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Talanta 66 (2005) 51–57
Talanta
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Selective detection of dopamine in the presence of ascorbic acid and uric acid by a carbon nanotubes-ionic liquid gel modified electrode

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Received 20 June 2004; received in revised form 22 September 2004; accepted 22 September 2004
Available online 23 November 2004

Abstract

The electrochemistry of dopamine (DA) was studied by cyclic voltammetry at a glassy carbon electrode modified by a gel containing multi-walled carbon nanotubes (MWNTs) and room-temperature ionic liquid of 1-octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$). The thickness of gel on the surface of the electrode has to be controlled carefully because the charging currents increase with the modified layer being thicker. The anodic peaks of DA, ascorbic acid (AA) and uric acid (UA) in their mixture can be well separated since the peak potential of AA is shifted to more negative values, while that of UA is shifted to more positive values due to the modified electrode. At pH 7.08 the three peaks are separated ca. 0.20 and 0.15 V, respectively; hence DA can be determined in the presence of UA and more than 100 times excess of AA. Under optimum conditions linear calibration graphs were obtained over the DA concentration range 1.0×10^{-6} to 1.0×10^{-4} M. The detection limit of the current technique was found to be 1.0×10^{-7} M based on the signal-to-noise ratio of 3. The modified electrode has been successfully applied for the assay of DA in human blood serum. This work provides a simple and easy approach to selectively detect dopamine in the presence of ascorbic acid and uric acid.

Keywords: Carbon nanotubes; Ionic liquid; Dopamine; Ascorbic acid; Modified electrode

1. Introduction

Since the discovery of carbon nanotubes (CNs) in 1991, they have been the targets of numerous investigations due to their unique properties [1,2]. Several authors have reported the excellent electrocatalytic properties of nanotubes for the redox reaction of different biomolecules [3–5]. Room-temperature ionic liquids (RTILs), which are compounds that consist only of ions, are liquids at around room temperature. They have great potential as the green reaction media due to the advantages such as no measurable vapor pressure, good thermal and chemical stability, high conductivity, and low toxicity [6–8]. Fukushima et al. have recently demonstrated that pristine single-walled carbon nanotubes can form gels when mixing them with imidazolium ion-based RTILs by grinding [9]. Our group has been involving in the development of chemically modified electrode based on CNs and RTILs to multi-walled carbon nanotubes gel of 1-butyl-3-ethylimidazolium hexafluorophosphate on a glassy carbon electrode and studying the direct electrochemistry of proteins. The preliminary investigation has demonstrated that such gel electrode is thermal stable with high conductivity, and that the proteins adsorbed on the electrode can still retain their activities [10]. This kind of modified electrode provides a platform for fabrication of biosensors, which shows promising application to detect various biomacromolecules.

DA is an important neurotransmitter in mammalian central nervous system [11]. In the extra-cellular fluid of the central nervous system the basal DA concentration is very low (0.01–1 μM) [12]. A major problem in its determination

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doi:10.1016/j.talanta.2004.09.019

is the lack of resolution between DA and coexisting AA, and its concentration is generally much higher than DA. At traditional solid electrodes, AA is oxidized at potentials close to that of DA, resulting in an overlapping voltammetric response. Various approaches have been made to overcome these difficulties [13–23]. For example, the voltammetric behavior of DA was studied at an unmodified, exfoliated graphite electrode [20] and surface modified electrodes with organic polymers [19,21,22] and metal complexes [15,16] and so on. Recently, carbon nanotubes as modified material on the electrodes have been developed to detect DA with satisfactory results [30–34]. Measurement at higher than ambient solution temperatures has also been made as an alternative approach to tackle such problem [35].

Here, we describe a cyclic voltammetric and differential pulse voltammetric studies of DA both in the absence and presence of AA at a MWNTs-ionic liquid gel modified electrode. Since the anodic peak potential of AA is shifted to more negative values than that of DA, their overlapped anodic peaks can be separated, which results in both compounds to be quantitatively determined. Moreover, the presence of UA has no effect on the detection of DA.

2. Experimental

2.1. Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a BAS 100B electrochemical workstation (Bioanalytical System, USA). The working electrode was a glassy carbon (GC) electrode or a modified GC electrode, the auxiliary and reference electrodes were platinum wire and saturated calomel electrode (SCE), respectively. The transmission electron microscope (TEM) image was obtained using a JEOL 200CX TEM (JEOL, Japan).

