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

Prosper Kanyong1\*, Sean Rawlinson1 and James Davis1

1School of Engineering, Ulster University, Jordanstown, Northern Ireland, BT37 0QB

\*corresponding author; p.kanyong@ulster.ac.uk

**Abstract**

A modified screen-printed carbon electrode (SPCE) was fabricated by electrodeposition of dopamine to create a suitable polydopamine (PDA) redox polymer 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 **~**6.1 x 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 3x the baseline noise) of 15.8 µM.

**Keywords**: square wave voltammetry, cyclic voltammetry, electrochemical impedance spectroscopy, dopamine, organocatalyst, thin films

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 ways 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 Cu2+ 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 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.

**Experimental**

* 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 to 0.1 Hz. The SPCE were printed using a Stainless Steel Screen Mesh (DEK: 159784, ASM Assembly Systems) in groups of eight onto a valox substrate. Valox substrate was purchased from Cardillac Plastics, UK. A Ag/AgCl (1.0 M KCl) reference electrode was used throughout.

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.

* 1. **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 seconds), no change in contact angle was observed. A variation of 5° is generally considered to be sufficient to differentiate materials [20].

* 1. **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 minutes. 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 seconds vs. Ag/AgCl in 5.0 mL 0.1M NaOH solution, under unstirred conditions. The electrodeposition of polydopamine (PDA) onto the SPCE was carried out from 5.0 mL of 5.0 mM of 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 nitrogen.

1. **Results and discussion**
   1. **Electropolymerization of PDA**

Figure 1A shows repetitive (30 scans) cyclic voltammograms (CV) for the electropolymerization of polydopamine (PDA) from 5.0 mM dopamine (DA) in Britton-Robinson buffer solution (pH 7.0) while Figure 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 the 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. Li et al proposed an “ECECEE” mechanism that involves 5,6-indolequinone as the polymerizable species [21, 22]. 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 dopaminechrome, respectively. In the second positive scan (from scans 5), a new oxidation peak (a2) (on scan 5) appeared at +0.5 V, and may be attributed to the oxidation of leucodopaminechrome (the reduction product of dopaminechrome) [21, 22]. During the cycle by cycle scans, the continuous drop in electrode activity due to the formation of PDA passivating layers is shown by the continuous decrease of the peak currents of peak (a1) and peak (c2). However, peak currents of peak (a2) and (c1) remained relatively constant. This relevant behavior demonstrates the fouling of the electrode by the PDA layers as it grows with each successive scan. When the potential scans reached 20 cycles, steady state voltammograms are obtained, where there is no more electron-transfer between the surface of the SPCE and species in the solution due to the total fouling of the electrode by the PDA. However, two redox peaks (a2 and c1), close enough to the surface of the SPCE to undergo electron-transfer, are still present and can be attributed to the oxidation and reduction of the catehols and quionones units present in PDA [7-9]. These results are consistent with recent measurements on the characterization of PDA polymer films [21, 23-24].



Figure 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.

* 1. **Characterization of the PDA redox polymer on SPCE**
     1. **Optimization of the number of cycles in electropolymerization**

The PDA film was synthesized onto the SPCE surface by cyclic voltammetry; thus, the number of scans during the electropolymerization process is related to the thickness of the PDA film [21, 24]. To ascertain the number of cycles required for optimum electrocatalytic response from the PDA-SPCE, cycle numbers from 5 to 30 were used to prepare the PDA-SPCE. Thereafter, the voltammetric response of the prepared electrodes were measured in buffer solution and the average values (n = 6) of both the anodic and cathodic peak currents were calculated. Figure 2 shows a plot of peak currents vs. the number of cycles.



Figure 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 = 2.15%, *n* = 6).

It can be seen in Figure 2 that the voltammetric response of the PDA-SPCE increased gradually cycle-by-cycle up to 20 scans. Subsequent scans did not show any increase in voltammetric response of the electrode. Consequently, 20 scans were chosen as the optimum number of cycles for preparation of the PDA-SPCE.

