Simultaneous determination of dopamine, uric acid and ascorbic acid at an ultrathin film modified gold electrode

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Well-separated square wave voltammetric peaks for uric acid, dopamine and ascorbic acid were observed at an ultrathin polypyrrole–tetradecyl sulfate film modified gold electrode, which can be used for simultaneous determination of these species in the range of 1 to 500 μM with good reproducibility.

Recently there has been a considerable effort in the development of voltammetric methods for the determination of uric acid (UA), dopamine (DA) and ascorbic acid (AA) in biological samples. It is generally believed that direct redox reactions of these species at bare electrodes are irreversible and therefore require high overpotentials.[1] Moreover the direct redox reactions of these species at the bare electrodes take place at very similar potentials and often suffer from a pronounced fouling effect, which results in rather poor selectivity and reproducibility. The ability to determine UA, DA and AA selectively has been a major goal of electroanalytical research.[2] Since the basal concentrations of UA, DA and AA in biological samples vary from species to species in an extremely wide range, from 1.0×10^{-7} to 1.0×10^{-3} M,[3] both sensitivity and selectivity are of equal importance in developing voltammetric procedures. Various approaches, mainly based on ion-exchange membrane coated electrodes, have been attempted to solve the UA, DA and AA determination problems.[4–8] Ion exchange membranes of both anionic and cationic nature have been developed to electrostatically accumulate/trap oppositely charged analyte molecules. Among them are Nafion,[5] poly(ester sulfonic acid),[6] poly(4-vinylpyridine)[7] *etc.* However, the drawbacks of these ion exchange membrane modified electrodes are their memory effect, non-uniform thickness and poor reproducibility arising from the solvent evaporation method used in the film preparation. Moreover, some of the valuable information is lost when working with these ion exchange membrane modified electrodes because the membranes only allow oppositely charged species access to the electrode.

The electropolymerization of conducting polymers generally results in polymer films which are uniform and strongly adherent to the electrode surface. In addition the polymer films can be deposited onto a small area with a high degree of geometrical conformity and controllable thickness; this aspect is particularly important in the manufacture of microsensors. In short, fabrication of conducting polymer films is flexible and easily controlled, hence provides an attractive means of overcoming the problems caused by the solvent evaporation method.

In this work, the feasibility of modifying gold electrodes in an attempt to develop a sensitive voltammetric procedure for UA, DA and AA was studied. A remarkable improvement in square wave voltammetric responses of UA, DA and AA (voltammetric peaks were separated by about 150 mV from each other) and a noticeable enhancement of voltammetric sensitivity were observed at the polypyrrole–tetradecyl sulfate (PPy–TDS) film modified gold electrode. All of these were brought about by the combined catalytic function of the PPy–TDS film and the minimized background current in square wave voltammetry.

The PPy–TDS film was deposited onto the gold electrode galvanostatically in a deaerated solution saturated with pyrrole and sodium tetradecyl sulfate. The film thickness was controlled in the range of 20–25 nm by measuring the charge passed during electrodeposition. The electrode was then rinsed thoroughly with water and conditioned by cycling the potential for 2 min between –0.20 and 0.50 V at a scan rate of 50 mV s^{-1} (*vs.* Ag/AgCl) in a 0.10 M pH 7.0 phosphate buffer solution. The electrode was ready after a final rinse with water. Under optimum experimental conditions for the deposition of PPy–TDS film, the gold electrode was perfectly covered with an ultrathin PPy–TDS film, confirmed by surface coverage measurement using the copper under potential deposition method.[9]

Fig. 1 shows square wave voltammograms of 0.50 mM DA, UA and AA at both bare gold and the PPy–TDS film coated gold electrodes. As can be seen in Fig. 1(*a*), a rather broad oxidation peak appeared at about 0.32V at the bare gold electrode and the peak potentials for UA, DA and AA were indistinguishable. It is impossible to deduce any conclusive information from the broad voltammetric peak. Depending on the history of the electrode surface and the concentration ratios of UA, DA and AA, the peak potential could vary from 0.30 to 0.5 V. As shown in Fig. 1(*b*), the presence of the PPy–TDS film at the electrode surface resolved the mixed voltammetric response into three well-defined voltammetric peaks at potentials of 0.32, 0.17 and 0.015 V, corresponding to the oxidations of UA, DA and AA, respectively. Furthermore, as indicated in Fig. 1(*b*), substantial increases in peak currents were observed due to the improvements in the reversibilities of the electron transfer processes.[10] This suggests an efficient catalytic reaction between the modified electrode and the three species in solution. When cyclic voltammetry was conducted with the modified gold electrode at different scan rates, good linearities between the peak currents and the square roots of the scan rates for UA, DA and AA were obtained, indicating diffusion-controlled processes in solution. Rotating disk electrode experiments also reached the same conclusions as those obtained by voltammetry for all modified electrodes. No