2.2. Reagents and solutions

MWNTs were produced by catalytic chemical vapor deposition (CCVD) method, and provided by the Department of Chemical Engineering of Tsinghua University of China as gifts. The details of synthesis were reported elsewhere [24,25]. The purity of the MWNTs is about 99%.

The ionic liquid of 1-octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$) was synthesized according to the procedures described in the references [26,27]. The $OMIMPF_6$ has been characterized by ^1H NMR and IR, and its purity was proven to be very high.

Dopamine (3-hydroxytyramine hydrochloride) was purchased from Fluka. L(+)-Ascorbic acid was purchased from Northeast Pharmacy Institute of China. Uric acid was purchased from Merck. Water was triply distilled with a quartz apparatus. Highly purity nitrogen was used for deaeration. All other reagents were of analytical grade.

The human blood serum was obtained from Campus Hospital of Peking University and was diluted 10 times with 0.1 M phosphate buffer (pH 7.08) before using.

The buffer and sample solutions were purged with highly purified nitrogen for at least 5 min prior to the experiments. Nitrogen atmosphere was maintained over the solutions during the experiments. All experiments were carried out at room temperature ($18 \pm 2\,^{\circ}C$).

2.3. Fabrication of the modified electrode

First, 12 mg MWNTs mixed with 0.2 mL $OMIMPF_6$ were ground with an agate mortar for about 20 min, and a black gel was formed [9]. Meanwhile, a glassy carbon disk electrode with the diameter of 4 mm was polished with alumina, followed with being washed in triply distilled water and ethanol, respectively. Then, the GC electrode was rubbed over the carbon nanotubes gel placed on a smooth glass slide, and the gel was mechanically attached to the electrode surface. Finally, after the gel on the electrode surface was smoothed with a spatula to leave a thin gel film on the GC electrode surface, the gel modified glassy carbon electrode (denominated as MWNTs-IL-Gel/GC electrode in this paper) was fabricated. All voltammograms of the MWNTs-IL-Gel/GC electrode were recorded after reaching equilibrium within the tested aqueous solution.

3. Results and discussion

3.1. Characterization of the MWNTs-IL-Gel/GC modified electrode

The MWNTs-IL-Gel/GC modified electrode is first characterized by the TEM. Fig. 1 shows the typical TEM image of the MWNTs, which were dispersed in ethanol by sonication. It is clear that MWNTs are highly entangled with the diameter of several tens of nanometers. As comparison, the MWNTs gel of the $OMIMPF_6$ was dispersed in triply distilled water by sonication, and its image of TEM (Fig. 2) indicates the MWNTs are untangled after being treated with

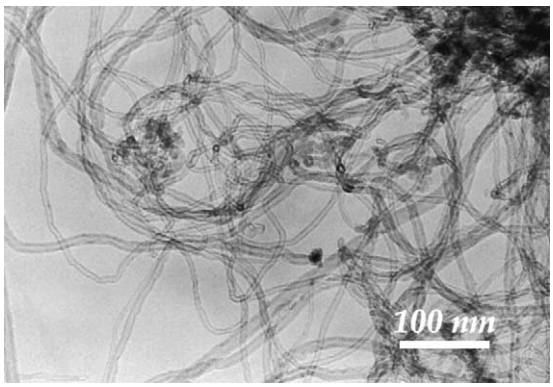

Fig. 1. TEM image of MWNTs dispersed in ethanol by sonication.

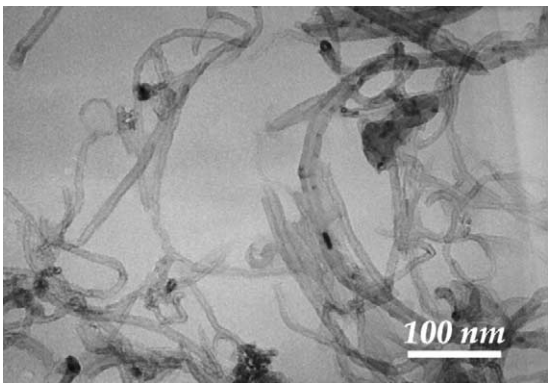

Fig. 2. TEM image of MWNTs gel of $OMIMPF_6$ dispersed in triply distilled water by sonication.

the $OMIMPF_6$, which is consistent with previous report [9].

