Electrochemical determination of dopamine and ascorbic acid at a novel gold nanoparticles distributed poly(4-aminothiophenol) modified electrode

Anantha Iyengar Gopalan\textsuperscript{a,b,c}, Kwang-Pill Lee\textsuperscript{a,b,*}, Kalayil Manian Manesh\textsuperscript{a}, Padmanabhan Santhosh\textsuperscript{a}, Jun Heon Kim\textsuperscript{a,b}, Jae Soo Kang\textsuperscript{a}

\textsuperscript{a} Advanced Analytical Science and Nanomaterials Lab, Department of Chemistry Education, Kyungpook National University, Daegu 702-701, South Korea
\textsuperscript{b} Nano Practical Application Center, Daegu 704-230, South Korea
\textsuperscript{c} Department of Industrial Chemistry, Alagappa University, Karaikudi-630 003, India

Received 11 April 2006; received in revised form 19 August 2006; accepted 19 August 2006
Available online 4 January 2007

Abstract

A modified electrode is fabricated by embedding gold nanoparticles into a layer of electroactive polymer, poly(4-aminothiophenol) (PAT) on the surface of glassy carbon (GC) electrode. Cyclic voltammetry (CV) is performed to deposit PAT and concomitantly deposit Au nanoparticles. Field emission transmission electron microscopic image of the modified electrode, PAT-Au\textsubscript{nano-ME}, indicates the presence of uniformly distributed Au nanoparticles having the sizes of 8–10 nm. Electrochemical behavior of the PAT-Au\textsubscript{nano-ME} towards detection of ascorbic acid (AA) and dopamine (DA) is studied using CV. Electrocatalytic determination of DA in the presence of fixed concentration of AA and vice versa, are studied using differential pulse voltammetry (DPV). PAT-Au\textsubscript{nano-ME} exhibits two well defined anodic peaks at the potential of 75 and 400 mV for the oxidation of AA and DA, respectively, with a potential difference of 325 mV. Further, the simultaneous determination of AA and DA is studied by varying the concentration of AA and DA. PAT-Au\textsubscript{nano-ME} exhibits selectivity and sensitivity for the simultaneous determination of AA and DA without fouling by the oxidation products of AA or DA. PAT and Au nanoparticles provide synergic influence on the accurate electrochemical determination of AA or DA from a mixture having any one of the component (AA or DA) in excess. The practical analytical utilities of the PAT-Au\textsubscript{nano-ME} are demonstrated by the determination of DA and AA in dopamine hydrochloride injection and human blood serum samples.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Gold nanoparticles; Conducting polymer; Cyclic voltammetry; Differential pulse voltammetry; Ascorbic acid; Dopamine; Real samples

1. Introduction

Dopamine, DA, belongs to the family of excitatory chemical neurotransmitter [1]. DA plays an important role in the function of central nervous, renal, hormonal and cardiovascular system. In the extra-cellular fluid of the central nervous system, the basal DA concentration is very low (0.01–1 μM) [2]. A major problem in its electrochemical determination is the coexistence of ascorbic acid (AA) in relatively high concentrations. Usually, the concentration of DA is in the range from $10^{-8}$ to $10^{-6}$ M. The concentration of AA in biological systems is as high as $10^{-4}$ M, while using conventional solid electrodes for the determination of DA, the main and foremost difficulty is the interference of AA, which is oxidized almost at the same potential as DA. As a result, an overlapping voltammetric response for the oxidation of mixture of DA and AA is obtained. Also, a large overpotential and fouling by oxidation products are the additional difficulties in the determination of DA [3,4]. Therefore, it is important to widen the potential range in which oxidation of AA and DA occurs. This warrants the use of modified electrode for this purpose.

Conducting polymers with entrapped metal nanoparticles [5,6] receive interest due to the probable electronic interactions between the nanoparticles and groups in the polymer. The porous structure of conducting polymer allows to disperse the metal particles into the polymer matrix and generates additional electrocatalytic sites. Gold nanoparticles anchored...
into certain substrates show catalytic activity for many reactions [7,8]. In particular, Au nanoparticles protected via self-assembly (in two or three dimensional lattices) are showing promise for the construction of nanodevices and nanocircuits [9,10]. Recently, Au nanoparticles entrapped into the matrix like amine terminated self-assembled monolayer, poly(3,4-ethylenedioxythiophene), sulfohydroxyl-terminated monolayer, carbon fiber electrode [11–14] have been widely used for the voltammetric sensing of DA and (or) AA.

