. Abnormalities in dopamine concentrations have been linked with several neurological disorders such as the debilitating ailment Parkinson's disease and the mental disorder schizophrenia [1,2]. Dopamine is also believed to play a central role in Huntington's disease, a fatal genetic neurodegenerative movement disorder and has also been associated with drug addiction and attention disorders [3–5].

Monitoring the concentration of dopamine is particularly challenging using electrochemical methods because dopamine co-exists with many interfering compounds in biological samples. These interfering compounds are usually present at concentrations much higher than dopamine and, moreover, they are oxidised at similar potentials to dopamine at most solid electrodes. This is particularly true of ascorbic acid, the main interfering compound in the determination of dopamine. The concentration of the ascorbate anion is typically 10^{-3} M, while the concentrations of dopamine are considerably lower, in the range of 10^{-8} to 10^{-6} M. Ascorbic acid is easily oxidised having a range of $E_{1/2}$ values between −100 and 400 mV vs. SCE on most solid electrodes. This lies in the same potential region as dopamine, which has a range of $E_{1/2}$ values between 100 and 250 mV vs. SCE for various electrode substrates [6]. Furthermore, ascorbic acid reacts with the oxidised dopamine product (dopamine-o-quinone) which is generated through the electrochemical oxidation of dopamine. This reaction leads to the regeneration of dopamine making it available for further electrochemical oxidation, complicating the analysis [7,8].

A number of modified electrodes have been used in an attempt to resolve these problems. The most popular strategies include polymer, self-assembled monolayer, metal nanoparticle, carbon nanotube and surfactant modified electrodes [9–13]. In particular, there has been much interest in the development of sensors based on electrodes modified with polymeric films. Electropolymerised films of pyrrole, aniline, 3-methylthiophene, acridine red, sulfosalicylic acid, 3,5-dihydroxy benzoic acid and acid chrome K have all been reported [14–18]. Overoxidised polymer modified electrodes have also been employed to sense dopamine and ascorbic acid [19]. However, the most common approach is to use Nafion®, a perfluorinated polymer. Nafion® has terminal sulfonate groups that can repel the negatively charged ascorbate anion from the electrode surface, enabling the discrimination of the ascorbate and dopamine oxidation waves [20].

Cyclodextrins are naturally occurring macrocyclic oligosaccharides built from α-1,4-linked D-glucopyranose units. Cyclodextrins are well-known to bind with suitable guest molecules in aqueous solutions to form inclusion complexes [21]. They also exhibit excellent biocompatibility and as a result have been incorporated into various dopamine sensors. For example, Izaoumen et al. [22] and Bouchta et al. [23] have used polymer films modified with neutral cyclodextrins and doped with perchlorate anions for the sensing of dopamine, while Alarcon-Angeles et al. [24] have modified multiwall carbon nanotubes with β-cyclodextrins for the sensing

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of dopamine. The electrochemical synthesis of polypyrrole doped with sulfonated β-cyclodextrins has been reported by Temsamani et al. [25], Bidan et al. [26] and Reece et al. [27]. However, there are no reports, to the best of our knowledge, on using these materials in the selective sensing of dopamine. The modified sensor used here differs from the majority of all other publications on cyclodextrin modified dopamine sensors, as the anionic cyclodextrin is introduced into the polymer matrix as an immobile dopant. Furthermore, it is the sole dopant, as no other anions are used in the electropolymerisation step.

In this paper, we show that polypyrrole films doped with sulfonated β-cyclodextrins are readily formed and that these materials have excellent selectivity in the determination of dopamine concentrations, facilitating the oxidation of dopamine, but inhibiting the oxidation of ascorbate. In addition, there is no evidence of the regeneration of dopamine through the ascorbate/dopamine-o-quinone reaction. Also, the exceptional biocompatibility properties of the materials used make the cyclodextrin-doped polypyrrole sensor considerably more suitable for *in vivo* detection compared to some of the more complex electrodes already considered in the sensing of dopamine.

2. Experimental

2.1. Materials

Dopamine, ascorbic acid, pyrrole, citric acid, disodium hydrogen phosphate and sulfonated β-cyclodextrin were obtained from Sigma–Aldrich or its subsidiary company, Fluka. All chemicals were used as supplied except for the pyrrole monomer which was distilled before use and stored at −4 °C. All solutions were prepared freshly before each experiment and were deoxygenated with nitrogen. Platinum rod (99.95%, 4 mm in diameter) and glassy carbon (4 mm in diameter) were supplied by Goodfellow or Alfa Aesar. A 250 mL citrate phosphate buffer solution (pH 6.0) was prepared by mixing 150 mL of 0.2 M disodium hydrogen phosphate and 100 mL of 0.1 M citric acid.

