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A selective voltammetric method for uric acid detection at β-cyclodextrin modified electrode incorporating carbon nanotubes

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Received 7th May 2002, Accepted 8th August 2002 First published as an Advance Article on the web 29th August 2002

A β -cyclodextrin-coated electrode incorporating carbon nanotubes was constructed and applied to the detection of uric acid in the presence of high concentration of ascorbic acid. The major obstacle of the overlapped oxidation potential of ascorbic acid was overcome owing to the distinct ability of the carbon nanotubes-modified electrode to yield a large anodic peak difference *ca*. 400 mV. The sensitive detection of uric acid has been further improved by the formation of a supramolecular complex between β -cyclodextrin and uric acid. A linear calibration curve was obtained for 5×10^{-7} to 5×10^{-5} M in 0.2 M HAc–NaAc buffer (pH 4.5) with correlation coefficient of 0.998 and detection limit of 0.2 μ M. The practical analytical application was illustrated by a selective measurement of uric acid in human urine without any preliminary treatment.

Introduction

Owing to their novel structural, electronic, mechanical and chemical properties, carbon nanotubes (CNT) are likely to have many potential applications.^{1,2} Depending on their atomic structure, CNT behave electrically as a metal or as a semiconductor. The subtle electronic properties suggest that CNT have the ability to promote electron-transfer reactions when used as an electrode in chemical reactions. Using nanomaterials to modify electrodes, in addition to the common effects of the inherent physical and chemical properties that are introduced, special properties such as the large specific surface area and the abundant functional groups help them to show specific catalytic action.³⁻⁵ It has been reported that the microelectrode was constructed from an individual single-wall carbon nanotube (SWNT) and its voltammetric response was characteristic of steady-state radial diffusion.⁶ An electrode constructed from multi-wall carbon nanotube (MWNT) mixed with bromoform can be used to catalyze the oxidation of dopamine (DA)7 and showed a favorable reversible electrochemical response to cytochrome c and azurin.⁸ The activity of enzymes can be stabilized well using CNT immobilization.9 A carboxylic SWNT solution was cast on a glassy carbon electrode to form a CNT film, which showed very stable electrochemical behavior and can be used to catalyze the electrochemical reactions of some biomolecules such as DA, epinephrine, ascorbic acid (AA),10 and 3,4-dihydroxyphenylacetic acid.11 DA and AA, however, have similar anodic peak potential ($E^{DA}pa = 0.182 \text{ V}, E^{AA}pa = 0.16 \text{ V}$).¹⁰ Surprisingly, very little research has been devoted to the application of nanotubes for chemical separation and molecular recognition. Recently, a voltammetric separation of DA and AA with the anodic peak difference ca. 270 mV has been reported with cyclic voltammetry at two kinds of carbon nanotubes-modified electrodes (coated and intercalated) in our group.¹² No other papers seem to have reported on the application of CNT for the voltammetric detection of uric acid (2,6,8-trihydroxypurine, UA), and this prompted us to investigate the electrocatalytic behavior of UA in the presence of AA at CNT-modified electrode.

In addition to these intrinsic, structurally induced differences of CNT, intercalation of CNT provides a route by which the electronic properties of CNT can be engineered, in analogy with the well-known examples of the graphite intercalation compounds and C_{60} . Alkali insertion by vapor^{13,14} or electro-chemical doping¹⁵ dramatically changes the electronic properties of SWNT, such as the conductivity and spin susceptibility due to charge transfer between the alkalis and the carbon host. It has been reported that a thermoelectric 'nano-nose' has been built from tangled bundles of SWNT, and the response is specific to the detail of the interaction of the adsorbed molecule with the nanotube wall.¹⁶ It is experimentally proved that the aggregated pores in MWNT play a much more important role in their adsorption and capillarity of nitrogen than other kinds of pores in some cases.¹⁷ Redox proteins immobilized on and within MWNT.9 So, aimed at improving the recognition ability of CNT, β -CD firstly immobilized with MWNT in the present work.

Uric acid, the primary end product of purine metabolism, and ascorbic acid (AA) are both present in biological fluids such as blood and urine. It has been shown that extreme abnormalities of UA levels are symptomatic of several diseases.¹⁸ As UA is electrochemically active at a carbon-based electrode, its electrochemical detection becomes one of the feasible methods.¹⁹ Earlier electrochemical procedures based on the oxidation of UA at carbon-based electrodes in acidic solutions suffered from interference from AA which can be oxidized at a potential close to that of UA.²⁰ Various methods, such as an adsorption/medium exchange approach,²¹ enzyme-based techniques,^{22,23} chemically modified electrode^{24–30} were developed to solve the UA detection problem. Until now, sensitive and selective methods still needed to be developed for the detection of UA due to its clinical significance.