4-Aminothiophenol (AT) has attracted significant attention in making 2D/3D assembly of nanoparticles via covalent or electrostatic interactions [15]. The difference in reactivity between the thiol and amine ends of AT [16] has been effectively utilized to design molecular assemblies leading to uniquemorphologies and chemical manipulations. In addition, the presence of phenyl group in AT enhances the electrical coupling between the electrode and nanoparticles. Self-assembled monolayer assembly of AT on Au electrode has been used for the selective determination of DA and AA [17].

In the present work, a new kind of modified electrode was fabricated by distributing Au nanoparticles into a conductive polymer matrix, poly(aminothiophenol), PAT over the surface of GC electrode. A simple, one-pot electrochemical approach was used for the fabrication of the modified electrode, PAT-Au\textsubscript{nano}-ME. PAT-Au\textsubscript{nano}-ME showed excellent selectivity for the electrochemical determination of AA and DA and the details are presented.

2. Experimental

2.1. Chemicals used

\(\beta\)-Cyclodextrin (CD), AT, HAuCl\(_4\), AA, DA and H\(_2\)SO\(_4\) were of analytical grade samples and used as received. For real sample analysis, human blood serum samples from single donor were obtained from Innovative Research, Inc, USA. Double-distilled water was used for the preparation of reagent solutions. Aqueous solutions of AA and DA were prepared afresh at the time of experiments in phosphate buffer (pH 7).

2.2. Preparation of inclusion complex

Inclusion complex of CD with AT was prepared by adopting the procedure detailed in the literature [18]. In a typical synthesis, 0.0626 g of AT was dissolved in 10 mL of ethanol and added to an aqueous solution containing 0.5676 g of CD in 40 mL of water. A homogenous solution was obtained after stirring. After distilling off the solvent, under reduced pressure, a white powder, CD/AT-IC was collected. The powder was washed with acetone to remove the excess of AT and dried.

2.3. Fabrication of PAT-Au\textsubscript{nano} modified electrode

A suspension was prepared by dissolving 50 mg of the inclusion complex (CD/AT-IC) in 10 mL of \(N,N'\)-dimethylformamide. Five microliter of the suspension was dropped on the surface of GC electrode and kept at 60 \(\degree\)C for 12 h in nitrogen atmosphere to evaporate the solvent. The electrode was washed with water and stored. Electrochemical deposition of Au particles into the GC/CD/AT-IC electrode surface was performed in 0.5 M H\(_2\)SO\(_4\) solution containing 2.0 \(\times\) 10\(^{-4}\) M HAuCl\(_4\) by applying a repetitive potential scan between 1000 and \(-100 \text{ mV (versus SCE)}\) at a scan rate of 50 mV s\(^{-1}\) for 100 cycles. Poly(aminothiophenol), PAT, and Au particles were simultaneously formed on the surface of GC electrode. Thus, the modified electrode (PAT-Au\textsubscript{nano}-ME) was fabricated. The steps involved in the fabrication of PAT-Au\textsubscript{nano}-ME are illustrated in Scheme 1.

**Scheme 1. Fabrication of PAT-Au\textsubscript{nano}-ME through a cyclic electrochemical process.**
2.4. Characterization

The morphology of PAT-Au_{nano-ME} was investigated by means of field emission transmission electron microscope (FETEM) (JEOL, JEM-2000EX) with a field emission electron gun operated at 200 kV. X-ray diffraction pattern of the sample was collected by employing a D8-Advanced Bruker AXS diffractometer using Cu Kα radiation.

2.5. Electrochemical measurements

Electrochemical measurements were performed in a cell consists of PAT-Au_{nano-ME} as working electrode, SCE and platinum wire as reference and auxiliary electrodes, respectively, using EG & G PAR 283 Electrochemical Analyzer. Cyclic voltammetry was used for the fabrication of the modified electrode and for following the electrochemical behavior of the modified electrode towards the detection of AA and DA. Simultaneous determination of AA and DA was performed using differential pulse voltammetry (DPV) at a scan rate of 50 mV s^{-1} with pulse amplitude of 25 mV, pulse rate of 0.5 s and pulse width of 60 ms.

3. Results and discussion

3.1. Fabrication of PAT-Au_{nano-ME}

The modification consists of the formation of electroactive PAT by the oxidation of AT present in the layer of CD/AT-IC on GC surface and deposition of Au nanoparticles by the reduction of H[AuCl_4] from the electrolyte solution. Importantly, PAT on the modified electrode plays dual role; as a conducting matrix and a stabilizer for Au nanoparticles. The -SH groups present in PAT stabilize the Au nanoparticles and prevent from aggregation. Scheme 1 represents the methodology of fabrication of PAT-Au_{nano-ME}.