Fig. 3 shows the cyclic voltammogram of $Fe(CN)_6^{3-}$ at the MWNTs-IL-Gel/GC electrode. A pair of well-defined redox peaks is observed with the formal potential of 0.185 V (versus SCE). The peak separation is 0.071 V at the scan rate of 0.05 V/s, which reveals that this redox reaction is a fast electron transfer (ET) process at this modified electrode. The result is consistent with the previous report at the MWNTs electrode [28,29]. The peak currents increase linearly with the square root of the scan rate in the range of 0.01–0.6 V/s, which shows the electrode reaction is controlled by the diffusion.

The thickness of the modified layer has great impact on the electrochemical properties of the MWNTs-IL-Gel/GC electrode. The cyclic voltammograms of $Fe(CN)_6^{3-}$ at the modified electrode with different weight of modified gel are shown in Fig. 4. The charging currents are much larger, as the modified gel gets heavier.

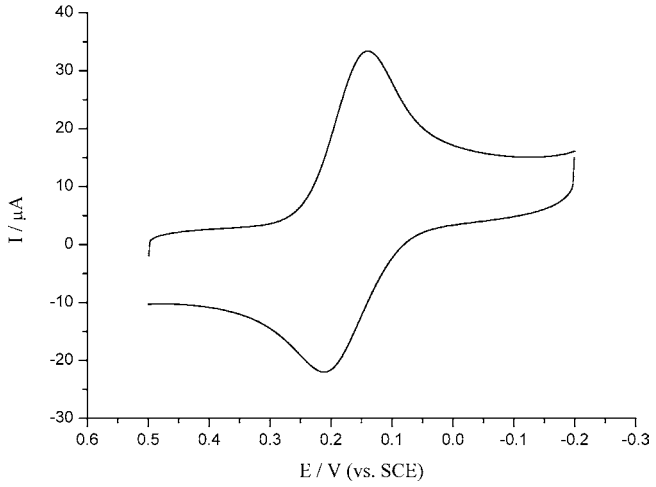

Fig. 3. Cyclic voltammogram of the MWNTs-IL-Gel/GC electrode in 1 mM $K_3Fe(CN)_6$ + 0.1 M KCl solution. Scan rate: 0.05 V/s. The weight of the gel modified on the electrode: 0.1 mg.

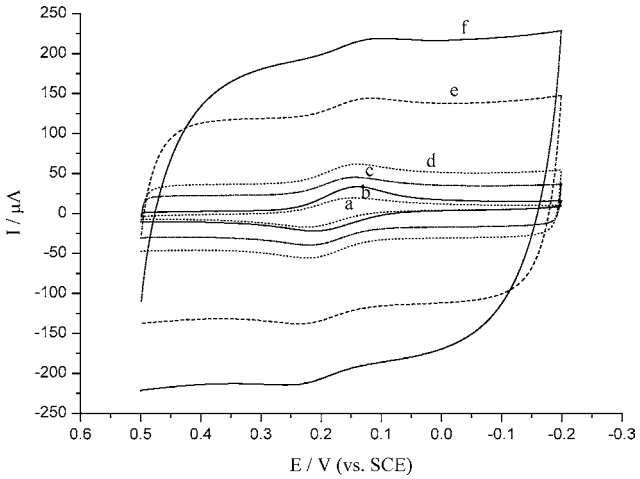

Fig. 4. Cyclic voltammograms of 1 mM $K_3Fe(CN)_6$ + 0.1 M KCl solution at (a) bare GC electrode, and MWNTs-IL-Gel/GC electrode with the gel weighting (b) 0.1 mg, (c) 0.7 mg, (d) 1.0 mg, (e) 1.6 mg, (f) 2.0 mg. Scan rate: 0.05 V/s.

When changing the ratio of $OMIMPF_6$ to MWNTs with more $OMIMPF_6$, the gel becomes more diluted. The cyclic voltammogram of $Fe(CN)_6^{3-}$ at this diluted modified electrode shows a peak separation of 0.084 V at the scan rate of 0.05 V/s, which is slightly bigger than the one described above.