Cyclodextrin (CD) is a macrocyclic glucose oligomer, consisting mostly of six, seven or eight D-glucose units forming α -, β - or γ -CD, respectively.³¹ It can bind a variety of guest

molecules inside their torus-shaped cavities and serve as a model host site. The interaction of molecular cavities with reactive guest molecules has been widely investigated with the aim of bringing more light to the specific recognition effects and reaction selectivity.

In this article, based on providing a new interfacial architecture that involves CNT and CD, we report the effect on selectivity and sensitivity during determination of UA in the presence of AA at β -CD-modified electrode incorporating CNT and its differential pulse voltammetric determination. The modified electrodes exhibited an attractive ability to separate UA and AA effectively and further greatly increased the sensitivity of UA.

Experimental

Apparatus

Cyclic and differential pulse voltammetric (CV and DPV) experiments were performed using a CHI-660 electrochemical workstation (CH, USA) with a conventional three-electrode cell. The working electrode was a graphite electrode or modified graphite electrode with an electrode area of 19.62 mm², the auxiliary electrode consisted of a platinum wire and the reference electrode was a saturated calomel electrode (SCE). All the potentials given in this paper were measured *versus* SCE. Scanning electron microscope (SEM) image was obtained using a thermal field emission scanning electron microscopy (LEO 1530, Germany). Fourier transform (FT) IR spectra were recorded on a Perkin-Elmer Spectrum GX spectrometer.

Chemicals

All reagents were of analytical-reagent grade. Uric acid was obtained from Merck. Ascorbic acid, β -CD and α -CD were purchased from Sigma. High-purity nitrogen was used for deaeration. All solutions were prepared with doubly distilled water. Spaghetti-like multi-wall CNT with an external diameter of 10 nm, denoted CNT, was kindly provided by Prof. Fan's research group (prepared by CVD method, purity >95%, Physics Department, Tsinghua University, Beijing, China). An experimental sample denoted CNT-1 (functionalized with carboxylic acid groups^{32–34}) was prepared as follows: 0.05 g CNT specimen was dispersed in 60 ml mixture of concentrated HNO₃ and H₂SO₄ (1 + 3 v/v) with the aid of ultrasonic agitation for 4 h in a water bath, then washed with distilled water to neutrality and finally dried.

Preparation of β -CD-coated electrodes incorporating CNT (β -CD/CNT/CE)

A pyrolytic graphite electrode was carefully polished with emery paper and chamois leather containing Al₂O₃ slurry (0.05 µm after 0.3 µm) and then ultrasonically cleaned in distilled water. The clean electrode was dried under an IR lamp and then smoothed on a weighing paper. One milligram of CNT was dispersed for 10 min with the aid of ultrasonic agitation in 10 ml β -CD aqueous solution (2%) to give a 0.1 mg mL⁻¹ black solution. A β -CD/CNT/CE was prepared by dropping 7 µL of the black solution with a finnpipette (2–20 µL volume) on the graphite electrode surface and then heating under an IR lamp to remove the solvent.

Procedures

All experiments were carried out at room temperature ($\sim 20 \,^{\circ}$ C) under nitrogen atmosphere. CV employed a scan rate of 50 mV

 s^{-1} . DPV were performed with pulse potential 50 mV, pulse duration 50 ms and pulse period 0.2 s. A 0.2 M HAc–NaAc buffer solution (pH 4.5) was used as a supporting electrolyte.

Results and discussion

Surface morphology

Homogeneous spaghetti-like CNT with a diameter of 10 nm can be observed at high magnification (Fig. 1 shows the SEM image of β -CD/CNT/CE), with a number of randomly tangled CNT to form stereo-porous interspaces, for the subtle tubule structure of carbon nanotubes.

