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Application of a Carbon Nanotube Modified Electrode in Anodic Stripping Voltammetry for Determination of Trace Amounts of 6-Benzylaminopurine

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Abstract. Carbon nanotubes were modified on the surface of a glassy carbon electrode (GC) and initially applied in semi-derivative anode stripping voltammetry for the determination of 6-benzylaminopurine. The experiments demonstrated that the presence of the carbon nanotube greatly increased the current of the oxidation peak of benzylaminopurine. Cyclic voltammetry (CV) and semi-derivative voltammetry were used in a comparative investigation into the electrochemical oxidation of benzylaminopurine with the modified electrode. Studies on the effect of pH on the peak current and potential were carried out over the pH range of $9.0 \sim 13.0$ with the NH_3–NH_4Cl buffer solution. A pH of 10.0 was chosen as the optimum pH. Other experimental parameters, such as film thickness, accumulation potential, temperature etc. were optimized. The anodic peak current was found to be linearly related to the concentration of benzylaminopurine over the range of 4.0×10^{-8} to 1.0×10^{-5} mol · L^{-1} with a detection limit of 5.0×10^{-9} mol · L^{-1} in an accumulation time of 5 min. Interferences of some inorganic and organic species on the response have been studied.

Key words: Carbon nanotube; chemically modified electrode; anodic stripping voltammetry; 6-benzylaminopurine.

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have attracted increasing attention due to their special properties, such as high electrical conductivity, high chemical stability and extremely high mechanical strength and modulus. At present, a number of investigations have been carried out to find potential applications of CNTs in catalyst support [2], hydrogen storage [3], quantum wire [4], electronic equipment [5], etc. The subtle electronic properties of carbon nanotube suggest that they have the ability to promote electron-transfer reactions when used as an electrode material in electrochemical reactions. It has been reported that carbon nanotube has better conductivity than graphite [6], the better performance has been found to be due to its dimensions, the electronic structure, and the topological defects present on the tube surface [7]. Britto et al. first fabricated carbon nanotube electrodes which were successfully used in the oxidation of dopamine [7], electrochemistry of protein [8], and electrocatalysis reduction of oxygen [9], its performance was superior to other carbon electrodes in terms of reaction rate and reversibility. The work of Luo et al. showed that after the CNTs were treated with nitric acid during the purification process, the carboxylic acid groups were introduced on the CNT surface; when cast on the GC electrode, the carbon

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nanotube modified electrode showed a stable electrochemical behavior and could be used to catalyze the electrochemical reaction of some biomoleculars such as dopamine, epinephrine, ascorbic acid and cytochrome c [10, 11]. Since carbon had been the most common electrode material in electrochemistry for a long time, as a new member of carbon, people gave intense attention to the CNTs. The application of CNTs in supercapacitors [12], the oxidation of dopamine and cytochrome c [10, 11], catalysis for reduction of oxygen and oxidation of methanol [11], etc. have been reported. However, carbon nanotube modified electrodes have rarely been applied in stripping voltammetry analysis.

6-benzylaminopurine is a kind of derivative of purine, and experiments have suggested that it can stimulate the growth of fruits. At the time of harvest (50% dry fruits), fruits treated with benzylaminopurine were longer, had thicker stems, more axillaries and branches, and larger fruits and leaves than control racemes [14]. The substance may, however, cause eye damage and irritation. Therefore, a sensitive and convenient method for the determination of 6-benzylaminopuine is desirable. At present, the method used for determining it is UV photometry [15], by which trace amounts of 6-benzylaminopurine could not be determined due to the lower sensitivity. Voltammetry, such as stripping voltammetry, is a suitable technique for the determination of trace compositions since it is highly sensitive. However, to date quantitative determination of 6-benzylaminopurine with voltammetry has not occurred. This paper presents a new method for the determination of 6-benzylaminopurine by semi-derivative anodic stripping voltammetry with a carbon nanotube modified electrode. The detection limit is $5.0 \times 10^{-9}\,\mathrm{mol \cdot L^{-1}}$ with 5 min accumulation. The method has been successfully applied to the determination of 6-benzylaminopurine residues on the surface of the fruits. The result shows that it is suitable for the determination of trace amounts of 6-benzylaminopurine and has the advantages of high sensitivity, quick response and stability.

