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ORIGINAL PAPER

Carbon electrode modified with ionic liquid and multi-walled carbon nanotubes for voltammetric sensing of adenine

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Abstract A voltammetric sensor was fabricated by applying a Nafion and multi-walled carbon nanotubes (MWCNTs) composite film on the surface of a carbon ionic liquid electrode (CILE), which was prepared by mixing 1-butyl-3-methylimidazolium hexafluorophosphate with graphite powder. The electrochemical behavior of adenine on the Nafion-MWCNTs/CILE was investigated in pH 5.5 buffer solution. Adenine showed an irreversible adsorption-controlled oxidation reaction with enhanced electrochemical response, which was due to the presence of high conductive MWCNTs on the CILE surface. The electrochemical parameters of adenine electro-oxidation were determined, and the experimental conditions were optimized. Under the optimal conditions, the oxidation peak current was linear to the adenine concentration over the range of 1.0×10^{-7} to 7.0×10^{-5} mol L^{-1} with a detection limit of 3.3×10^{-8} mol L^{-1} (signal/noise=3). The electrode showed good stability and selectivity, and was further applied to milk powder samples with satisfactory results.

Keyword Adenine · 1-butyl-3-methylimidazolium hexafluorophosphate · Multi-walled carbon nanotubes · Cyclic voltammetry · Carbon ionic liquid electrode

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Introduction

Room temperature ionic liquids (RTILs) are ionic compounds composed of an organic cation and either an organic or an inorganic anion, which exist in the liquid state over a wide temperature range [1]. Due to their unusual properties, such as high electrochemical stability, good ionic conductivity and wide electrochemical windows, RTILs have been widely used in the fields of electrochemistry and electroanalysis [2]. RTILs can be used as the supporting electrolyte, or the binder in the carbon paste electrode, or the modifier on the chemically modified electrodes [3–7]. Wei et al. reviewed the recent application of RTILs in the electrochemical sensor [8]. Makeli et al. applied n-octylpyridinum hexafluorophosphate (OPFP) as binder to fabricate a carbon composite electrode, which provided a remarkable increase in the electron transfer rate and decreased the overpotentials of some organic substances [9]. The electrooxidation of some electroactive compounds was further investigated on this kind of IL modified electrode [10, 11]. Our group also applied a series of IL modified carbon paste electrodes in the investigation of protein electrochemistry and the detection of electroactive molecules [12–15].

Carbon nanotubes (CNTs) modified electrodes have been widely used in recent years due to the specific characteristics of CNTs such as high ratio of surface area, excellent electrical conductivity and good chemical stability. Wang et al. have reviewed the application of CNTs in the electrochemical biosensor [16]. A large number of compounds such as theophylline, DNA, uric acid, Cytochrome c and NADH have been investigated on different CNTs based electrodes [17–21].

In the present work, a multi-walled carbon nanotubes (MWCNTs) modified CILE was designed and used for the investigation of the electrochemical behaviors of adenine. Adenine is a kind of nucleoside with important physiological functions. Since the direct electrochemistry of DNA was discovered in the 1960s [22], many efforts have been made to investigate the electrochemical behavior of DNA and its related bases [23]. For example, different kinds of working electrodes, such as electrochemically pretreated carbon paste electrodes (CPE) or glassy carbon electrodes (GCE), polycrystalline gold electrodes and modified electrodes had been used for the investigation of the direct electrochemical oxidation of the bases in DNA molecules [24–28]. Adenine is recognized as a molecule that has wide ranging biological significance and plays a vital role in biochemical processes. It regulates the renal function and is an inhibitory neurotransmitter which plays a role in promoting sleep and suppressing arousal. So it is necessary to establish a sensitive method for adenine detection. It was found that the MWCNTs modified CILE displayed good electrochemical activity to the oxidation of adenine in pH 5.5 B-R buffer solution with increased electrochemical responses. So the electrochemical behaviors of adenine on the modified electrode were carefully investigated by employing differential pulse voltammetric method.

