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# Fabrication and electrochemical characterization of polydopamine redox polymer modified screen-printed carbon electrode for the detection of guanine

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ABSTRACT

A modified screen-printed carbon electrode (SPCE) was fabricated by electrodeposition of dopamine to create a suitable polydopamine (PDA) redox polymer film for sensing applications. The fabricated sensor, designated as PDA-SPCE, was characterized by electrochemical impedance spectroscopy, contact angle measurements and chronoamperometry. The surface coverage of redox species on the polymer film was optimized and found to be $\sim 6.1 \times 10^{-6}$ mol cm$^{-2}$. Using square wave voltammetry, the PDA-SPCE was used to facilitate and observe the electrocatalytic oxidation of guanine at different concentrations. A calibration curve for guanine was constructed, with a sensitivity of 90.5 μA μM$^{-1}$ cm$^{-2}$ and a limit of detection (based on 3× the baseline noise) of 15.8 μM.



## 1. Introduction

Polydopamine (PDA) is a polymer formed by the oxidation of dopamine (DA). PDA films can form on any materials including metals, silica, metaloxides, glass and polymers [1–5]. The deposition of polydopamine (PDA) films, especially from aqueous solution constitutes a new and versatile way to functionalize surfaces [6]. PDA films are considered to be robust, non-poisonous, relatively inert and biocompatible. Although, a fundamental understanding of the mechanism of PDA formation as well as its structure is still under discussion, there is a general consensus that it consists of *o*-quinone and *o*-hydroquinone subunits including their semi-oxidized/semi-reduced forms [7–9]. Hence, these subunits can undergo electron-transfer reactions. The reductive nature of the catechol/*o*-quinone moieties in PDA has been exploited to enable reactions involving thiols or amines; thus, it has served as a medium for the immobilization of enzymes and other biomolecules [3,10–13], and allows the electroless metallization of easily reduced metal salt solutions without the need for an exogenous reducing agent to form metal films on substrates [1,14–17]. More recently, PDA films were used to anchor $Cu^{2+}$ onto glassy carbon electrode and utilized for the selective detection of uric acid in urine [18].

In this study, we demonstrate the possibilities of using the redox species of PDA as a sensing tool for the detection of specific biomarkers such as guanine. Guanine is one of the four standard nitrogenous bases which pairs to make up the DNA helix; thus, investigation of its electrochemical behavior and quantitative measurement is relevant for the direct electroanalysis of DNA. The PDA films were formed through electrodeposition of dopamine hydrochloride in Britton-Robinson buffer solution onto screen-printed carbon electrodes (SPCEs). This study is of great importance in electrocatalysis and in fields where PDA films are presumed to be an inert coating polymer.

## 2. Experimental

### 2.1. Apparatus and reagents

Electrochemical experiments were conducted using VSP-300 Multichannel Potentiostat/Galvanostat/EIS (Bio-Logic Science Instruments, France) with a standard three-electrode configuration. Electrochemical impedance spectroscopy in potassium ferrocyanide was carried out at open circuit within the frequency range 200 kHz–0.1 Hz. The SPCE were printed using a Stainless Steel Screen Mesh (DEK: 159784, ASM Assembly Systems) onto a valox substrate. Valox substrate was purchased from Cardillac Plastics, UK. A Ag/AgCl (1.0 M KCl) reference electrode was used throughout.

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The working electrode was either the bare SPCE or PDA-SPCE with a platinum wire as the counter electrode. Guanine, ascorbic acid and uric acid were purchased from Alfa Aesar, UK. Dopamine hydrochloride and NaCl were purchased from Sigma Aldrich, UK. All other chemicals were of analytical grade and used without further purification.

### 2.2. Sessile contact angle measurements

The contact angle measurements were carried out by the sessile drop technique [19]; a water droplet was placed onto a flat surface of the bare SPCE and PDA-SPCE, and the contact angle of the droplet with the surface measured using a CAM200 Optical Contact Angle Meter (KSV Instruments Ltd., Finland). Reported values are the average contact angle (right and left) of 10 droplets. During the measurement time (~60 s), no change in contact angle was observed. A variation of 5° is generally considered to be sufficient to differentiate materials [20].

### 2.3. Fabrication of the PDA-SPCE

The base unmodified screen-printed carbon electrode (SPCE) transducer was prepared using graphite ink (GEM Product code: C205010697) and the sensors were screen-printed in groups of eight onto valox substrate and cured at 70 °C for 90 min. A dielectric material was used to define the working area of the electrode. Prior to modification, each SPCE was anodized by applying a potential of 1.6 V for 60 s vs. Ag/AgCl in 5.0 mL 0.1 M NaOH solution, under unstirred conditions. The electrodeposition of polydopamine (PDA) onto the SPCE was carried out from 5.0 mL of 5.0 mM dopamine hydrochloride in Britton-Robinson buffer (pH 7.0) by cycling the potential from −0.5 V to +1.5 V vs. Ag/AgCl [21]. The resulting PDA-SPCE was then copiously rinsed in doubly distilled water and dried in a stream of free-flowing $N_2$.