* + 1. **Sessile contact angle measurements**

Beside this, the measurement of water contact angle for the PDA on the surface of the SPCE was performed. The contact angle of water at the surface of the bare SPCE was found to be ~73.9 °. However, it decreased after coating the SPCE with PDA to ~58.1 °. This increase in the hydrophilicity of the coated electrode means that the PDA polymer properties can be manipulated in buffer solution; thus, making it a suitable surface for biofunctionalization, which is of considerable relevance for a variety of applications including sensors and biosensors and for studying biointerfaces [25].

* + 1. **Cyclic voltammetry**

Figure 3A shows a voltammetric behavior of the bare SPCE and the PDA modified SPCE (PDA-SPCE) in Britton-Robinson buffer (pH 7.0). No redox peaks were observed when a voltammogram of the bare SPCE in buffer solution was recorded. However, a pair of reversible peaks could be seen on the PDA-SPCE electrode; this confirms the presence of redox species which were previously attributed to the oxidation and reduction of the catechols and quinones units present in PDA [7-9]. The anodic and cathodic peak potentials were located at ~ +0.245 V and ~ +0.184 V, respectively and the peak separation was found to be ~61 mV; which is considerably close to the 59 mV value expected for Nernstian one-electron reactions [26].



Figure 3: Cyclic voltammograms obtained at (A) bare SPCE and PDA-SPCE in Britton-Robinson buffer (pH 7.0), 50 mV.s-1 scan rate; (B) PDA-SPCE in Britton-Robinson buffer (pH 7.0) at scan rates of 10, 25, 50, 100, 150 and 200 mV.s-1’ (C) plot of Ip vs. *v*1/2; (D) Epa vs log *v* and log Ipa vs log *v*.

* + 1. **Effect of scan rate**

The effect of scan rate on the voltammetric behavior of the PDA-SPCE was examined by cyclic voltammetry (Figure 3B). At the scan rates investigated, the oxidation and reduction peak currents (Ip) increases linearly with the scan rate (Figure 3C) suggesting a behavior consistent with surface confined voltammetry and corresponding ‘thin layer’ type voltammetry [27].

To further evaluate the electrochemical behavior of the PDA-SPCE, the influence of scan rate on both the anodic peak potentials and peak currents were analyzed. With increase in scan rate, the anodic peak potential shifted towards a positive value and a linear relationship was observed in the range of 25 to 200 mV.s-1 as shown in Figure 3D. The equation of this behavior can be expressed as:

(2)

According to Laviron’s expression for an electrochemical process [28-30], Ep is governed by:

where *v* is the scan rate, *nʹ is* the number of electrons transferred before the rate-determining step, α is the transfer coefficient, *E0*ʹ is the formal standard redox potential and *k0* is the standard heterogeneous rate constant of the reaction, and the other symbols have their usual meaning. The value of *αn* can be calculated using the slope of *E*p vs log *v* plot (the slope = 0.082). Taking *R* = 8.314J.K-1.mol-1, *T* = 298 K, and F = 96480 C.mol-1, the value of *αn* was calculated to be ~0.7.

According to Bard and Faulkner [31],

where Ep-Ep/2 is the potential at which the current is at half its peak value. From this, the value of α was calculated to be 0.8. Consequently, the number of electrons (*n*) involved in the electrochemical process was calculated to be ~1.0; thus, confirming the fact that the reaction is a one-electron transfer process.

Assuming the PDA is fully saturated with redox species, and using the Laviron expression:

where *Г* is the surface coverage of the redox species, *v* scan rate, *A* is the electrode surface are (here ~5.0 x 10-3 cm2) and using the average values of both the anodic and cathodic peak currents (for scan rates ≥100 mV.s-1), *Г* values of ~6.1 x 10-6 mol.cm-2 was derived; which is considered to be satisfactory for sensitive analytical sensing applications.

* + 1. **Effect of pH**

The electrode reaction can be affected by the pH of the medium; thus the effect of pH was studied over the pH range of 2.0 to 10.0 in Britton-Robinson buffer solution by cyclic voltammetry. The solution pH influenced both the anodic and cathodic peak potentials considerably. However, there was no significant change in both the anodic and cathodic peak currents. With increase in pH of the solution, the peak potentials shifted to less positive values (Figure 4A), and obeys the following equations:

(6)

(7)

The slope of these equations, 57.7 mV/pH and 54.5 mV/pH for the anodic and cathodic peak potentials, respectively are close to the expected theoretical value of 59 mV/pH [26]; thus, suggesting that the number of electrons transferred is equal to the number of hydrogen ions participating in the electrode reaction.