Experimental

Reagents

Multi-walled carbon nanotubes (diameter: 10–20 nm, length: 5–15 μm, purity: ≥95%, Shenzhen Nanoport. Co. Ltd., China, http://www.nanotubes.com.cn), ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$, 98%, Hangzhou Kemer Chemical Limited Company, China, http://www.chemer.com/), graphite powder (average particle size 30 μm, Shanghai Colloid Chemical Company, http://www.cheminfo.gov.cn/UI/yellowpage/Showhy.aspx?hyid=2363) were used as received without further purification. 0.5% Nafion solution was prepared by diluting 5% Nafion (Sigma, USA, http://www.sigmaaldrich.com/) in ethanol (AR). Adenine was the products of Sigma (http://www.sigmaaldrich.com/) and the stock solution (1.0 mmol L^{-1}) was prepared with doubly distilled water. 0.2 mol L^{-1} Britton-Robinson (B-R) buffer solutions with various pH values were used as the supporting electrolyte. All the other chemicals were of analytical reagent grade, and doubly distilled water was used in the experiments.

Apparatus

All the electrochemical experiments were performed on a CHI 1210A electrochemical workstation (Shanghai CHI Instruments, China, http://chi.chemshow.cn). A three-electrode system was used with a Nafion-MWCNTs/CILE as working electrode, a saturated calomel electrode (SCE) as reference electrode, and a platinum wire as auxiliary electrode.

Preparation of modified electrodes

Ionic liquid modified carbon paste was fabricated by mixing 4.0 g of graphite powder, 1.0 g of $[BMIM]PF_6$ and 1.0 g of paraffin oil thoroughly in a mortar to form a homogeneous carbon paste. A portion of carbon ionic liquid paste was filled into one end of a glass tube (Φ=4 mm) and a copper wire was inserted through the opposite end to establish an electrical contact. The CILE surface was smoothed on a piece of polishing paper just before use. For comparison, the traditional carbon paste electrode (CPE) was prepared by hand-mixing graphite powder with paraffin oil at a ratio of 70/30 (w/w).

Multi-walled carbon nanotubes (MWCNTs) were purified by refluxing in a 68% HNO_3–98% H_2SO_4 (volume ratio: 1:1) mixture, washing with double distilled water and drying under vacuum. A 1.0 g mL^{-1} MWCNTs stock solution was prepared by dissolving 1.0 g of MWCNTs in 1.0 mL of 0.5% Nafion solution. Finally, a 5 μL volume of the Nafion-MWCNTs mixture was transferred to a smoothed CILE surface and dried at room temperature to obtain a Nafion-MWCNTs film coated carbon ionic liquid electrode (denominated as Nafion-MWCNTs/CILE).

Experimental procedure

The three-electrode system was immersed in an electrochemical cell containing 10 ml of 0.2 mol L^{-1} B-R buffer solution containing 1.0×10^{-5} mol L^{-1} adenine. After an accumulation of 270 s at +0.3 V, the voltammograms were recorded in the potential range of 0.7 to 1.3 V. Before or after every measurement, the potential scan was repeated successively for three cycles in a blank buffer solution to regenerate the electrode surface. All the experiments were carried out at a room temperature of 20°C.

Sample preparation

The milk powder sample was produced by Inner Mongolia Yili Industrial Group Co. Ltd., and obtained from a local market. Its pretreatment procedure is described as reference [29]. Skim milk powder (0.5 g) was dissolved in 4.0 mL double distilled water (25°C). After adding 2.0 mL acetic acid (3% v/v) and letting it stand for 15 min, it was diluted to 10.0 mL with double distilled water. Then it was centrifuged for 10 min at approximately 4000 r min^{-1}. Part of the sample solution was transferred to the cell with pH 5.5 B-R for analysis.

Results and discussion

Characteristics of the Nafion-MWCNTs/CILE

Figure 1 shows the typical cyclic voltammograms of different electrodes in $K_3[Fe(CN)_6]$ solution, and the results can be used to evaluate the performance of the modified electrodes. On the traditional CPE (curve a) a quasi-reversible redox behavior of ferricyanide was observed with the peak-to-peak separation (ΔE) of 207 mV. While on the CILE (curve b) an increase of the redox peak current and a decrease of ΔE (103 mV) was observed. This was due to the presence of high conductive IL in the carbon paste, which accelerated the electron transfer rate. While the response on the Nafion-MWCNTs/CILE (curve c) was better than that of CILE with the increase of peak current and the decrease of the ΔE value to 84 mV, the presence of MWCNTs on the electrode surface further increased the electron conductivity due to the specific characteristic of Nafion-MWCNTs composite film present on the electrode surface.