Fig. 1 represents the CVs of CD/AT-IC coated GC electrode recorded in a solution containing 2.0 × 10^{-4} M H[AuCl_4] (in 0.5 M H_2SO_4) by scanning the potential from 1000 to −100 mV at a scan rate of 50 mV s^{-1}. The mechanism of formation of PAT-Au_{nano} is as follows. At the first cycle, during the cathodic scan of potential, two reduction waves were noticed at ~870 and ~400 mV. These two waves correspond to adsorption of AuCl_4^- and reduction of AuCl_4^- to Au particles, respectively. In the subsequent anodic scan, a peak at ~750 mV was observed which corresponds to the formation of AT radical cation from the oxidation of AT in the self assembled monolayers (Scheme 1) [19,20]. On the subsequent potential scans, two anodic peaks, at ~670 and ~900 mV, were observed and that are attributed to the formation of polaronic and bipolaronic forms of PAT. The peak current values for the polaronic and bipolaronic transitions of PAT showed continuous increase with increase in number of potential cycles. These observations inform the simultaneous formation of electroactive PAT and Au nanoparticles on the GC electrode.

3.2. Characterization of PAT-Au_{nano-ME}

3.2.1. FETEM analysis

Fig. 2 shows the FETEM image of PAT-Au_{nano}. Spherically shaped Au particles having an average size of about 8–10 nm can be seen. FETEM image also indicates that the Au nanoparticles are uniformly distributed in the entire region of the surface of electrode. Generally, Au nanoparticles tend to aggregate to form bigger metallic particles. The type and structure of catalyst support influence the agglomeration of Au nanoparticles [21–23]. In present study, Au nanoparticles are uniformly distributed since the -SH functional groups present in PAT helps to anchor the Au nanoparticles (Scheme 1). Further, the interactions between -SH groups and Au nanoparticles prevent them from aggregation [24–26].
3.2.2. XRD analysis

Crystalline structure and size of the Au nanoparticles present in PAT-Au\textsubscript{nano} were examined by XRD analysis (Fig. 3). Peaks observed around 38.0°, 48.2°, 64.5° and 77.4° are attributed to (111), (200), (220) and (311) facets of the fcc crystal structure of Au\textsuperscript{27}. From the full width measured at the half-maximum of the peak at 2\(\theta\) = 38°, the average crystallite size of the Au particles was evaluated to be \(\sim\)10 nm using Scherer’s equation\textsuperscript{28}.

3.3. Electrochemical behavior of AA and DA at PAT-Au\textsubscript{nano}-ME

CVs recorded for the oxidation of AA (1.5 \(\times\) 10\(^{-4}\) M) at the bare GC electrode (Fig. 4A(i)) and PAT-Au\textsubscript{nano}-ME (Fig. 4A(ii)) in aqueous phosphate buffer (pH 7) are presented. Oxidation of AA occurs at a lower potential (153 mV) at PAT-Au\textsubscript{nano}-ME in comparison to oxidation at bare GC electrode (376 mV). The enhanced electrocatalytic activity of PAT-Au\textsubscript{nano}-ME for AA arises probably due to electrostatic binding between protonated amine/imine groups in PAT and carboxylic groups in AA prior to oxidation. Enhanced anodic current was noticed at PAT-Au\textsubscript{nano}-ME in comparison to the current values noticed at the bare GC electrode. An increase of nearly 20% current for the oxidation of AA was noticed at PAT-Au\textsubscript{nano}-ME than at bare GC electrode.

Further, it is inferred that oxidation of AA and DA occur at closer potentials (376 mV for AA and 326 mV for DA) on bare GC electrode. However, oxidation of AA and DA occurs at potentials (153 mV for AA and 300 mV for DA) with a difference of 150 mV on PAT-Au\textsubscript{nano}-ME. Hence, it is inferred that PAT-Au\textsubscript{nano}-ME can be used for the simultaneous electrochemical determination of AA and DA.

The morphology of the PAT-Au\textsubscript{nano}-ME after the detection of AA or DA was analyzed by FETEM. There is no apparent change in the morphology of PAT-Au\textsubscript{nano}-ME after using the electrode for the detection of AA or DA. This indicates that PAT-Au\textsubscript{nano}-ME is not susceptible for fouling by the oxidation products or by pH or ionic strength of the electrolyte medium.