Experimental

Apparatus

All electrochemical experiments were carried out on a CHI-660 electrochemical workstation (CH Instrument Inc., USA) with a three-electrode system. The work electrode used here was a glassy carbon electrode (GCE, geometric area of $0.07\,\mathrm{cm}^2$) modified with CNTs. A platinum plate was used as the counter-electrode (CE), and SCE was used as the reference electrode (RE) against which all potentials were measured and reported in this article. TEM was performed on a JEOL model JEM-2010 instrument (JPA). UV spectroscopy measurement was performed using a UV250 ultra-visible recording spectrophotometer (JPA).

Reagents

CNTs were obtained from Tsinghua University. Benzylaminopurine was purchased from Shanghai Reagent Factory. All solvents and reagents were of analytical analysis reagent grade unless otherwise indicated. Solutions for voltammetric study were made with doubly distilled water. All experiments were carried out at room temperature (about 20 °C).

Purification of CNTs

CNTs were refluxed in the mixture of concentrated H_2SO_4 and HNO_3, then washed with distilled water and dried under vacuum at room temperature.

Preparation of Modified Electrode

The GCE was polished on the microcloth pads, rinsed thoroughly with distilled water in an ultrasonic bath, and finally allowed to dry at room temperature. The electrode surface was then coated with a desired volume of $2.5\,\mathrm{mg\,mL^{-1}}$ CNTs dispersed in water and dried at room temperature. The modified electrode was washed with distilled water and then cyclically scanned between 1.0 and -0.8 V in NH_3–NH_4Cl buffer solution a few times before use.

Analytical Procedure

A 10 mL volume of NH_3–NH_4Cl buffer solution containing a suitable amount of benzylaminopurine was added to the sample cell. The solution was degassed with nitrogen for 10 minutes. For CV study, the electrode was scanned between 1.0 and -0.6 V; for semi-derivative voltammetry, the electrode was kept at the desired accumulation potential for a given period of time, while the solution was stirred at about 400 rpm throughout the entire period. Stirring was then stopped, and the solution was allowed to rest for 15 seconds, after which a positive-going scan was initiated at 0 V and terminated at 1.0 V. After each electrochemical measurement, the electrode was cycled in the NH_3–NH_4Cl buffer solution for several cycles to renew the surface of the electrode.

Results and Discussion

TEM Image of the Purified CNTs

Figure 1 is the TEM image of purified CNTs. In the IR spectrum, compared to CNTs prior to purification, we can find a new peak at $1700\,\mathrm{cm}^{-1}$, which belongs to the carboxylic acid group. It was introduced during purification, which had been referred to in the literature [10]. The image clearly shows that the CNTs are purified and distributed uniformly, the diameter is $10 \sim 20$ nm and the length is several micrometers.

