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Electrochemical Sensing of Dopamine using a Dodecylsulfate Doped Polypyrrole Film

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A polymer-modified electrode was fabricated by the electropolymerisation of pyrrole from an ethanol solution using sodium dodecylsulfate as a dopant. The modified electrode is a highly sensitive electrochemical sensor for dopamine with a limit of detection measured as 3.8×10^{-8} mol dm^{-3}. The sensor did not sense the common interferant ascorbic acid showing a single redox peak for dopamine in the presence of excess ascorbic acid.

Introduction

Dopamine (DA) is an important neurotransmitter in the mammalian central nervous system (CNS), and abnormalities in its concentration can be linked to several disorders, such as Parkinson's, Alzheimer's, Schizophrenia and a number of other CNS disorders. Accordingly, there is much interest in the development of new, rapid, selective and simple methods for the detection of DA. Many of these are based on electrochemical detection, as DA is easily oxidised into the corresponding quinone with good reversibility, to give a quasi-reversible system [1]. However, electrochemical detection methods suffer from selectivity. In particular ascorbic acid (AA), which is present at relatively high concentrations in biological systems, is oxidised in the same potential region as DA. This gives rise to overlapping oxidation peaks that are difficult to resolve [2, 3]. In an attempt to resolve the oxidation peaks of DA and AA, various modified electrodes have been proposed and reported [4-6]. However, few of these have met with sufficient success to enable the development of a selective dopamine sensor.

In this paper we present results on the formation of a polymeric material that has the potential to selectively detect DA in the presence of high concentrations of AA. This polymeric material was formed in ethanol using pyrrole as the monomer and dodecylsulfate (SDS) as the dopant, to give a highly adherent polypyrrole film.

Experimental

All reagents used were of analytical grade and were obtained from Sigma-Aldrich or its subsidiary, Fluka. The pyrrole was purified by distillation before use and all other reagents were used without further purification.

Conductivity measurements were carried out using a Jenway 4510 conductivity meter. All electrochemical experiments were carried out in a three-electrode cell using a Solartron 1287 or a CH Instruments potentiostat, model 700C. Constant potential amperometry was performed using a pine instruments ring disc electrode system model 636. A gold electrode was used as the working electrode. Platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

The gold electrode was prepared by polishing to a mirror finish with 1 μm diamond paste, rinsed and then sonicated in distilled water. A 0.1 M phosphate buffer with a pH of 5.85 was used in all electrochemical experiments. Cyclic voltammetry experiments were performed at a scan rate of 100 mV s^{-1}, DPV measurements were carried out at 20 mV s^{-1}, while the constant potential amperometry experiments were carried out at 0.65 V vs. SCE and at a rotation rate of 2000 rpm.

The polymer was grown by electropolymerisation of pyrrole in an ethanol solution containing 0.02 mol dm^{-3} dodecylsulphate (SDS) and 0.08 mol dm^{-3} tetrabutyl ammonium perchlorate using cyclic voltammetry (CV), by cycling from a potential of -0.35 V to 0.80 V vs. SCE at 20 mV s^{-1}. The polymer was overoxidized in a 0.1 mol dm^{-3} NaOH solution at 1.0 V vs. SCE until the current flow decreased to 4 x 10^{-6} A. SEM measurements were carried out with a Hitachi S-3200N scanning electron microscope.

Results and discussion

The SDS-doped polypyrrole film was electrosynthesized from an ethanol solution containing 0.02 mol dm^{-3} sodium dodecylsulfate (SDS) as the dopant species by cycling the gold substrate electrode between -0.35 V and 0.80 V vs. SCE at 20 mV s^{-1}. A highly adherent polymer film was deposited, and as shown in Fig. 1(a), the polymer adopts the usual cauliflower-like morphology, as evidenced from scanning electron microscopy. However, when the polymer was formed from an aqueous solution containing a similar concentration of SDS the adherence of the polymer was very poor, as shown in Fig. 1(b).