Electrocatalytic behavior of UA at β-CD/CNT/CE

The role of CNT was: (i) to transfer electrons between the electrode surface and UA based on the intrinsic property of CNT; (ii) to increase the conductive area based on the high specific surface of CNT; (iii) for CD doping into the modified layer since CD cannot be directly modified at bare graphite electrode due to its solubility. When CD with a diameter of less than 1 nm mixed with CNT in the case of ultrasonic agitation, they would penetrate the aggregated pores (distributed, 20-40 nm) which were formed by the interaction of isolated MWNTs due to van der Waals force,17 and be adsorbed and attached to the wall of CNT. CD can immobilize in the aggregated pores of CNT due to steric hindrance and the binding force. To verify the case of CD immobilization, a preliminary experiment was performed. The β -CD/CNT sample was washed extensively with distilled water, and then dried. The microscopic FTIR spectra of the sample of β -CD/CNT were shown in Fig. 2. In the range from 1000 to 1180 cm⁻¹, the FTIR spectrum of CNT showed no sharp absorbance peaks, and the FTIR spectrum [Fig. 2(b)] showed three typical peaks of β -CD at 1157, 1080 and 1031 cm⁻¹.^{35,36} Compared with the spectrum of β -CD, the microscopic FTIR spectrum of β-CD/CNT showed a new peak at 1112 cm⁻¹, while a peak at 1157 cm⁻¹, corresponding to the C-O-C stretching vibration, showed much less intensity. It is speculated that β -CD attached to the CNT wall, and the lone electron pair of the oxygen atom (C–O–C) in the β -CD ring conjugate with the carbon p electron of CNT due to the mesomeric effect, resulting in the peak of C-O-C stretching modes shifted to a lower wavenumber. Another interaction may originate in hydrophobic property. The surface of carbon nanotubes is substantially more hydrophobic and may interact strongly with the non-polar regions of β -CD.

The CVs of UA at β -CD/CNT/CE, CNT/CE and a bare graphite electrode (GE) are shown in Fig. 3. As can be seen, UA



Fig. 1 SEM image of the $\beta\text{-CD/CNT/CE}$ surface. Magnification $\times 150000.$

gives a broad and small CV peak response at 0.45 V at the bare electrode [Fig. 3(a)], while CNT/CE and β -CD/CNT/CE leads to a spiky anodic peak at the same potential, and the peak current increased greatly. The interesting aspect of the CNT electrode is the large background current attributable to the catalytically active surface. The reason for the better performance of the CNT-modified electrodes may originate in the nanometer dimensions (of the tubes, the channels that are inherently present in the tubes and the pores that are formed by the interaction of isolated MWNTs), the electronic structure and the topological defects present on the tube surfaces. The high aspect ratios³⁷ of the tubes may also present a steric (template) effect for biomolecules for more efficient oxidation reactions. The oxidation peak height of UA at β -CD/CNT/CE is the highest, which means the concentration of UA at β -CD/CNT/ CE was higher than that at CNT/CE. It can be explained that the CD–UA apparent concentration in the β -CD/CNT/CE film was much higher due to the β -CD encapsulation effect of UA.²⁶ Then, β-CD-UA complex in β-CD/CNT/CE dissociated and diffused rapidly through the porous layer of CNT to the graphite surface. These phenomena demonstrated that β -CD/CNT/CE not only showed the advantage of CNT, but also exerted the ability of β-CD including organic molecules. The anodic peak current I_{pa} exhibited a linear dependence on the square root of 5 to 500 mV s⁻¹, which is typical for the signal of a diffusioncontrolled electrode process.



Fig. 2 Microscopic FTIR spectra of solid (a) β -CD/CNT, (b) β -CD and (c) CNT.



Fig. 3 CVs of 2×10^{-5} M UA at the bare electrode (a), CNT/CE (b), β -CD/CNT/CE (c). Electrolyte: 0.2 M HAc–NaAc solution (pH 4.5). Scan rate: 50 mV s⁻¹.

The pH of the solution has a significant influence on the UA oxidation at β -CD/CNT/CE by altering both the peak current and peak potential. Fig. 4 illustrates the dependence of the DPV peak potentials of the UA on the pH. The slope of the *E*–pH dependence is -60.6 mV pH^{-1} , which indicates that the number of electrons and protons involved in the UA oxidation mechanism is the same. As UA oxidation is a two-electron process, the number of protons involved is also predicted to be two. Therefore, a mechanism of the UA oxidation can be proposed in Scheme 1.

Differential pulse voltammetry of UA at $\beta\text{-CD/CNT/CE}$ in the presence of AA

Fig. 5 shows a series of DPVs of a UA/AA binary mixture. Only one rather broad and small wave at 0.30 V appeared at the bare electrode [Fig. 5(a)]. Preliminary tests employing a modified electrode showed an interesting behavior in the presence of UA



Fig. 4 Dependence of the peak potential of UA on pH in DPV.



Scheme 1 Mechanism of UA oxidation at β -CD/CNT/CE.