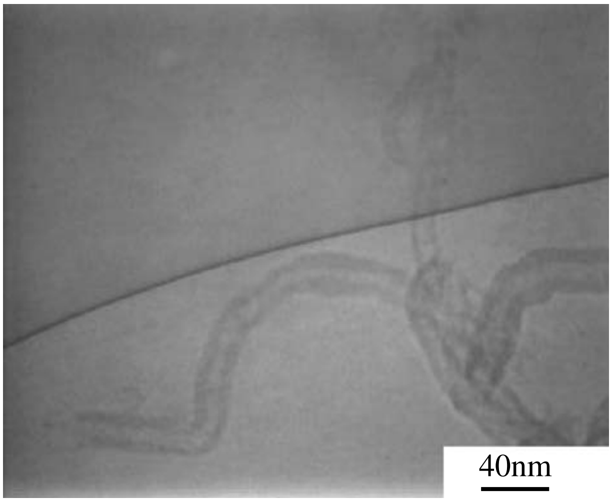

Fig. 1. TEM image of the CNTs

Electrochemical Behavior of CNTs

When the CNT modified electrode was placed into a pH 10.0 NH_3–NH_4Cl buffer solution, a pair of reduction/oxidation waves was observed as compared to the bare electrode. At a scan rate of 0.1 V/s, the cathodic and anodic peak potentials were −0.4 V and −0.03 V, respectively. The peaks might be the redox of the carboxylic acid groups introduced during purification, which had been discussed in the literature [10]. The reduction and reoxidation waves were extremely broad. Similarly to the microelectrode reported previously [7, 8], the background current was apparently large. This might be attributed to the increased surface area due to the catalytically active surface and high aspect ratio (length over diameter) of carbon nanotube. In a series of different media, such as HAc-NaAc, B.R., KCl, Na_2SO_4, KH_2PO_4–Na_2HPO_4, sodium citrate, and potassium acid phthalate, the electrochemical behavior is similar to that in NH_3–NH_4Cl. The electrochemical behavior in different pH values of NH_3–NH_4Cl showed that with increasing pH both the cathodic and anodic peak potentials shifted negatively, which is in accordance with the literature [10].

Electrochemical Behavior of 6-Benzylaminopurine

Cyclic Voltammetry of 6-Benzylaminopurine

The cyclic voltammetry behavior of 6-benzylaminopurine at a bare GC and CNT-modified GC was studied. Figure 2 shows the cyclic voltammetry of 1.0×10^{-4} mol · L^{-1} 6-benzylaminopurine in pH 10.0 NH_3–NH_4Cl. Only an oxidation peak at about 0.65 V can be seen, which indicates that the oxidation of benzylaminopurine is irreversible. Comparing the response on the modified GC with bare GC, the peak current increased greatly, suggesting that the CNT's film enhanced the preconcentration of benzylaminopurine. When scanned sequentially, the current decreased a little and became stable after several cycles, from which we can deduce that 6-benzylaminopurine had been adsorbed on the electrode surface.

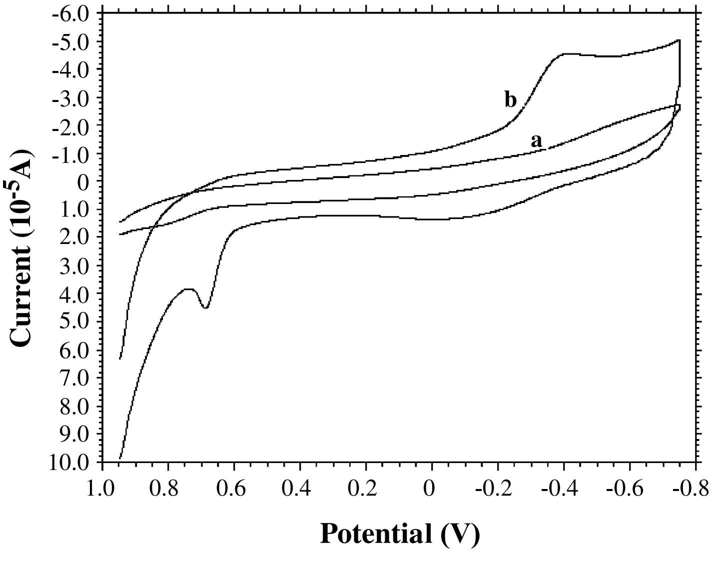

Fig. 2. Cyclic voltammograms for 1.0×10^{-4} mol · L^{-1} of benzylaminopurine (a) bare GC (b) CNT-modified GC. Scan rate 0.1 v s^{-1}

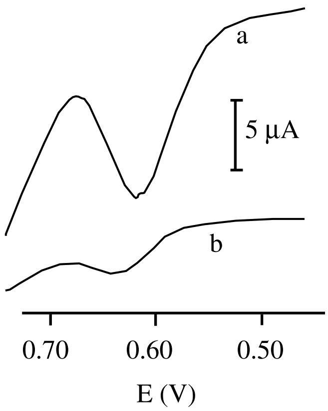

Fig. 3. The semi-derivative (a) and normal (b) linear sweep voltammograms of 1.0×10^{-6} M benzylaminopurine