Electrochemical responses of adenine on Nafion-MWCNTs/CILE

Cyclic voltammetric responses of 1.0×10^{-5} mol L^{-1} adenine on the CPE, CILE and Nafion-MWCNTs/CILE were recorded in pH 5.5 B-R buffer, and the results are shown in Fig. 2. On the bare CPE (Fig. 2 Inset A) an irreversible oxidation peak appeared with the oxidative peak current (Ipa) equal to 0.94 μA, and the oxidative peak potential (Epa) equal to 1.08 V (vs. SCE), while on the CILE (Fig. 2 Inset B) the values of Ipa and Epa were equal to 15.55 μA and 1.12 V (vs. SCE), respectively. The peak current was about 17 times that of CPE, indicating that the presence of ionic liquid in the carbon paste electrode greatly improved the electrocatalysis of adenine. On the Nafion-MWCNTs/CILE (Fig. 2) a better electrochemical response of adenine was observed with Ipa equalling 48.8 μA and Epa equalling 1.12 V. The peak current was about 50 times higher than that of CPE, indicating that the presence of MWCNTs on the CILE surface further improved the electrochemical reaction of adenine. MWCNTs possess excellent electrical conductivity with high surface area, so the presence of MWCNTs on the electrode surface increases the interfacial conductivity and the corresponding electrochemical response. Therefore Nafion-MWCNTs/CILE could be used as a sensitive sensor for adenine quantification.

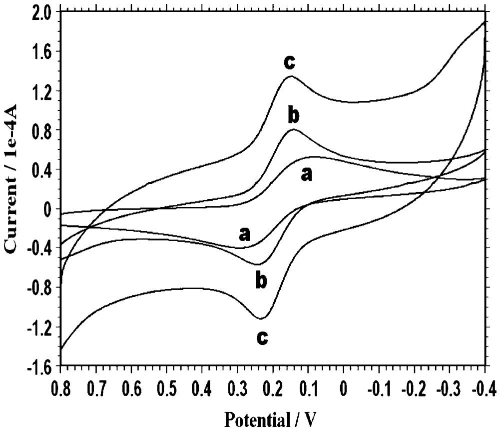

Fig. 1 Cyclic voltammograms of CPE (**a**), CILE (**b**) and Nafion-MWCNTs/CILE (**c**) in a solution of 1.0×10^{-3} mol L^{-1} $K_3[Fe(CN)_6]$ +0.5 mol L^{-1} KCl at a scan rate of 100 mV s^{-1}

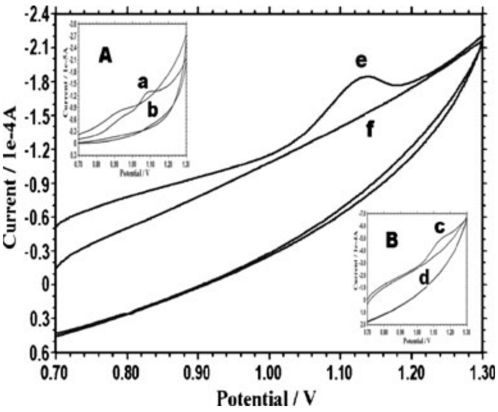

Fig. 2 Cyclic voltammograms of 1.0×10^{-5} mol L^{-1} adenine on different electrodes, (a) CPE, (c) CILE, (e) Nafion-MWCNTs/CILE, and pH5.5 B-R buffer solution (b) CPE, (d) CILE, (f) Nafion-MWCNTs/CILE after preconcentration at +0.30 V for 270 s; scan rate: 100 mV s^{-1}

Effect of pH

The effect of pH on the electrochemical response of adenine was investigated in the range of 3.0 to 8.0, the results are shown in Fig. 3. The oxidation peak currents increased with