3.2. Electrochemical investigation of dopamine at the MWNTs-IL-Gel/GC electrode

As shown in Fig. 5a and c, in the 0.1 M phosphate buffer (pH 7.08), no redox peak appears for both the bare GC electrode and the MWNTs-IL-Gel/GC electrode. When 0.2 mM DA was added into the solution and the first CV scan toward positive direction was performed, a pair of redox peaks

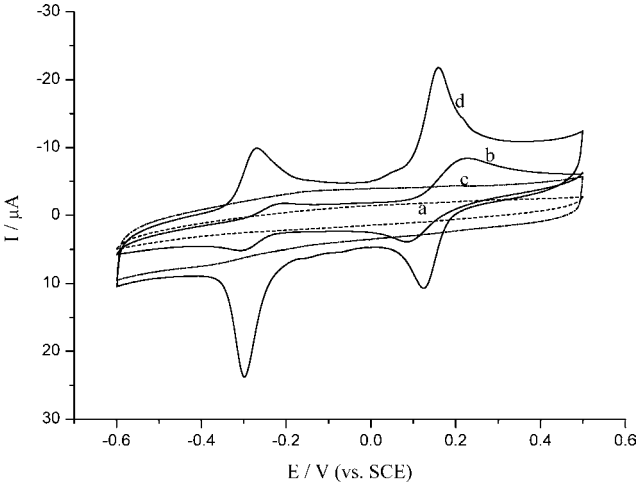

Fig. 5. Cyclic voltammograms in the absence (a, c) or in the presence (b, d) of 0.2 mM DA at bare GC electrode (a, b) or MWNTs-IL-Gel/GC electrode (c, d). Blank buffer: 0.1 M phosphate buffer solution (pH 7.08). Scan rate: 0.05 V/s. The weight of the gel modified on the electrode: 0.1 mg.

appeared at about 0.14 V. From the second scan, two pairs of well-defined redox peaks could be observed (see Fig. 5b and d). In comparison, the peak currents at the modified electrode are much larger than those at the bare GC electrode, and the peak separations are much smaller. It means the electrochemical behavior of DA can be improved by this modified electrode. Moreover, this electrochemical response has good stability, as the peaks remain unchanged after consecutive 40 CV scans. The formal potential of DA estimated from the average value of anodic and cathodic peak potentials [23], $(E_{p_a} + E_{p_c})/2$, were 0.14, −0.28 and 0.16, −0.26 V versus SCE corresponding to the MWNTs-IL-Gel/GC electrode and the bare GC electrode, respectively. Almost the same peak potential differences (ca. 0.03 V) suggest that dopamine is both undergoing two-electron oxidation during the two processes occurring at the modified electrode.

The peak potentials keep constant with different thickness of the modified layer, and the charging currents are enhanced as mentioned previously. Based on the right anodic peak, the detection limit of DA is ca. 8.0×10^{-8} M in above buffer solution.

The anodic peak currents increase linearly with the square root of the scan rate in the range of 0.01–0.6 V/s. After washing the electrode with a large amount of triply distilled water and afterwards putting it in a blank solution (0.1 M phosphate buffer), the currents of the right pair of peaks were getting much lower and the left nearly disappeared. This result shows that DA is hardly adsorbed at the surface of this modified electrode and that the two electrode reactions are both controlled by the diffusion of DA in the solution.

The right pair of peaks of DA (at 0.14 V) is well behaved in 0.1 M phosphate buffer solution in the range of pH 4.60–9.30. The relation between the anodic peak potential and pH was directly investigated and a linear regression equation for $E_{p_a} = 0.612 - 0.065$ pH (E_{p_a}, V; correlation coefficient, $r = -0.9987$) was obtained, which showed that the uptake of electrons was accompanied by an equal number of protons. In addition, the other pair of peaks (at −0.28 V) diminished as the pH lowered down, and disappeared at pH 4.60. The result is consistent with the redox procedure of dopamine. As shown in Fig. 6, a product of two electrons oxidation of DA (Eq. (1)) can undergo follow-up ring closure reaction (Eq. (2)) leading to leucodopaminechrome, which in turn oxidized to dopaminechrome (Eq. (3)). When pH < 7, the DA oxidation cannot undergo follow-up ring closure reaction (Eq. (4)).

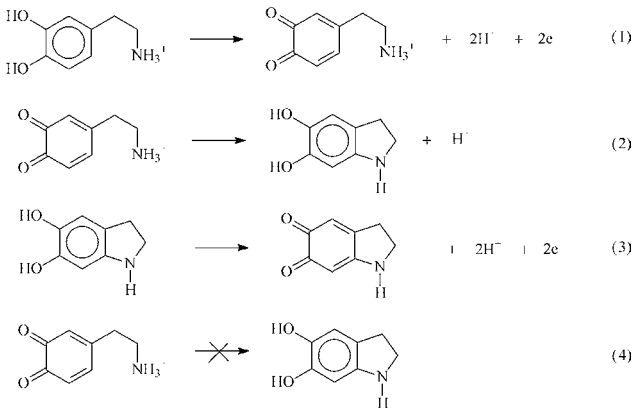

Fig. 6. The reaction mechanism for the redox process of DA.