## 3. Results and discussion

### 3.1. Electropolymerization of PDA

Fig. 1A shows repetitive (30 scans) cyclic voltammograms (CV) for the electropolymerization of polydopamine (PDA) from 5.0 mM dopamine hydrochloride in Britton-Robinson buffer solution (pH 7.0) while Fig. 1B shows the 1st and 20th scans; four redox peaks are present in the CV. During the first positive scan, an oxidation peak (a1) at +0.7 V was observed, which is attributed to the oxidation of dopamine (DA) leading to dopaminequinone. Dopaminequinone is known to undergo several chemical reactions (denoted by "C") and electrochemical (denoted by "E") transformations, which then leads to PDA. Loget et al. [21] and Li et al. [22] proposed an "ECECEE" mechanism that involves 5,6-indolequinone as the polymerizable species. In the subsequent reverse scan, two reduction peaks c1 and c2, were observed at +0.1 V and −0.02 V, respectively. According to the "ECECEE" mechanism, these reduction peaks (c1 and c2) can be attributed to the reduction of dopaminequinone and

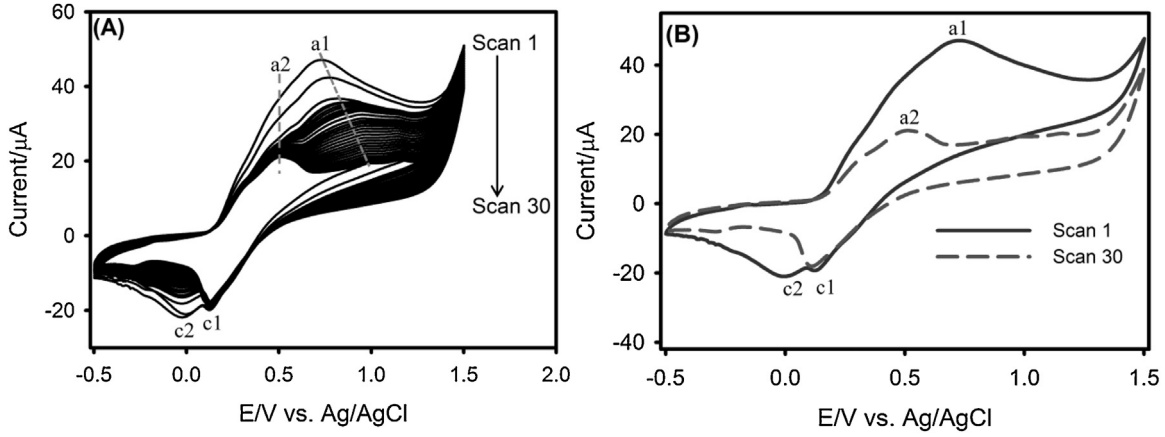


**Fig. 1.** Electropolymerization of polydopamine onto SPCE by cyclic voltammetry; (A) cyclic voltammograms of 5.0 mM dopamine hydrochloride in Britton-Robinson buffer solution (pH 7.0) on SPCE at scan rate of 100 mV $s^{-1}$; (B) the 1st and 30th scans.

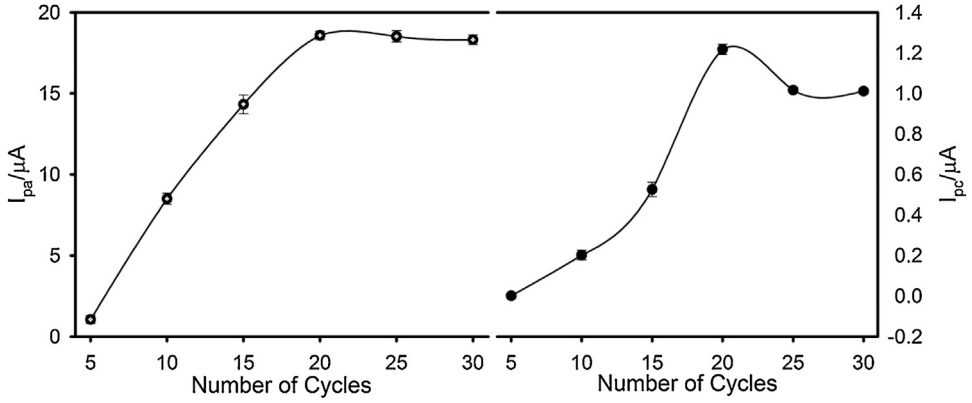


**Fig. 2.** Optimization of the number of cycle in electropolymerization of PDA onto SPCE. Electrodes were prepared in 5.0 mM dopamine hydrochloride in Britton-Robinson buffer solution (pH 7.0) at scan rate of 100 mV $s^{-1}$. Each point represents the mean ± (standard deviation, SD = 2.2%, $n$ = 6).