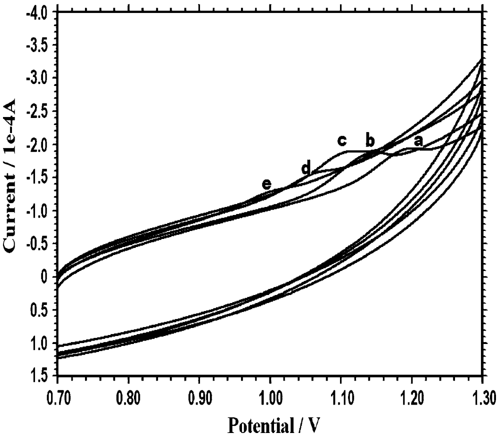

Fig. 3 Cyclic voltammograms of 1.0×10^{-5} mol L^{-1} adenine with different pH (from a to e: 4.0, 5.0, 5.5, 6.0, 7.0)

the increase of pH up to 5.5, then the peak currents decreased gradually with a further increase of the pH value. So pH 5.5 B-R buffer was used as the supporting electrolyte in the following experiments. Different kinds of buffers, such as Na_2HPO_4-KH_2PO_4, HOAC-NaOAC, KCl etc., were tested, and the electrochemical responses were found to be best in B-R buffer solution. With increasing pH the oxidation peak potentials shifted to the negative direction, and a linear regression equation was obtained as Epa (V)=−0.063pH + 1.44 (γ=0.997), with the slope value of −63 mV pH^{-1}, suggesting that the same amount of electrons and protons are involved in the electrode reaction [30].

Effect of scan rate

The influence of the scan rate on the electrochemical response of 1.0×10^{-5} mol L^{-1} adenine was further studied. With an increasing scan rate the oxidation peak current increased with the positive shift of the oxidation peak potential, indicating an irreversible process. The oxidation peak current increased linearly with the scan rate in the range of 10 to 150 mV s^{-1}, with the linear regression equation being:

$$\mathrm{Ipa}(\mu\mathrm{A}) = -111.5\mathrm{v}\left(\mathrm{Vs}^{-1}\right) - 2.3(\gamma = 0.994),$$

which indicated a surface-controlled process resulting from the adsorption of adenine on the MWCNTs modified electrode. Based on the equation [31, 32]:

$$Ip = \frac{nFQ\upsilon}{4RT} = \frac{n^2F^2A\Gamma_T\upsilon}{4RT},$$

where n is the number of electrons transferred, F (C mol^{-1}) is the Faraday's constant, A (cm^2) is the area of the electrode, Γ_T (mol cm^{-2}) is the surface concentration of the electroactive substance, Q (C) is the quantity of charge and υ (V s^{-1}) is the scan rate. The value of n was estimated to be 3.06, which suggested that a total of three electrons were involved in the oxidation reaction, and the result was in accordance with the reported value [33]. Also, the value of surface coverage (Γ_T) of adenine was calculated to be 1.4×10^{-10} mol cm^{-2}. The relationship of the oxidation peak potential (Epa) with ln υ was further constructed as:

$$\mathrm{Epa}\,(\mathrm{V}) = 0.03\ln\,\mathrm{v}\left(\mathrm{Vs}^{-1}\right) + 1.15(\gamma = 0.993).$$

According to Laviron's equations [34]:

$$Epa = E^{0'} + \frac{RT}{(1-\alpha)nF}\ln\upsilon$$

$$\log k_s = \alpha\log(1-\alpha) + (1-\alpha)\log\alpha - \log\frac{RT}{nF\upsilon} - \frac{(1-\alpha)\alpha nF\Delta Ep}{2.3RT}$$

The values of α and k_s were calculated to be 0.72 and 9.25×10^{-6} s^{-1}, where α is the charge transfer coefficient and k_s is the standard rate constant electrode reaction.

Effect of accumulation time and accumulation potential

Since the electrode process was adsorption-controlled, the conditions for adenine were optimized. With the increase in accumulation time the peak current increased and reached a maximum value at 270 s. This value was used as the accumulation time. When the accumulation potential changed from 0.3 V to 0.8 V, no obvious changes appeared for the oxidation peak current. Hence, 0.3 V was used as the accumulation potential.