Is well known that SDS forms micelles in water [7], and accordingly, conductivity measurements were used to explore the nature of SDS in the ethanol solution and to determine if this had an influence on the adherence of the film. Similar measurements were carried out to calculate the critical micelle concentration (CMC) of SDS in water with added pyrrole, and to compare this with the concentrations used to form the polymer. The SDS was added to the ethanol and the water systems and the conductivity was monitored as a function of the SDS concentration. Representative plots of the conductivity plotted as a function of the SDS concentration in water, with 0.2 mol dm^{-3} pyrrole, and in 40% ethanol solution are shown in Fig. 1(c). There is a linear increase in the conductivity as the SDS concentration is increased between 0.0 and 0.01 mol dm^{-3} for both the water and the ethanol solutions. Although the conductivity continues to increase at the same rate in the ethanol solution, there is a clear inflection in the trace recorded for the water system with increasing SDS concentration. This inflection point corresponds to the concentration of SDS at which micelles are formed. As higher concentrations of SDS are added to the solution and the micelles continue to form, there is a decrease in the rate at which the conductivity increases as the large micelles are less mobile than the SDS anions. The critical micelle concentration (CMC) was extrapolated from this inflection point to give a value of 11.0 x 10^{-3} mol dm^{-3} for the CMC. This value is somewhat higher than the values previously reported in pure water, which are typically in the region of 8 x 10^{-3} mol dm^{-3} [7]. However, this can be explained by the presence of the pyrrole. The behaviour in the ethanol solution is very different and there is no evidence for the formation of micelles. It is generally accepted that disruption of the structured water around the hydrophobic group favours demicellization [7]. This indicates that the polymer formed in the ethanol solution is doped with SDS anions and not micelles and also explains the excellent adherence of the film formed in ethanol compared to the poor adherence observed from the water system, where the SDS forms micelles.

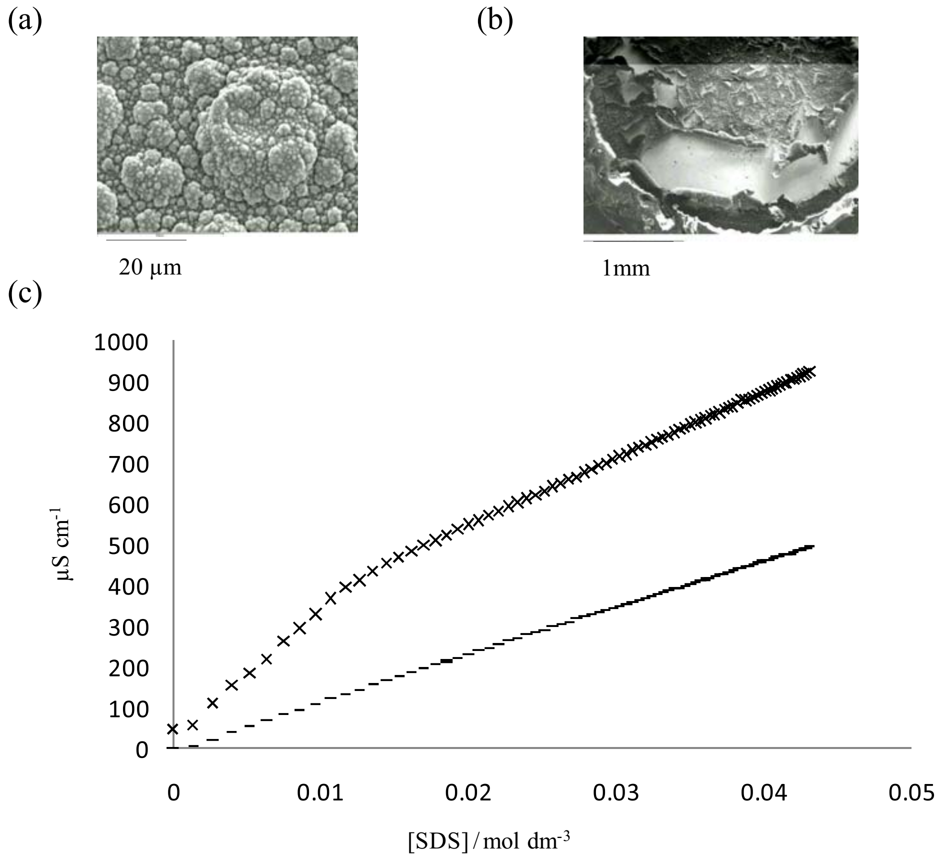

Figure 1. SEM micrographs of polypyrrole films electrodeposited from (a) ethanol with 0.02 mol dm^{-3} SDS, 0.2 mol dm^{-3} pyrrole and 0.08 mol dm^{-3} tetrabutyl ammonium perchlorate (b) water with 0.02 mol dm^{-3} SDS and 0.2 mol dm^{-3} pyrrole and (c) conductivity as a function of the concentration of SDS in xx water and -- ethanol.