The focus of the present study is to electrochemically oxidize DA without having concurrent influence from AA. Hence, experiments were performed to understand the electrocatalytic behavior of PAT-Au\textsubscript{nano}-ME for the mixture of AA and DA. Previous reports inform that there is a shift in the potential for the oxidation of AA and DA in each other’s presence\textsuperscript{29–32}. Voltammetric pulse techniques have been established to be very sensitive in the detection of micromolar amounts of this analyte\textsuperscript{33}. More electrochemical methods such as differential pulse voltammetry can be used for obtaining better resolved voltammetric characteristics for mixture of components. We employed DPV to understand the inter-dependence in the electrochemical signals on the oxidation of AA or DA in the mixture. Further, DPV was used for the simultaneous determination of AA and DA in the mixture.
3.4. Factors influencing the electrochemical response of AA and DA

3.4.1. Influence of solution pH

The effect of pH in the electrolytic solution on the determination of AA and DA in the mixture at the PAT-Au nano-ME was studied in the range of pH 4–8.5 using DPV. The peaks corresponding to the oxidation waves of AA and DA appeared with larger differences in potentials, as the pH was changed from 4 to 6.5. It was found that at a pH of 7.0 the peak separation was maximum. Hence, the phosphate buffer with a pH of 7 was chosen as the supporting electrolyte for the selective determination of AA or DA in the mixture.

3.4.2. Influence of the potential scan rate and potential pulse amplitude

The effect of the scan rate on the current response of DPV at the PAT-Au nano-ME in phosphate buffer (pH 7) was investigated. The ratio of peak current to peak half width \(j_p/W_{1/2}\) showed a linear increase with the scan rate between 10 and 50 mV s\(^{-1}\). On the other hand, when the scan rate is higher than 50 mV s\(^{-1}\), the increase of the peak current values was accompanied by broadening and distortion of the peaks. From these results, the scan rate of 50 mV s\(^{-1}\) was chosen as it gives the best voltammetric profile with higher sensitivity and subsequently used throughout the present study.

The current values of peak were also found to vary with pulse amplitude (10–75 mV) applied on DPV at a scan rate of 50 mV s\(^{-1}\) at the PAT-Au nano-ME. The use of a pulse amplitude larger than 25 mV led to an increase in the capacitive current. In this sense, the best voltammetric sensitivity was obtained with 25 mV and therefore, this value was chosen for further studies.

3.5. Electrochemical determination of AA and DA in the mixture at PAT-Au nano-ME

Sensitivity and selectivity of PAT-Au nano-ME for the simultaneous determination of AA and DA were evaluated for a mixture of AA and DA at the PAT-Au nano-ME. Fig. 5 shows the DPVs recorded for a mixture of AA (15 μM) and DA (10 μM) at the bare GC electrode (line (i)) and PAT-Au nano-ME (line (ii)) in phosphate buffer. A poor current response with a broad overlapped peak around 380 mV was observed for the oxidation of AA and DA at the bare GC electrode (Fig. 5(i)). Almost, it was impossible to distinguish the peak potential for the independent oxidation of AA and DA at the bare GC electrode. Hence, bare GC electrode could not effectively discriminate the voltammetric signals from AA and DA.

On the other hand, two well-defined anodic peaks around the potential of 75 and 400 mV were observed for the oxidation of AA and DA, respectively, at the PAT-Au nano-ME (Fig. 5(ii)). It is interesting to note that oxidation of AA occurs at a less positive potential (75 mV) in the mixture in comparison to the oxidation peak noticed at 153 mV for a electrolyte solution contain AA alone. However, the oxidation peak potential of DA in the mixture was shifted to more positive potential (400 mV) in comparison to the oxidation potential (300 mV) noticed for simple DA. Thus, oxidation of AA and DA occur with a difference in potential of 325 mV (400–75 mV) at PAT-Au nano-ME. Presence of PAT and Au nanoparticles in the modified electrode favors preferential electrostatic interactions with negatively-charged ascorbate anions. Thus, AA is expected to preconcentrate at the surface of PAT-Au nano-ME prior to oxidation. Subsequently, oxidation of AA becomes facile and occurs at a less positive potential (75 mV). On the other hand, the existence of protonated amine/imine nitrogen in PAT excludes DA from the electrode site due to electrostatic repulsion between amine sites in PAT and DA. As a result, oxidation of DA occurs at a much more positive potential (400 mV). This causes a large separation of potential (325 mV) for the oxidation of AA and DA. The larger potential difference in the oxidation potentials of AA and DA makes the simultaneous determination of AA and DA as feasible from the mixture.