In a word, the right pair of redox peaks (at 0.14 V) is corresponding to the redox process of Eq. (1) and the left (at −0.28 V) is corresponding to Eq. (3).

3.3. Electrochemical investigation of ascorbic acid and uric acid at the MWNTs-IL-Gel/GC electrode

As shown in Fig. 7, at the MWNTs-IL-Gel/GC electrode, the anodic peak potential of ascorbic acid is shifted about 0.31 V (from 0.27 to −0.04 V) to more negative values comparing with that at the bare GC electrode. Moreover, the peak is getting sharper. The anodic peak potential is correlated with the thickness of the modified layer. When the weight of the modified gel is more than 0.2 mg, the anodic peak potential trends to shift towards negative potential direction with the thicker gel coated onto the electrode. However, thicker modified layer brings out more charging currents and worse peak shape. Like the previous experiment, 0.1 mg was chosen as the optimal weight of the gel modified on the electrode. The detection limit of AA is ca. 2.0×10^{-6} M in neutral solution.

At the bare GC electrode, there is an irreversible electrochemical reaction process of uric acid. The charging currents increase at the MWNTs-IL-Gel/GC electrode, and the peak current is much larger at this modified electrode than that at the bare GC electrode (see Fig. 8). The anodic peak potential is shifted slightly to the positive values (from 0.09 to 0.11 V) at pH 7.72.

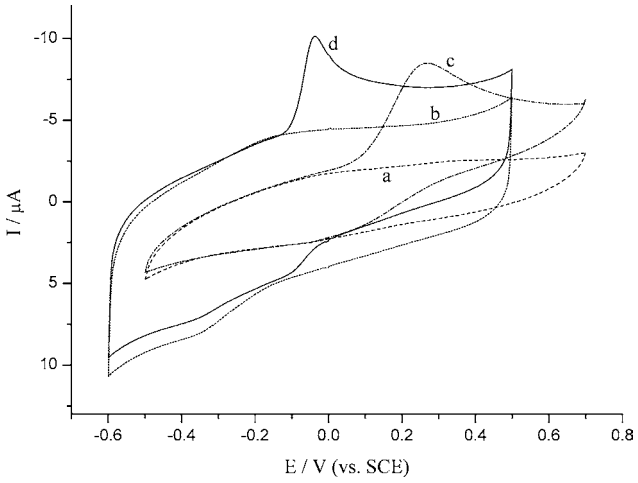

Fig. 7. Cyclic voltammograms in the absence (a, b) or in the presence (c, d) of 0.4 mM AA at bare GC electrode (a, c) or MWNTs-IL-Gel/GC electrode (b, d). Measurement conditions are the same as in Fig. 5.

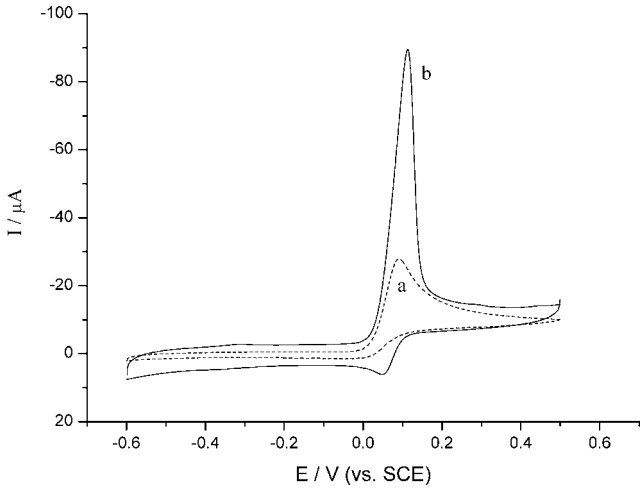

Fig. 8. Cyclic voltammograms of (a) 1.0 mM UA at bare GC electrode, (b) 1.0 mM UA at MWNTs-IL-Gel/GC electrode. Measurement conditions are the same as in Fig. 5.

3.4. Electrochemical investigation of dopamine in the presence of ascorbic acid and uric acid at the MWNTs-IL-Gel/GC electrode

Fig. 9 shows the CV curves obtained with the bare GC electrode in 3.0×10^{-4} M DA solution containing 4.0×10^{-4} M AA. The anodic peaks of DA and AA overlap completely. Consequently, it is impossible to measure the anodic current of DA in the presence of a little excess of AA with a bare GC electrode.