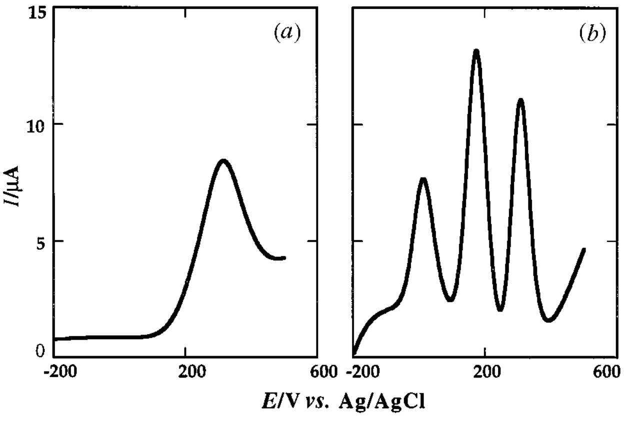

Fig. 1 Square wave voltammograms of 0.50 mM UA, DA and AA at (*a*) a bare gold and (b) a PPy–TDS film modified gold electrode (0.10 M pH 7.0 phosphate buffer, initial potential = −0.2 V, SW amplitude = 25 mV, SW frequency = 15 Hz, SW step = 2 mV)

obvious changes in the peak currents were observed when increasing the film thickness from 20 nm to 1.0 μm, suggesting that the PPy–TDS film has genuine catalytic function towards the oxidation of UA, DA and AA, and that the electron transfer processes within the film and at the film–solution interface are sufficiently fast that they do not affect the catalytic currents of UA, DA and AA. However, the charging current increased with increasing film thickness, thus preventing us from determining UA, DA and AA at micromolar levels. A similar catalytic effect was also observed at PPy films doped with other anions, but large charging currents were observed at PPy films doped with small anions such as chloride, nitrate and sulfate.[11] For practical purpose, in order to minimize the charging current, the PPy–TDS film should be kept as thin as possible, as long as the electrode is completely covered by the PPy–TDS film. Moreover, there is no memory effect at all since analytes cannot penetrate into the highly compact and conductive PPy–TDS film and the electron exchange process takes places at the PPy–TDS film–solution interface.

The overall facility of the modified electrode for simultaneous determinations of UA, DA and AA was demonstrated in solutions with simultaneous changes of concentrations. The peak currents obtained increased linearly with increasing UA, DA and AA concentrations in the range of 1.0 to 500 μM with a correlation coefficient of 0.997–0.998. The detection limits (signal-to-noise ratio = 3.0) for UA, DA and AA were found to be 0.4, 0.4 and 0.6 μM respectively. The modified electrode showed excellent anti-fouling properties. A series of 50 repetitive voltammetric determinations of sample solutions containing 25 μM UA, DA and AA were used to evaluate the stability of the modified electrode. The coefficient of variation was found to be 5.5%, indicating that the modified electrode is not subject to surface fouling by the oxidation products, which are notorious for their surface fouling effects at the bare electrodes.[12] High stability was also observed in phosphate buffer solutions containing high concentrations of chloride. For example, no obvious deterioration was observed after 50 repetitive voltammetric runs in a 0.10 M pH 7.0 phosphate buffer solution containing 0.15 M NaCl. The advantages accruing from the catalytic function of the film improved the selectivity of the voltammetric measurement of UA, DA or AA in the presence of the other two. As demonstrated in Table 1, the peak current obtained for a 25 μM of UA, DA or AA sample solution was practically constant in the presence of a wide range of concentrations of the other two species. In addition the slopes of the calibration curves were almost the same as those obtained with simultaneously changing concentrations of UA, DA and AA.

Table 1 Square wave voltammetric data (SW amplitude = 25 mV, SW frequency = 15 Hz, SW step = 2 mV) for 25 μM UA, DA and AA in mixed solutions at the PPy–TDS film modified gold electrode

AA		DA		UA	
DA + UA/ μM	ip_{AA}/μA	UA + AA/ μM	ip_{DA}/μA	DA + AA/ μM	ip_{UA}/ μA
0.0 + 0.0	0.250	0.0 + 0.0	0.600	0.0 + 0.0	0.510
10 + 10	0.247	10 + 10	0.590	10 + 10	0.512
50 + 50	0.248	50 + 50	0.608	50 + 50	0.505
200 + 200	0.247	200 + 200	0.575	200 + 200	0.498
500 + 500	0.245	500 + 500	0.580	500 + 500	0.490
1000 + 500	0.225	500 + 1000	0.535	1000 + 1000	0.445

In conclusion, we have demonstrated the possibility of using the PPy–TDS film modified electrode for the simultaneous determination of UA, DA and AA. The modified electrode showed excellent sensitivity, selectivity and anti-fouling properties. The high selectivity was proved to be mainly attributed to the catalytic function of the PPy–TDS film.

Notes and References

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