Calibration curve

Under the selected conditions given above, differential pulse voltammetry (DPV) was used to record the oxidation peak current with a higher sensitivity for quantitative detection of adenine. Two calibration curves were obtained between the oxidation peak currents and the adenine concentration with the equations being:

$$\begin{aligned}\mathrm{Ipa}(\mu\mathrm{A}) &= 1.30\mathrm{C}(\mu\mathrm{mol\,L}^{-1}) + 0.36(\gamma = 0.992)\\ &\quad \text{in the range of } 1.0\times10^{-7} - 8.0\times10^{-6}\mathrm{mol\,L}^{-1};\\ \mathrm{Ipa}(\mu\mathrm{A}) &= 0.25\mathrm{C}(\mu\mathrm{mol\,L}^{-1}) + 7.88(\gamma = 0.994)\\ &\quad \text{in the range of } 8.0\times10^{-6} - 7.0\times10^{-5}\mathrm{mol\,L}^{-1}.\end{aligned}$$

The detection limit was estimated to be 3.3×10^{-8} mol L^{-1} (3σ).

Repeatability and stability

The stability and repeatability of Nafion-MWCNTs/CILE was further evaluated by measuring the electrochemical response of 1.0×10^{-5} mol L^{-1} adenine. After the modified electrode was stored at 4°C in a refrigerator for 3 weeks, only a small

Table 1 Influence of coexisting substances on the determination of 1.0×10^{-5} mol L^{-1} adenine (*n*=3)

Potentially interfering substances	Concentration (molL^{-1})	Relative error (%)
Adrenalin	1.0×10^{-5}	3.39
Ascorbic acid	1.0×10^{-5}	9.30
Uric acid	1.0×10^{-5}	−3.32
L-Glutamic acid	1.0×10^{-5}	−3.54
L-Leucine	1.0×10^{-5}	−2.31
Glycin	1.0×10^{-5}	3.76
Cytosin	1.0×10^{-5}	1.34
Uracil	1.0×10^{-5}	1.67
Thymidin	1.0×10^{-5}	1.49
Mg^{2+}	1.0×10^{-5}	2.43
Al^{3+}	1.0×10^{-5}	−0.74
Zn^{2+}	1.0×10^{-5}	1.57
Cu^{2+}	1.0×10^{-5}	0.34

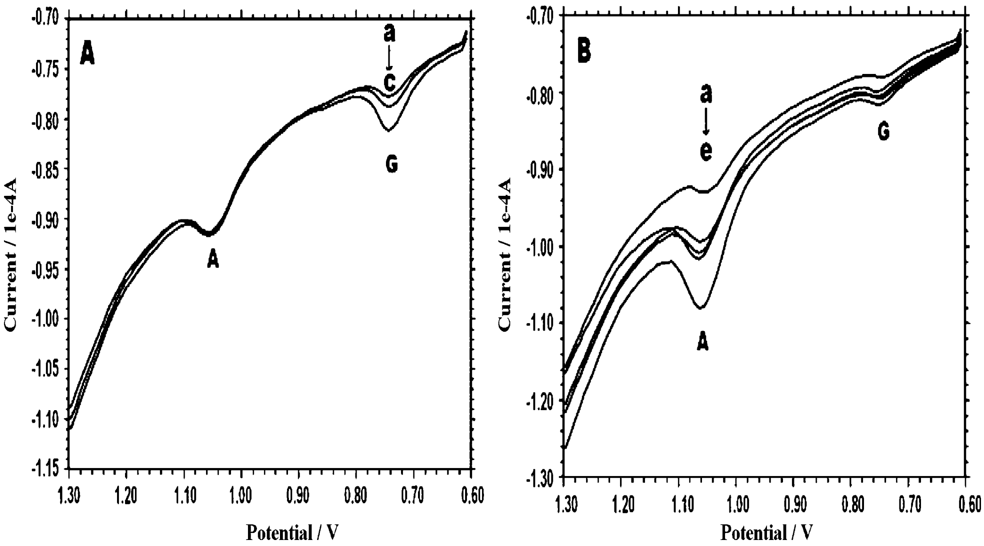

Fig. 4 **a** Differential pulse voltammograms of a mixture of guanine (a to c: 3.0, 8.0, 30.0 μmol L^{-1}) with 7.0 μmol L^{-1} adenine at the Nafion-MWCNTs/CILE; **b** differential pulse voltammograms of a mixture of adenine (a to e: 5.0, 8.0, 10.0, 15.0, 20.0 μmol L^{-1}) with 7.0 μmol L^{-1} guanine at the Nafion-MWCNTs/CILE