However, at the MWNTs-IL-Gel/GC electrode, the redox currents of DA and AA can be detected simultaneously. As shown in Fig. 10, the peak potential of AA is more negative than the one of DA. If mixing MWNTs with triply distilled water instead of $OMIMPF_6$, the MWNTs-IL gel would not be formed and the mixture could not be modified on the GC electrode as aforementioned. It showed almost the same electrochemical behaviors of DA and AA at this electrode as at bare GC electrode.

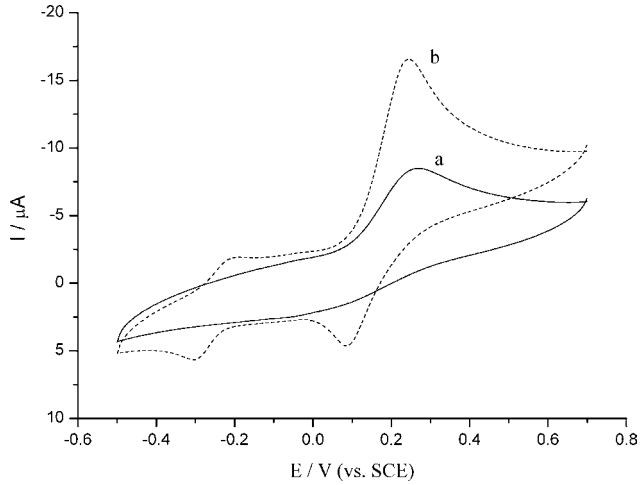

Fig. 9. Cyclic voltammograms of (a) 0.4 mM AA and (b) 0.4 mM AA + 0.3 mM DA at bare GC electrode. Measurement conditions are the same as in Fig. 5.

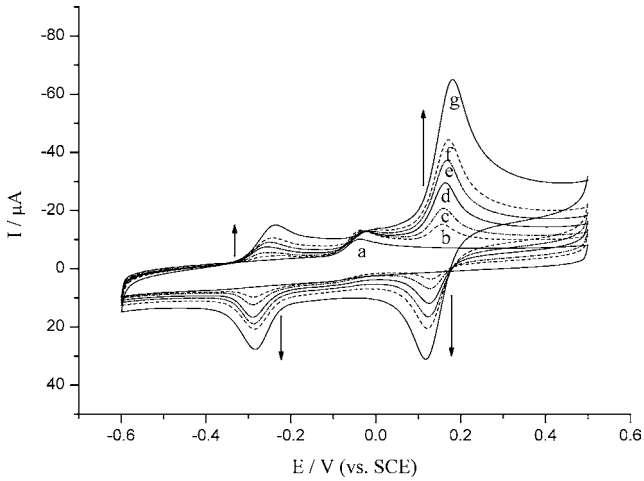

Fig. 10. Cyclic voltammograms for different concentrations of DA in the presence of 0.4 mM AA at MWNTs-IL-Gel/GC electrode. The concentration of DA (mM): (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.3, (f) 0.4, (g) 0.8. Measurement conditions are the same as in Fig. 5.

In addition, when using the method of drop-coating 1.5 mg of MWNTs dispersed in 1 mL triply distilled water on the GC electrode, the formal potentials of DA are 0.27 and −0.17 V at this modified electrode. The anodic peak potential of AA is 0.06 V (see Fig. 11). The result is consistent with the previous report at the MWNTs modified GC electrode [30]. Comparing with the drop-coating MWNTs modified electrode, the anodic peak potentials of both DA and AA at the MWNTs-IL-Gel/GC electrode shifted more negatively, which illuminates that the MWNTs-IL-Gel/GC electrode has better electrocatalytic oxidative property to both DA and AA. We suppose the presence of MWNTs cause the positive shift of the DA peak potentials and negative shift of the AA peak potential, while