The oxidation of DA was investigated at the SDS-doped polypyrrole film formed in ethanol and at a bare gold electrode using CV. The electrodes were cycled in 5.0 x 10^{-4} mol dm^{-3} DA solution between -0.2 V and 0.8 V vs. SCE at a scan rate of 100 mV s^{-1}. Typical voltammograms are shown in Fig. 2. Oxidation of DA is observed at both electrodes with a peak potential, E_p^A, at about 250 mV vs. SCE, which corresponds to the oxidation of the DA to the dopamine-o-quinone. Upon reversal of the potential, a cathodic peak, E_p^C, at 125 mV vs. SCE is observed, corresponding to the reduction of dopamine-o-quinone back to DA. This is consistent with the well-known quasi-reversible electrochemistry of DA [1]. Although the peak potentials are similar at the bare and polymer-modified electrode, it is evident that the peak currents are significantly higher at the SDS-doped polypyrrole film, clearly showing that the DA is oxidized at the polymer interface and not at the gold substrate.

Cyclic voltammograms were recorded as a function of the concentration of DA, however the detection limit was found to be 5.0 x 10^{-6} mol dm^{-3}. This is not sufficient for the detection of DA in biological samples, where the concentration of DA varies from 1.0 x 10^{-6} to 1.0 x 10^{-8} mol dm^{-3} [3]. In an attempt to improve the detection of DA, differential pulse voltammetry (DPV) and constant potential amperometry (CPA) were used. Typical calibration plots are presented in Fig 3(a) for the DPV measurements, with the voltammograms presented in the inset, and in Fig. 3(b) for the CPA, with the amperometric response of the SDS-doped polypyrrole film to successive additions of DA shown in the inset. Linear calibration curves were obtained over a wide concentration range, with correlation coefficients of 0.99. In particular very good sensitivity with a current to concentration ratio of 0.8319 μA cm^{-2}/μmol dm^{-3} was obtained for the CPA measurements. Moreover, the response time in the CPA measurements was less than 1 s, which indicates a rapid response of the polypyrrole-modified electrode to DA. This compares very well with the typical response times of DA at other modified electrodes [8]. The limit of detection was measured at 3.98×10^{-8} mol dm^{-3} with the CPA technique. This compares very favorably with the typical concentrations of DA in biological samples [3].

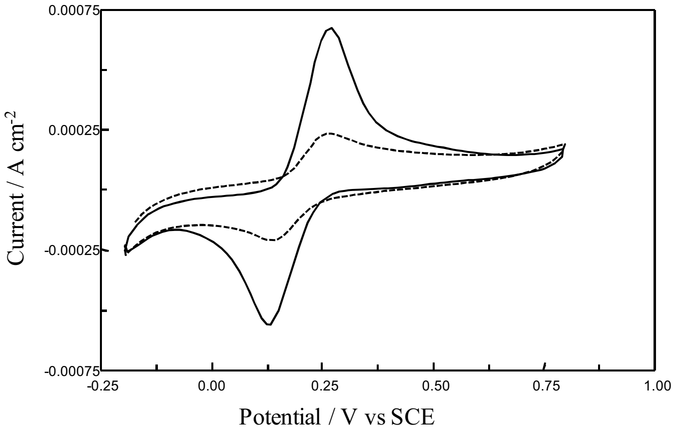

Figure 2. Cyclic voltammograms recorded in 5.0×10^{-4} mol dm^{-3} DA —— at the polymer modified gold electrode and ---- at a bare gold electrode.