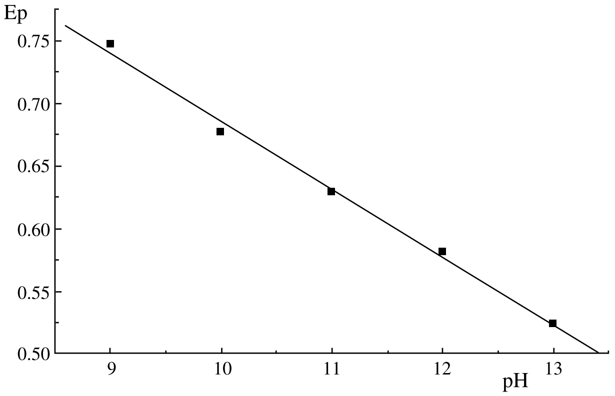

Fig. 4. Relationship between pH of NH_3–NH_4Cl and peak potential (Ep)

A lot of media were tried out, and the results showed that in NH_3–NH_4Cl the peak was sharp and the current was the largest, so it was chosen for further study. The effect of other factors on the peak were also investigated. Figure 3 shows semi-derivative and normal sweep voltammograms for $1.0 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$. 6-benzylaminopurine with a CNT modified electrode. A higher stripping peak (a), which increased linearly with increasing benzylaminopurine content, appeared at 0.62 V measured with semi-derivative voltammetry, and a smaller one (b) appeared at 0.65 V with normal linear sweep voltammetry under the same conditions. It is obvious that semi-derivative voltammetry improves the sensitivity for determination of trace amounts of benzylaminopurine.

Furthermore, the electrochemical behavior of 6-benzylaminopurine was studied by cyclic voltammetry at a Pt electrode modified with CNTs, and the results were the same as those obtained from a CNT modified GC electrode. The results indicate that the potential range of a Pt electrode could be expanded toward either positive or negative.

Influence of pH

In NH_3–NH_4Cl solution the effect of pH on the response of 6-benzylaminopurine was investigated by CV. With increasing pH, the anodic peak potential shifted negatively. From the analysis of pH variation, a linear relation was obtained between the peak potential and pH (Fig. 4), indicating the participation of the protons in the reaction of electro-oxidation. For pH levels between 9.0 and 13.0, the linear dependence fits the equation: $\mathrm{Ep} = 1.23–0.054\ \mathrm{pH} \sim \mathrm{R} = 0.998$. The peak current also changed with an increase in pH. First it increased, and then it decreased, arriving at the maximum of $\mathrm{pH} = 10.0$. It was therefore chosen for further study.

Influence of the Scan Rate (v)

With an increase in v, the peak potential shifted positively, and in the range of 10–200 mV/s the relationship was $\mathrm{Ep} = 0.576 + 0.022 \ln v$. In the concentrated solution, the peak current is proportional to $v^{1/2}$ in the range of 10–100 mV/s, indicating a diffusion-controlled reaction. In thin solution, the peak current is proportional to v, which also suggested the adsorption of 6-benzylaminopurine on the electrode.

Influence of Temperature

In the range of 15–500 °C with the temperature increasing, the peak potential shifted negatively, and the peak current increased slowly. This suggested that the increase in temperature accelerated the oxidation of 6-benzylaminopurine on the electrode surface.

Influence of the Surfactants

The stripping signal is also affected by surfactants. Experiments proved that surfactants such as OP, Tribon-100, sodium dodecyl benzene sulfonate, carboxymethyl cellulose, etc. strongly depressed the peak current. It can be deduced that the 6-benzylaminopurine was adsorbed on the electrode surface. When the surfactants exist, competitive adsorption was produced on the surface of the electrode, causing the stripping current of 6-benzylaminopurine to be depressed.

Analysis of Stripping Voltammetry of 6-Benzylaminopurine

Influence of the Amount of CNTs

The amounts of CNTs used for preparing the modified electrode also affect the peak current. Comparative tests using various amounts of CNTs (2 μL, 3 μL, 4 μL, 5 μL and 6 μL) were conducted. The results showed that the amount of 3 μL was the best. It was therefore chosen for further study.