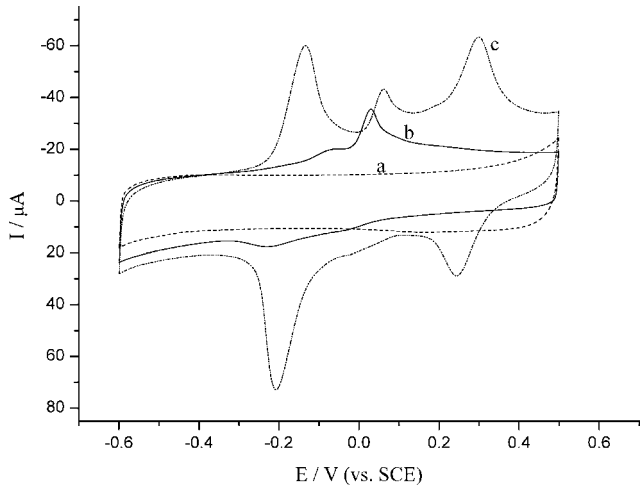

Fig. 11. Cyclic voltammograms of (a) blank buffer, (b) 0.8 mM AA and (c) 0.8 mM AA + 0.1 mM DA at drop-coating MWNTs modified GC electrode. Scan rate: 0.05 V/s.

the ionic liquid shifts the peak potentials of both DA and AA to more negative values.

In the recent researches of Compton and co-workers [36,37], the authors compared carbon nanotubes and graphite powder as electrocatalysts and pointed out that the electrocatalytic behavior of nanotube-modified electrodes shows enhanced currents and reduced peak-to-peak separations in the voltammetry in comparison with naked basal plane pyrolytic graphite, similar catalytic behavior is also seen at the graphite powder-modified electrodes. However, the carbon nanotubes are utilized in this work not only because of their higher electrocatalytic behavior they have showed to AA, DA and UA, but also because of the formation of a gel when mixing nanotubes with imidazolium ion-based room-temperature ionic liquid by grinding. While other forms of carbon, such as graphite power and C_{60}, the gel cannot be formed by the same processes [9]. Therefore, it provides a more convenient and effective method to make modified electrode.

As the pH condition and the different ratio of $OMIMPF_6$ and MWNTs are concerned, DA in the presence of AA shows the best electrochemical behavior at the acidic and neutral pH with the modified gel consisting of less ionic liquid. We suppose the excessive ionic liquids decrease the density of the MWNTs, hence the diluted gel results in worse peak shape.

In order to obtain a better resolution among the voltammograms, differential pulse voltammetry (DPV) has been employed. As shown in Fig. 12, a series of well-defined peaks for DA are obtained owing to its good reversibility. The presence of AA has no effect on the determination of DA. After the correction of background current, the detection limit of DA is ca. 1.0×10^{-7} M in the presence of a large excess of ascorbic acid in neutral pH solution, and linear calibration graphs were obtained over the DA concentration range 1.0×10^{-6} to 1.0×10^{-5} and 1.0×10^{-5} to 1.0×10^{-4} M, respectively. The linear equations and the correlation coefficients are listed in Table 1. Fig. 13 shows the DPV curves without correction of background current in the presence of 0.3 mM AA.

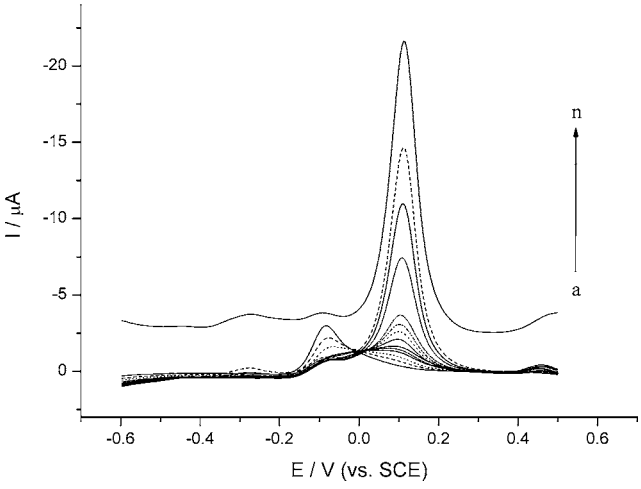

Fig. 12. Differential pulse voltammograms with correction of background current for different concentrations of DA in the presence of 0.1 mM AA at MWNTs-IL-Gel/GC electrode. The concentration of DA (μM): (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0, (g) 3.0, (h) 5.0, (i) 7.0, (j) 10.0, (k) 30.0, (l) 50.0, (m) 70.0, (n) 100. Scan rate 0.02 V/s. The weight of the gel modified on the electrode: 0.1 mg.