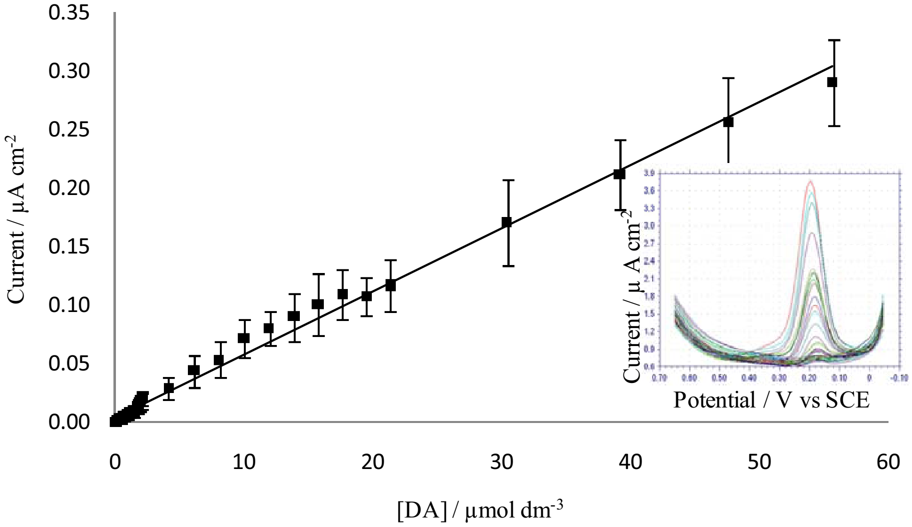

Figure 3(a). Calibration curve generated from a DPV measurements. Inset shows the voltammograms with current plotted as a function of potential.

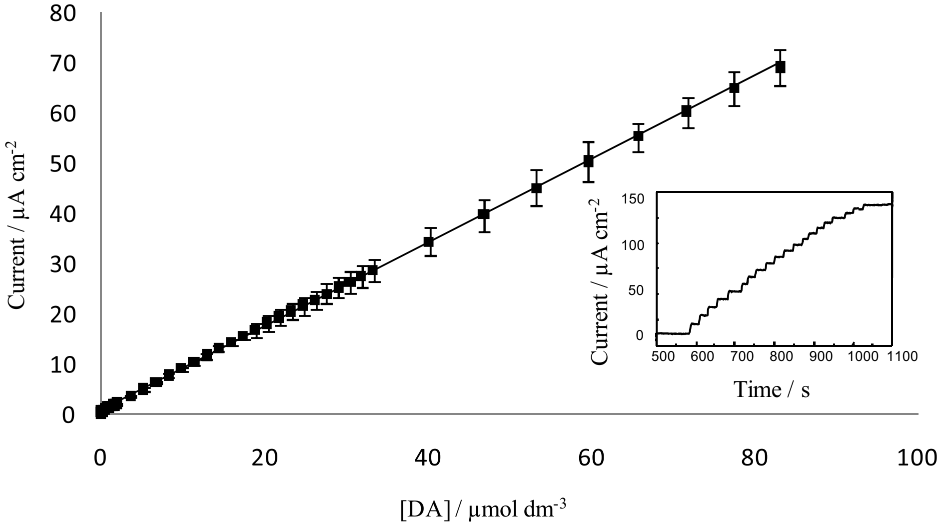

Figure 3(b). Calibration curve generated from a CPA measurement. Inset shows the CPA with current plotted as a function of time and as a function of successive additions of dopamine.

The selectivity of the SDS-doped polypyrrole film was tested with an excess concentration of AA. In Fig. 4(a) cyclic voltammograms of the polymer modified electrode cycled in a solution containing 5.0 x 10^{-4} mol dm^{-3} DA and in a solution containing both 5.0 x 10^{-4} mol dm^{-3} DA and 1.0 x 10^{-3} mol dm^{-3} AA are presented. No oxidation peak is observed for the ascorbate anion, which is oxidized readily at most electrode surfaces between -100 and 400 mV vs. SCE [1]. Only the oxidation wave of the DA is seen. It is also clear that the high concentration of AA has little influence on the peak oxidation currents. This is more clearly evident from the calibration curves presented in Fig. 4(b), where it is seen that the gradients of the calibration curves are identical. There is a slight decrease in the peak oxidation current in the AA-containing solution. This shows that the well known catalytic regeneration of DA through the oxidation of AA is not taking place at the polymer modified film [9, 10]. The % decrease in the peak current is only 11 % in the presence of a high concentration of AA, 1.0 x 10^{-3} mol dm^{-3}. This decrease in the sensitivity toward dopamine may be due to the physical interference of the high concentration of AA which is much higher than the maximum concentration of AA in biological systems which can be as high as 1.0 x 10^{-4} mol dm^{-3}. The % change in the DA peak currents is negligible at this concentration of AA.