Influence of the Accumulation Potential

The study of the accumulation potential at which pre-concentration was affected was performed between -0.2 V and 0.6 V. It was found that the peak current arrived a maximum of 0 V, so an accumulation potential of 0 V was chosen for the subsequent determination. After each stripping experiment, the electrode surface must be renewed. It was found that the surface of the electrode can be renewed after each electrochemical measurement, if the electrode was cycled in the NH_3–NH_4Cl buffer solution for several cycles.

Influence of the Accumulation Time

The effect of accumulation time had a great influence on the height of the peak current during which the potential of 0 V was applied. We used a solution of 5.0×10^{-7} mol L^{-1} 6-benzylaminopurine and accumulated different times. The result is shown in Fig. 5. It is obvious that the peak current increased linearly up to 180 s, after which it turned stable.

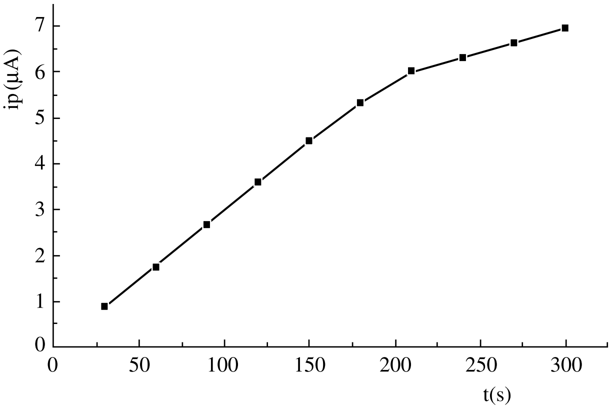

Fig. 5. Relationship between accumulation time t (s) and peak current ip (μA)

Reproduction and Stability of the CNT Modified Electrode

In the experiment the electrode surface is easily renewed. The results of six times cleaning/accumulating/measuring showed that reproduction is good with a deviation of 0.49%. The peak current was still unchanged even after a week with the same electrode, which suggests that the electrode is stable.

Calibration Curve

Voltammograms at different concentrations of 6-benzylaminopurine were recorded using the optimum conditions. From this experiment, linear calibration plots were obtained for the oxidation peak current in a concentration range of 4.0×10^{-8} to 1.0×10^{-5} mol L^{-1}, using an accumulation potential of 0 V, pH 10.0, and a pre-accumulation time of 1 min. The peak current depends on the concentration according to the equation $ip\ (\mu A) = 0.45 + 1.90\,c\ (\mu mol\,L^{-1})$, correlation coefficient, $r = 0.997$. The detection limit was found to be 5.0×10^{-9} mol L^{-1} in 5 mins accumulation time.

Interference

In a 2.0×10^{-6} mol L^{-1} 6-benzylaminopurine solution, some inorganic and organic compounds were experimented with. The results showed that a 100-fold amount of Ca^{2+}, Mn^{2+}, Cd^{2+}, Zn^{3+}, Cu^{2+} and ascorbic acid, cystine serine, citrulline, tryptophane, benzoic acid, glycine, dopamine and tyrosine did not interfere with the determination of 6-benzylaminopurine, which suggest that the modified electrode has a strong resistance to interferences.

Determination of the Samples

The surface of the fruits was squirted with the 6-benzylaminopurine solution, and after some time they were dipped in NH_3–NH_4Cl. Then the electrochemical experimental was performed to determine the content under optimum conditions. We also found that in

Table 1. Determination of 6-benzylaminopurine

Number of samples	Found (mol L^{-1})	UV (mol L^{-1})
1	1.79×10^{-5}	1.90×10^{-5}
2	1.43×10^{-6}	1.35×10^{-6}
3	7.26×10^{-6}	7.60×10^{-6}

UV spectra, 6-benzylaminopurine has its maximum absorption at 272 nm and there were no interferents in the sample, so the content was also determined with this method. The results obtained by our method agree well with those obtained by UV as shown in Table 1.

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