Fig. 5 DPVs of a mixture of 2×10^{-5} M UA and 8×10^{-4} M AA at bare electrode (a, solid line); α -CD/CNT/CE (b, dash-dotted line); CNT/CE (c); β -CD/CNT/CE (d).

and AA. The current enhancement was remarkable and in addition, a decrease in the oxidation potential of AA occurs. AA and UA can be discriminated with a large anodic peak potential difference ($\Delta E \ge 360 \text{ mV}$), which were large enough for the selective determination of UA. The results showed the prominent role of CNT for distinguishing UA from AA. The electrocatalysis of CNT-modified electrodes toward AA was mainly attributed to the stereo-porous interfacial layer of CNT discussed in detail in ref. 12. The negative shift of AA may occur for different reasons, and another possible explanation is the kinetic effect.³⁸ When using macrocyclic compounds as a doping reagent, the changes of two variables (potential and current) showed as follows: E_{pa}^{UA} had little change, whereas $E_{\rm pa}^{\rm AA}$ at α -CD/CNT/CE shifted positively compared with that at CNT/CE [Fig. 5(b)]. The anodic peak current ratios of UA/ AA differed considerably (listed in Table 1), and the highest current response towards UA occurred at β -CD/CNT/CE [Fig. 5(d)]. As β -CD showed more affinity towards UA than α -CD did, β -CD/CNT/CE increased the sensitivity for UA. While α -CD showed more affinity towards AA, higher sensitivity of AA at α -CD/CNT/CE was obtained compared with UA. These phenomena further demonstrated that carbon nanotubes being coupled with CD could enhance the molecular recognition function.

Fig. 6 showed DPVs of UA and AA at different pH values. It can be seen that the ΔE_{pa} has decreased from 0.412 through 0.408 to 0.384 V, corresponding to pH 3.6, 4.5 and 6.0. The peak current maximum for UA is at pH 4.5. A mechanism is proposed of β -CD sensitivity determination of UA in the presence of AA. In the buffer solution of pH 4.5, AA exists in a monoanionic form, while UA exists in a neutral form, since their pK_a values are 4.1 and 5.4, respectively. As neutral UA interacts more strongly with β -CD than HA⁻, β -CD immobilized on the CNT/CE encapsulates UA, while it repels HA⁻ being thus sensitive with respect to UA. At pH 3.6, UA and AA both exist in a neutral form, and thus β -CD encapsulates UA under the case of existence of competition with AA, resulting in a decrease of the sensitivity for UA.

 Table 1
 Effect of macrocyclic compounds as doping reagents on the electrochemical behavior of DPV at CNT/CE

Electrode	$E_{\rm pa}^{\rm UA}/{\rm V}$	$E_{\rm pa}^{\rm AA}/{\rm V}$	$\Delta E_{\mathrm{pa}}/\mathrm{V}$	$I_{\rm UA}/I_{\rm AA}$
CNT/CE	0.400	0.012	0.388	0.60
α-CD/CNT/CE	0.408	0.056	0.352	0.48
β-CD/CNT/CE	0.404	0.004	0.400	1.18

Fig. 6 DPVs of a mixture of 2×10^{-5} M UA and 8×10^{-4} M AA at different pH values. (a) pH 6.0, (b) pH 4.5, (c) pH 3.6.

Effect of functionalized CNT on the electrochemical behavior of UA in the presence of AA

To study the effect of the functional groups (attached to CNT by treating with acid) on the electrochemical behavior, IR and DPV experiments were further performed, which has been shown in Fig. 7 and Fig. 8, respectively. As we can see in Fig. 7, the signal at 1635 cm⁻¹ attributed to contaminating water; two peaksone at 1557 cm⁻¹ and a broader one at *ca*. 1152 cm⁻¹—were assigned to the carbon skeleton.³⁹ One peak at 1713 cm⁻¹ was associated with C=O stretching of carboxylic acids, which occurs in the CNT-1 specimen. These results indicated that concentrated acid could oxidize CNT to attach a carboxylic acid group under the present conditions. Fig. 8 shows the DPVs of UA at β -CD/CNT/CE and β -CD/CNT-1/CE in the presence of AA. Compared with the case of β -CD/CNT/CE [Fig. 8(a)], the β -CD/CNT-1/CE response towards UA decreased and the potentials of AA shifted positively with a worsened wave [Fig. 8(b)]. It might be explained that the carboxylic acid group of CNT-1 enhances the electrostatic repulsion towards negatively charged AA and decelerates the oxidation reaction. On the other hand, the carboxylic acid group of CNT-1 suppresses the β -CD immobilized on CNT to some extent and lowers the sensitivity for UA.

Analytical application for the determination of UA

As the charging current contribution to the background current is a limiting factor in the analytical determination, experiments



Fig. 7 FTIR spectra of CNT-1 (a) and CNT (b).