decrease in the current response with a relative standard deviation (RSD) of 2.86% was found. After 8 weeks of storage, the current response decreased by 7.34%, indicating good stability of the modified electrode. The repeatability of the modified electrode was investigated based on nine successive scans in the same adenine solution, and an RSD value of 2.42% was obtained, indicating good repeatability of the modified electrode. The modified electrode can be regenerated for the next measurement after a continuous sweep for three cycles in the buffer solution.

Selectivity of the Nafion-MWCNTs/CILE

The effect of some interference, which maybe coexisted in the real samples, on the determination of 1.0×10^{-5} mol L^{-1} adenine was investigated, and the results are summarized in Table 1. Negligible interference appeared for adenine detection except in the presence of ascorbic acid, which may be due to its oxidation on the modified electrode at the same time.

The electrode was further applied to the simultaneous determination of adenine and guanine mixture. Figure 4a shows the differential pulse voltammograms for the different concentrations of guanine in the presence of a fixed concentration of 7.0 μmol L^{-1} adenine. It can be seen that the differential pulse voltammetric signal of guanine appeared at 0.752 V and increased with increasing concentration. At the same time no change of response of adenine was observed. Similarly, Fig. 4b shows the differential pulse voltammograms with the concentration of adenine changed by keeping the guanine concentration constant. The results indicate that the electrochemical signals of adenine and guanine are independent of each other at the Nafion-MWCNTs/CILE with the oxidation peak potential separation being 0.304 V, which is large enough for simultaneous detection. So the method was suitable for the simultaneous detection of a mixture of adenine and guanine.

Real sample determination

To evaluate the validity of the Nafion-MWCNTs/CILE, the recovery of adenine in milk samples was tested. Various amounts of adenine were added to the diluted milk samples and detected with the procedure. Table 2 shows the results with the recovery in the range of 93.5% to 104.4%, indicating that the Nafion-MWCNTs/CILE could be efficiently applied to the adenine detection.

Conclusion

MWCNTs were used to modify the surface of CILE with the help of Nafion. Benefiting from MWCNTs, CILE and

Table 2 Analytical results of adenine in milk powder samples (n=6)

Sample[a]	No.	Spike (μmol L^{-1})	Found (μmol L^{-1})	Confidence intervals[b]	Recovery (%)
Milk powder	1	2.0	1.87	1.78–1.95	93.5
		4.0	4.18	4.00–4.45	104.4
		8.0	7.25	7.17–7.35	90.6
	2	2.5	2.50	2.30–2.65	100.2
		5.0	5.20	4.87–5.49	104.1
		10.0	9.40	8.40–10.64	94.0

[a] Number of samples assayed: 6

[b] Confidence level: 97.8%

the special characteristics of Nafion film, the fabricated Nafion-MWCNTs/CILE showed good stability and excellent electrocatalytic ability. The electrochemical behaviors of adenine on the modified electrode were carefully investigated with electrochemical parameters such as surface coverage (Γ_T), charge transfer coefficient (α) and standard rate constant (k_s) as 1.4×10^{-10} mol cm^{-2}, 0.72 and 9.25×10^{-6} s^{-1}. Based on the DPV response, a sensitive electroanalytical method for adenine detection was proposed with a concentration range of 1.0×10^{-7} to 7.0×10^{-5} mol L^{-1}. Due to the specific characteristics of the modifier used, the Nafion-MWCNTs/CILE has potential for application in the field of electrochemical biosensors, and the proposed method was successfully applied to the detection in milk powder samples with satisfactory results.

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