Figure 4: (A) Influence of pH on the peak potential obtained at PDA-SPCE in Britton-Robinson buffer solution at scan rate of 50 mV.s-1; (B) Nyquist plots observed for electrochemical impedance measurements at bare SPCE and PDA modified SPCE (PDA-SPCE) in Britton-Robinson buffer (pH 7.0) containing 2.0 mM potassium ferrocyanide and 0.1 M KCl; (C) Determination of the coverage rate of PDA functionalized SPCE.

* + 1. **Electrochemical impedance analysis of PDA-SPCE**

Electrochemical impedance spectroscopy was also used to examine the PDA modified SPCE (Figure 4B). In the Nyquist plot impedance spectra, the diameter of the semicircle represents the charge-transfer resistance (RCT) at the electrode surface [32]. Figure 4B shows the impedance spectra of the PDA polymer modified SPCE and the bare SPCE. There was an increase in the RCT value after PDA electrodeposition onto the bare SPCE indicating enhanced resistance to charge-transfer occurring at the PDA-SPCE surface; thus, further confirming the successful electrodeposition of the PDA film.

* + 1. **Determination of the coverage rate of PDA on SPCE**

The determination of the coverage (*θ*) rate may provide information regarding the morphology of the surface of the PDA-SPCE and the porosity of the active PDA layer electrodeposited on the SPCE [33]. The coverage of PDA layer was determined by electrochemical impedance spectroscopy and can be described as follows:

) (8)

Figure 4C represents the impedance of the real part of the bare SPCE and PDA-SPCE as a function of the inverse of the square root of the sinusoidal excitation pulsation. The extrapolation of the linear zone to the high frequencies provides the sum of the charge transfer resistance (RCT), the PDA layer resistance (R*m*) and the resistance of the electrolyte solution (Rs). The latter resistances (R*m* and Rs) are generally considered negligible when compared with the first one (RCT); thus, the calculated fractional coverage area for PDA on the SPCE surface was found to be ~31.2%. This low coverage values indicate that the electrodeposited PDA film is thin, sparse, irregularly dispersed and contains several pores [33, 34].

* 1. **Analytical application of PDA-SPCE to guanine analysis**

To evaluate the suitability of the polydopamine redox polymer for use in electrocatalytic processes of relevant biological molecules, the electrochemical behavior of the PDA-SPCE towards guanine was examined by cyclic voltammetry. Figure 5A shows cyclic voltammograms of the bare SPCE and the PDA-SPCE recorded in aqueous solution of Britton-Robinson buffer (pH 7.0) containing 2.0 mM guanine at 50.0 mV.s-1 scan rate. A well-defined irreversible anodic peak for guanine was observed at ~0.4 V on the PDA-SPCE; similar electrochemical behavior of guanine has been **reported elsewhere** [35]. According to Li et al. 2010 [35], guanine oxidation is a complex mechanism involving the oxidation of the free guanine base and is thought to be a -4e-, -4H+ system, in which the guanine initially undergoes an EE (-2e-, -2H+) process followed by a chemical step to form 8-oxoguanine.

The peak broadened and shifted to a more positive potential (~0.5 V) with a significant decrease in the peak current at the bare SPCE. In comparison to what occurred at the bare SPCE, the PDA-SPCE exhibited a characteristic increase of the anodic peak currents for guanine. This more than five-fold increase in the anodic peak current of guanine at the PDA-SPCE can be attributed to the electrocatalytic effect of the polydopamine redox polymer.

The catalytic rate constant (*K*cat) and diffusion coefficient (*D*) of guanine for PDA-SPCE were estimate by chronoamperometry. Chronoamperometric measurements were carried out in Britton-Robinson buffer solutions containing various concentrations of guanine (1.0, 2.5, 5.0 and 10.0 mM) at an applied potential of +0.4 V vs. Ag/AgCl (Figure 5B).