Generally, for a given concentration of DA, a comparatively large oxidation current was noticed in the presence of AA at conventional electrode. This is due to the fact that oxidation product of DA, dopamine-o-quinone, catalytically reacts with AA and reduces the dopamine-o-quinone back to DA [34–36]. Therefore, determination of concentration of DA could not be done accurately in the presence of AA. However, in the present investigation, oxidation of AA occurs ahead of DA due to the preferential preconcentration of AA at PAT-Au nano-ME. Hence, in addition to the wider potential difference (325 mV) for the oxidation of AA and DA at PAT-Au nano-ME, the interference from oxidation product of DA is minimized. Thus, the combined presence of PAT and Au nanoparticles in PAT-Au nano-ME helps in the simultaneous determination of AA and DA.

3.5.1. Selective determination of DA in the presence of fixed concentration of AA

DPVs recorded for different concentrations of DA (15–45 μM) at PAT-Au nano-ME keeping a constant concentration of AA (12.5 μM) are presented (Fig. 6). There is an increase...
in the voltammetric peak current corresponding to the oxidation of DA with the increase of the concentration of DA. The current response with concentration of DA seems to be linear with a correlation coefficient of 0.9963 in the concentration range: 15–50 µM (Fig. 6, inset). Further, DPVs were recorded at PAT-Au nano-ME, while changing the concentration of DA from 0.01 to 1 µM in the presence of 0.1 mM AA (∼1000 times higher concentration than DA). It is observed that the peak current for DA was increased linearly with the increase in DA concentration between 0.01 and 1 µM with the correlation coefficient of 0.9983. It is to be noted that in the presence of AA at millimolar level (0.1 mM), the PAT-Au nano-ME can sense the increase of DA at micromolar concentration (0.01–1 µM) which is close to the physiological condition. Thus, the selective and sensitive detection of DA in the presence of high concentration of AA is achievable at this electrode.

3.5.2. Selective determination of AA in the presence of a fixed concentration of DA

Fig. 7 shows the DPVs recorded for increasing concentration of AA (20–45 µM) for a fixed concentration of DA (12.5 µM). The current for the oxidation of AA shows an increasing trend with an increase in the concentration of AA and no significant changes is observed in the oxidation current of DA. Also, the oxidation current of AA shows linearity with the concentration of AA (Fig. 7, inset). These results suggest that the PAT-Au nano-ME can effectively be utilized for the determination of AA in the presence of DA.

3.5.3. Simultaneous determination of AA and DA in the mixture

DPV experiments were performed (Fig. 8) while changing the concentration of AA and DA simultaneously at the micromolar levels. The peak current values were proportional to the concentration of AA and DA in the mixture. As can be seen from the inset of Fig. 8, the oxidation current of AA increases linearly with its concentration between 10 and 50 µM. For the regression plot of \( i_p \) versus AA concentration, the slope is 0.4 µA µM\(^{-1}\), the y-intercept is 2.3 µA, and correlation (\( r^2 \)) is 0.9967. At the same time, the calibration plot of DA is linear between 10 and 50 µM with slope, intercept and correlation of 0.22 µA µM\(^{-1}\), 5.5 µA and 0.9954, respectively. Further, the oxidation potentials of AA and DA are not influenced much (Fig. 8). Hence, it is confirmed that for the oxidation of AA or DA at PAT-Au nano-ME, the other component does not give any interference to the electrochemical signal. Interestingly, \( \Delta E_s \) does not change with concentration of AA and DA in the mixture.

3.6. Interference study

It is well known that uric acid (UA) coexists with DA in the extracellular fluid of the central nervous system and its concentration is much higher than that of DA. Hence, UA and AA are the two important interfering substances for the electrochemical
detection of DA. The interference from AA and UA was investigated. Fig. 9 shows the DPV of 25 μM AA + 25 μM DA + 25 μM UA in phosphate buffer (pH 7). Well defined anodic peaks at 10, 210 and 475 mV for the oxidation of AA, DA and UA, respectively were observed at the PAT-Au nano-ME. However, the oxidation of AA and UA does not modify or influence the current response of the oxidation of DA. Interference studies were also performed with other compounds. In the case of 25 μM DA, no interference could be observed for glucose (200), glutamic acid (200), citric acid (100), tartaric acid (100), NaCl (500) and KCl (500), where the data in the brackets were the concentration ratios. These results indicate that selective and sensitive determination of DA is possible at PAT-Au nano-ME.