Table 1
Experimental results for the linearity of peak currents and dopamine concentration at MWNTs-IL-Gel/GC electrode in the presence of AA in 0.1 M pH 7.08 phosphate buffer solution

Concentration range	Linear equation	Correlation coefficient	Annotate
0.01–0.1 mM	$I_{p_a} = 1.88 + 169.4C_{DA}$	0.9986	DPV, Fig. 12
1–10 μM	$I_{p_a} = 0.97 + 0.237C_{DA}$	0.9990	DPV, Fig. 12

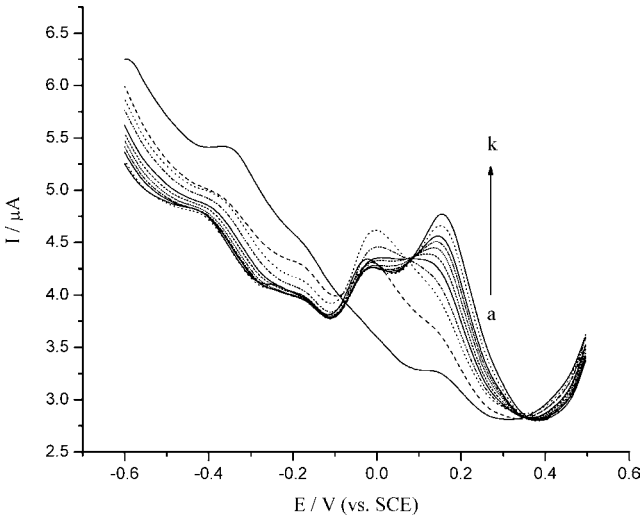

Fig. 13. Differential pulse voltammograms without correction of background current for different concentrations of DA in the absence (a) or the presence (b–i) of 0.3 mM AA at MWNTs-IL-Gel/GC electrode. The concentration of DA (μM): (b) 0, (c) 0.05, (d) 0.10, (e) 0.20, (f) 0.30, (g) 0.40, (h) 0.50, (i) 0.60, (j) 0.80, (k) 1.0. Measurement conditions are the same as in Fig. 12.

As shown in Fig. 14, DA, AA and UA are clearly separated in the same solution. The three peaks are separated by ca. 200 and 150 mV at pH 7.08, respectively. The presence of AA and UA has no effect on the determination of DA.

3.5. Determination of dopamine in human blood serum at the MWNTs-IL-Gel/GC electrode

In human blood serum, the presence of UA and some other interfering substances, such as proteins and glucose do not

Table 2
Experimental results for the determination of DA in human blood serum

No.	DA spiking ($\times 10^5$ M)	DA found ($\times 10^5$ M)	Recovery (%)
1	2.0	1.94	97
2	2.0	1.85	93
3	2.0	1.91	96
Mean		1.90	95

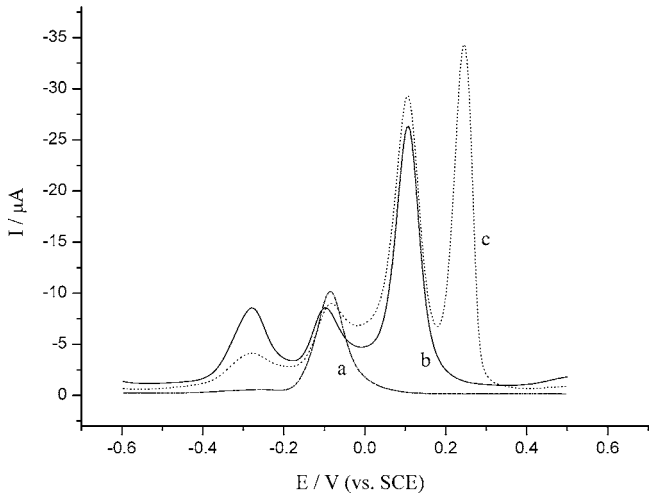

Fig. 14. Differential pulse voltammograms with correction of background current of (a) 0.4 mM AA, (b) 0.4 mM AA + 0.05 mM DA and (c) 0.4 mM AA + 0.05 mM DA + 0.05 mM UA at MWNTs-IL-Gel/GC electrode. Measurement conditions are the same as in Fig. 12.

interfere with the determination of DA. The satisfactory results are shown in Table 2.

4. Conclusions

A simple, quick and sensitive electrochemical technique has been developed for the first time for the dopamine detection in the presence of uric acid and large quantities of ascorbic acid, based on the application of the MWNTs-IL-Gel/GC electrode. This technique has been used in the determination of dopamine in human blood serum with satisfactory result.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20305001 and No. 50134020). We also appreciate Prof. Guohua Luo, Department of Chemical Engineering of Tsinghua University of China, for the generous gifts of MWNTs.

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