The catalytic rate constant *K*cat, was calculated using the equation [36]:

where *i*cat and *i*BRB are the currents obtained at the PDA-SPCE for guanine and Britton-Robinson buffer (BRB) solutions, respectively, *C* is the concentration of guanine and *t* is time in seconds.

The catalytic rate constant was calculated from the slope of the plot of *i*cat/*i*BRB vs. *t*1/2 (insert of Figure 5B) for 1.0 mM guanine concentration. A value of ~6.0 x 104 M-1.s-1 was calculated for the PDA-SPCE, which reveals the fact that the PDA film is suitable for developing analytical (bio)sensing surfaces [37].

The slope of the linear parts of *i* vs. *t-*1/2 plots (Figure 5 C) for the different concentrations of guanine (1.0, 2.5, 5.0 and 10 mM) were selected and used to construct the *i.t*½ vs *C*gunaine plot (Figure 5D). The slope of *i.t*½ vs *C*gunaine plot was used in conjunction with the Cottrel equation [36]:

to estimate the diffusion coefficient (D) for guanine and was calculated to be ~8.4 x 10-7 cm2.s-1.



Figure 5: (A) Cyclic voltammograms recorded using the (a) bare SPCE and (b) PDA-SPCE in 2.0 mM guanine solution in Britton-Robinson buffer (BRB, pH 7.0) at a scan rate of 50 mV.s-1; (B) Chronoamperograms obtained at PDA-SPCE in the presence of (a) 0; (b) 1.0; (c) 2.5; (d) 5.0 and (e) 10.0 mM guanine in Britton-Robinson buffer (pH 7.0). Insert; *i*cat/*i*BRB vs. *t*-½ plot derived from chronoamperomeric data for BRB (a) and 1 mM guanine (b); (C) Linear segments of the plot *i* vs. *t*-½ for (a) 1.0; (b) 2.5; (c) 5.0 and (d) 10.0 mM guanine and; (D) plot of the slopes from graph C vs. the concentration of guanine.

A calibration graph was then performed for varying concentrations of guanine from 0.1 to 10.0 mM (Figure 6) using square wave voltammetry. A linear range was recorded from 0.1 to 10.0 mM with a sensitivity of 90.5 μA.μM-1.cm-2 and a calculated limit of detection (based on 3x the baseline noise) of 15.8 µM.



Figure 6: (A) Square wave voltammograms recorded for different concentrations [(a) 0.1; (b) 1.0; (c) 2.5; (d) 5.0; (e) 7.5 and (d) 10 mM of guanine at the PDA-SPCE in Britton-Robinson buffer (pH 7.0); (B) corresponding calibration plots. Sensitivity for guanine was found to be 90.5 μA.μM-1.cm-2 with coefficients of variations of 1.3 %; each data point is the mean of three replicates and error bars are the corresponding standard deviations.

It should be mentioned that the electrochemical behavior of guanine was tested in the presence of a binary mixture of uric acid and ascorbic acid (2.0 mM each) by SWV. It was found that the voltammetric peak current for guanine was not significantly altered; indicating that the PDA-SPCE has a high selectivity for guanine.

1. **Conclusions**

This study showed that polydopamine polymer film can be electrodeposited onto the surfaces of screen-printed carbon electrodes. The redox species of polydopamine polymer was determined to be surface-bound and could be further optimized by varying the number voltammetric cycles. The surface coverage of redox species on the electrodeposited polydopamine polymer film was found to be 6.1 x 10-6 mol.cm-2; which is anticipated to be suitable for sensitive analytical sensing applications. By taking advantage of the electrocatalytic oxidation of guanine, the modified screen-printed carbon electrode show enough distinction for varying concentrations for a calibration curve to be constructed. This makes it suitable for quantitative analyses, often required in bioanalytical applications. To the best of our knowledge, this is the first time where the electrocatalytic activity of electrodeposited polydopamine films has been fully characterized. This study is of particular relevance in electrocatalysis and in fields where polydopamine is often presumed to be an inert coating. In the future, we hope to combine the disposability of screen-printed electrodes with the unique electrochemical properties of polydopamine film for the development of electrochemical biosensors/immunosensors for clinical applications.

**Conflict of interest**

The authors declare no conflict of interest.

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