3.7. Reproducibility, repetition and stability

We have checked the reproducibility and stability of the PAT-Au nano-ME for a period of operation. The performance of PAT-Au nano-ME for the detection of DA was tested in phosphate buffer (pH 7) for a longer period. Over the first 2 days, the signal showed a 2% decrease of its initial response, over 10 days, the current response decreased by about 5% and in the following 15 days, the decrease was 10%. PAT-Au nano-ME retains 90% of its original activity after 15 days and continued to exhibit excellent response to both AA and DA. Thus, PAT-Au nano-ME does not tend to foul by the oxidation products of AA or DA and exhibits high sensitivity for the simultaneous determination of AA and DA. Further, it was found that the anodic peak currents for the oxidation AA and DA in the mixture remain unchanged after successive measurements at PAT-Au nano-ME. For instance, peak current values of 20.22, 19.38 and 17.19 μA (for AA) and peak currents values of 12.70, 12.19 and 11.46 μA (for DA) were observed for the 1st, 3rd and 30th measurements, respectively. These results indicated that PAT-Au nano-ME electrode is stable and the measurement can be repeated for the selective determination of AA or DA.

3.8. Real sample analysis

3.8.1. Determination of DA and AA in the mixture

The PAT-Au nano-ME was applied to the determination of DA and AA in dopamine hydrochloride injection sample. DOPADIC®—dopamine hydrochloride injection solution (concentration of DA 200 mg mL⁻¹, 5 mL per injection) was diluted to 10 mL with water. 1 mL of this diluted solution or some amount of standard DA or AA (from vitamin C tablet) solutions were injected into each of a series of 5 mL volume flasks and made up to volume with phosphate buffer (pH 7). An aliquot of 2 mL of this solution was placed in an electrochemical cell for the determination of DA and AA using DPV method. The results are listed in Table 1.

3.8.2. Determination of DA in human blood serum

Most of the previously reported modified electrodes were reported on the detection of DA in dopamine hydrochloride injection [37–39]. Few reports are available for the determination of DA in human blood serum [40]. At PAT-Au nano-ME, DA was not detected in human blood serum. However, when the DA standard solution was spiked, the presence of AA, UA and some other interfering substances, such as albumin and glucose did not interfere with the determination of DA (Table 2). PAT-

### Table 1

<table>
<thead>
<tr>
<th>Determination of DA in dopamine hydrochloride injection (n = 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dopamine</strong></td>
</tr>
<tr>
<td><strong>Content (mg mL⁻¹)</strong></td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Fig. 9. DPV of 25 μM AA, 25 μM DA and 25 μM UA mixtures at PAT-Au nano-ME in phosphate buffer (pH 7). Scan rate: 50 mV s⁻¹, pulse amplitude: 25 mV, pulse rate: 0.5 s, pulse width: 60 ms.
Table 2

Determination of DA in human blood serum (n = 5)

<table>
<thead>
<tr>
<th>Samples Added (µM L⁻¹)</th>
<th>Found (µM L⁻¹)</th>
<th>R.S.D. (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3</td>
<td>0.32</td>
<td>2.3</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>0.57</td>
<td>2.4</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>0.89</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Au nano-ME responds well for the recovery of spiked DA with high sensitivity and selectivity in comparison to other reported methods. This implies a promising feature for the applicability of the PAT-Au nano-ME for the selective and sensitive determination of DA in the real samples.

4. Conclusions

A newer modified electrode, PAT-Au nano-ME, was fabricated by embedding Au nanoparticles into conducting PAT matrix on the GC electrode and used for the simultaneous determination of AA and DA. PAT-Au nano-ME shows two well-defined anodic peaks for the oxidation of mixture of AA and DA with a larger peak potential difference of 325 mV. The combined presence of PAT and Au nanoparticles provide synergic influence for the simultaneous oxidation of AA and DA with a wider potential difference (ΔEₐ ≈ 325 mV). Stable electrochemical response for a longer period (>15 days) and minimum interference form the oxidation product of AA or DA were observed at PAT-Au nano-ME. Thus, PAT-Au nano-ME seems to be a promising electrode for the simultaneous determination of AA and DA.

Acknowledgements

This work was supported by Korean Research Foundation Grant (KRF-2006-J02402). The authors acknowledge Korea Basic Science Institute (Daegu) and Kyungpook National University Center for Scientific Instrument.

References