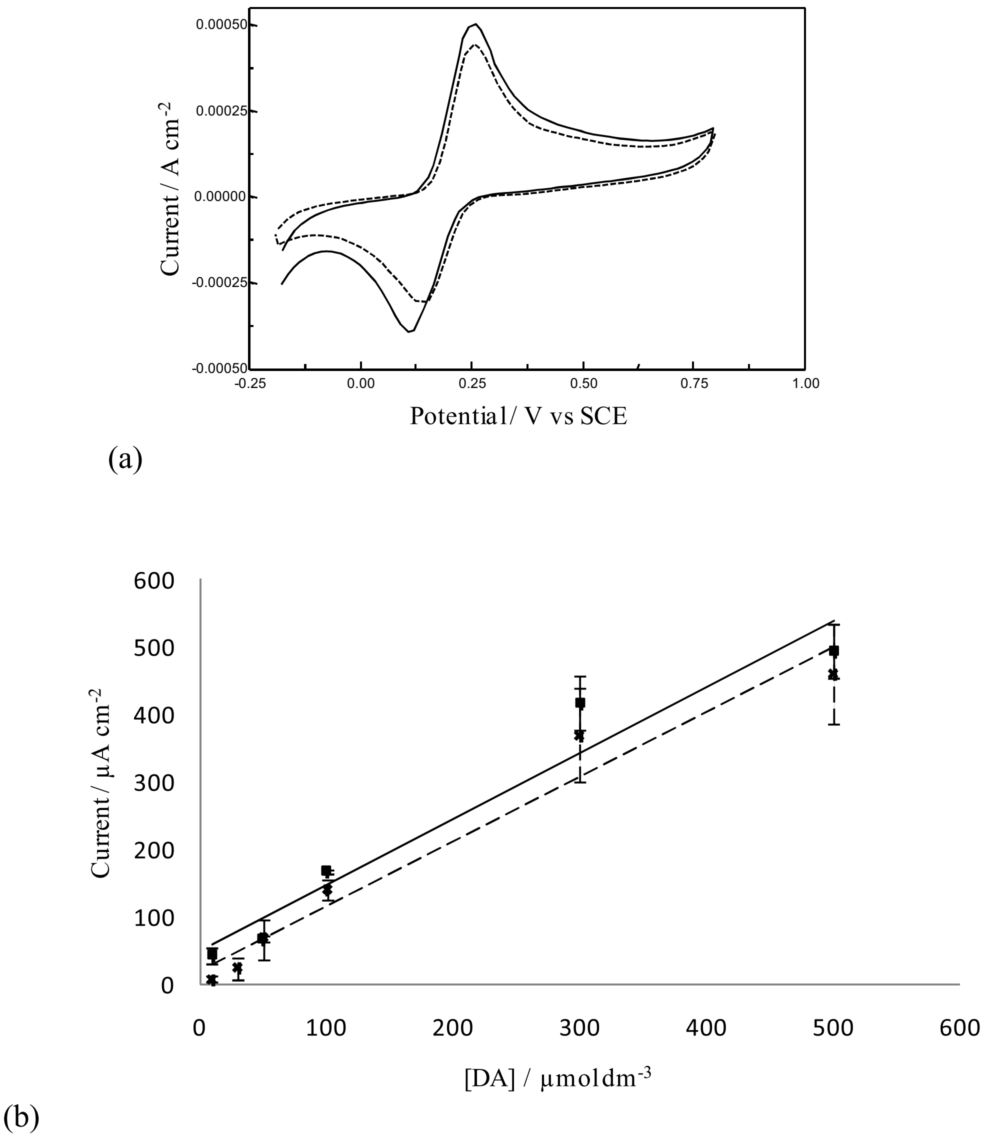

Figure 4. (a) Cyclic voltammograms recorded in 5.0 x 10^{-4} M dopamine — and in a mixed solution of 5.0 x 10^{-4} mol dm^{-3} DA and 1.0 x 10^{-3} mol dm^{-3} AA --- (b) Calibration curves with the peak oxidation current plotted as a function of the concentration of DA in the absence — ■■ and in the presence of 1.0 x 10^{-3} mol dm^{-3} AA --- xx.

Conclusions

A highly adherent SDS-doped polypyrrole film was electrodeposited from ethanol. The presence of the SDS anions gave rise to enhanced selectivity while maintaining the sensitivity of the polymer for DA detection in the presence of a high concentration of AA. A linear calibration curve was obtained with a sensitivity of 0.8319 µA cm^{-2}/µmol dm^{-3} and a limit of detection of 3.98 x 10^{-8} mol dm^{-3} for DA.

Acknowledgments

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