2.2. Apparatus

The performance of the sensor was evaluated using both cyclic voltammetry measurements and constant potential amperometry. All data were recorded using a Solartron 1285A potentiostat at room temperature in a 0.10 M Na_2SO_4 supporting electrolyte, pH 6.0. The constant potential amperometry was performed by rotating the electrode at 2000 rpm using a rotating disc electrode assembly, EG&G Model 363. A platinum rotating disc electrode was used as the working electrode. In each case, the modified electrodes were first cycled in the background electrolyte, between −0.10 V vs. SCE and 0.90 V vs. SCE for 10 cycles to ensure the release of any pyrrole or oligomers from the surface.

A standard three-electrode electrochemical cell configuration was employed for all electrochemical experiments. A platinum or glassy carbon rod electrode was used as the working electrode. These were embedded in epoxy resin in a Teflon holder with electrical contact being achieved by means of a wire threaded through the holder to the rod substrate. A platinum wire was used as an auxiliary electrode and a saturated calomel electrode (SCE) was used as the reference electrode. Tencor analysis was carried out on a Tencor Veeco Dektac 6M Stylus Profilometer in the Tyndall National Institute, University College Cork.

2.3. Fabrication of polymers

Prior to each experiment, the platinum electrode was polished to a mirror finish, using successively smaller sizes of diamond paste, down to a 1 μm sized diamond paste, rinsed with distilled water and finally cleaned in an ultrasonic bath. The cyclodextrin doped polypyrrole films were prepared at the platinum electrode from a 0.20 M pyrrole and 0.01 M sulfonated β-cyclodextrin solution[1] at a constant potential of 0.80 V vs. SCE until a charge of 0.24 C cm^{-2} was passed (approximately 35 s). The polypyrrole sulfonated β-cyclodextrin modified electrode was finally washed with distilled water and dried.

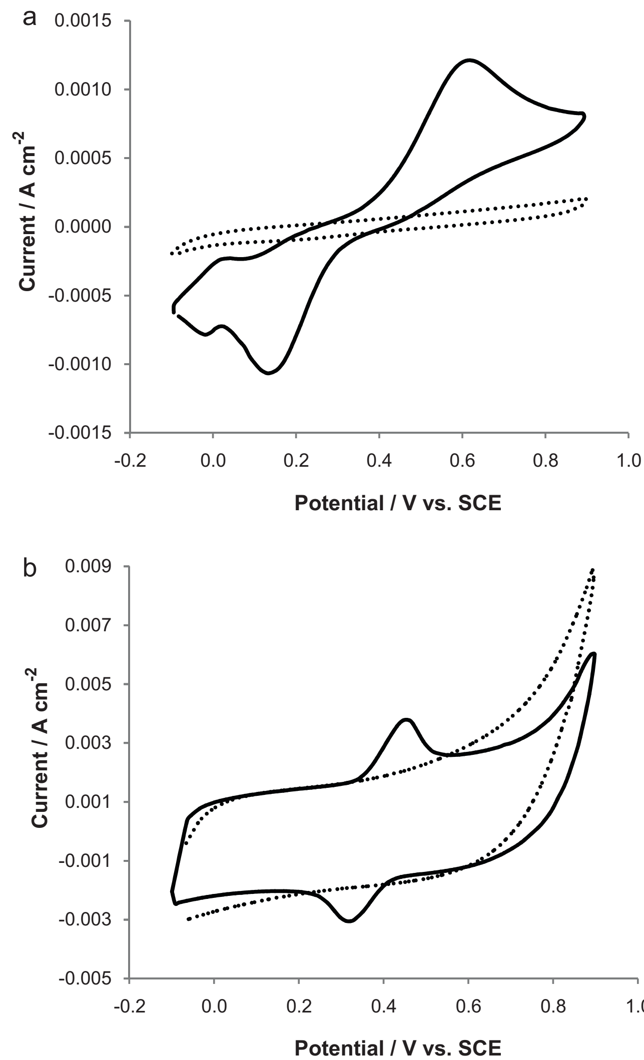

Fig. 1. Cyclic voltammograms of (a) bare platinum electrode and (b) a polypyrrole sulfonated β-cyclodextrin modified electrode in (···) a 0.10 M Na_2SO_4 solution and in (–) a 1.0×10^{-3} M dopamine/0.10 M Na_2SO_4 solution. Scan rate = 100 mV s^{-1}.

3. Results and discussion

3.1. Oxidation of dopamine at the polypyrrole sulfonated β-cyclodextrin film

The dopamine response at the bare platinum electrode and at the polypyrrole sulfonated β-cyclodextrin film was examined using cyclic voltammetry, Fig. 1(a) and (b), respectively. The electrodes were cycled in a 1.0×10^{-3} M dopamine solution dissolved in a

[1] Commercially available sulfonated β-cyclodextrin has approximately 7–11 sulfonated groups per cyclodextrin. A mean value of 9 sulfonated groups was assumed when calculating the molecular weight.