Fig. 8 DPVs of a mixture of 2×10^{-5} M UA and 8×10^{-4} M AA at β -CD/CNT/CE (a) and β -CD/CNT-1/CE (b).





Fig. 9 DPV recordings of UA at β -CD/CNT/CE. UA concentration (μ M): (a) 1, (b) 6, (c) 11, (d) 21, (e) 31, (f) 41, (g) 51. Inset: graph of current *vs.* UA concentration.

Table 2 Influence of potential interferents on the UA response. UA concentration = 20 μM

Interferent	Concentration/mM	Signal change ($i_{\text{UA}} = 100\%$)
AA	1.0	-0.5
Cytosine	0.1	-2.1
Cysteine	0.1	-1.2
Purine	0.1	+0.4
Urea	0.2	-1.5
Glucose	0.2	-1.8
Oxalate	0.5	+0.7
Acetaminophen	0.05	+1.5

were carried out using the DPV technique. The oxidation peak current was related to the concentration of UA. A linear relation between I_{pa} and the UA concentration was over the range of 5 × 10⁻⁷ to 5 × 10⁻⁵ M, the slope was 2.7 µA µM⁻¹, with a correlation coefficient of 0.998 (Fig. 9). The detection limit was 0.2 µM UA at the signal to noise ratio equal to 3. The slope of the calibration curve of UA in the presence of 5 × 10⁻⁴ M AA was the same as that obtained for the species alone, confirming that no interaction occurs between AA and UA.

Since the procedure of electrode preparation was easy and rapid, it was not so important for the electrode to be stable for a prolonged period of time. However, we checked its lifetime of β -CD/CNT/CE. Our experiment has demonstrated that the β -CD/CNT film retained 98% of its initial response after 4 d of storage in dry conditions. Such stability seems to be acceptable for most practical applications. Practical work required the electrode to be reversible, *i.e.*, able to be used many times in samples with different analyte concentrations. Because of the porous structure, AA and UA could easily penetrate into the interfacial layer that would affect the subsequent measurements. But it was found that the renewal of the electrode surface was easily accomplished by soaking the modified electrode in a buffer and cycling its potential between -0.2 V and 0.8 V ca. 3 scans, which indicated that UA and AA at β-CD/CNT passed in and out rapidly and adsorbed little. The reproducibility was measured with the same electrode, using the renewal way after each use, and the RSD were 1.5% (n = 7). The modified electrode was prepared repeatedly five times, and the RSD was 0.78%.

The interference effect was studied. As AA is a serious interferent, its effect was investigated in detail previously. A few other common co-existing substances were examined for their effect on the determination of 20 μ M UA. There was no substantial change in the peak current. The data are summarized in Table 2.

Table 3 Determination of UA in urine samples with β -CD/CNT/CE^a

	Urine 1	Urine 2	Urine 3
Detected/µM	10.99	9.83	12.34
Spike/µM	10	10	10
After spike/µM	21.12	19.48	22.10
Recovery (%)	100.6	98.2	98.9
Total value ^b /mg L-1	369.51	330.50	414.90
^{<i>a</i>} Number of samples as	309.31 saved 5. ^b Tota	330.30 l value was obtaine	414.90 d by multiply

the detected value and the dilution factor.

As an example of the analytical performance of the modified electrode, the method was applied to the direct analysis of urine samples. Three human urine samples from laboratory personnel were determined with the method presented above. To fit into the linear range, all the samples used for detection were diluted 200 times. The dilution process can actually help reducing the matrix effect of the urine samples. The results obtained are listed in Table 3. To ascertain the correctness of the results, the samples were spiked with certain amounts of UA in about the same concentration as found in the samples themselves. The recovery rates of the spiked samples were determined and ranged between 98 and 101% for urine.

Conclusions

The modification of the electrode surface by carbon nanotubes reduced the overpotential of AA by obtaining a large peak potential difference of UA and AA ($\Delta E = 0.40$ V), and the incorporation of β -CD with CNT significantly increased the sensitivity of UA. The linear dependence of the DPV peak current on the UA concentration over the range of 5×10^{-7} to 5×10^{-5} M can be used for the determination of UA with a low detection limit of 2×10^{-7} M. Using a macromolecule as a dispersant, the coated layer of CNT showed the sensitive, steady and repetitive ability for the determination of UA. With its low cost and ease of preparation, the β -CD-modified electrode incorporating carbon nanotubes will hopefully be of good application for further sensor development.

Acknowledgements

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (Grant No. 20075015). They thank Dr Jiang and Professor Fan for providing carbon nanotubes species.

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