

Electrocatalysis at a Thin Multi-Wall Carbon Nanotube Film Modified Glassy Carbon Electrode

J. Fei, Y. Sun, S. Hu and Z. Gao^{1*}

Department of Chemistry, Wuhan University, Wuhan, 430072, China.

¹Institute of Bioengineering and Nanotechnology, 51 Science Park Road, Singapore 117586 Republic of Singapore, *Corresponding author: zqgao@ibn.a-star.edu.sg

ABSTRACT

A sensitive and selective amperometric procedure, based on a glassy carbon electrode (GCE) modified with a thin multi-wall carbon nanotube (MWNT) film, for the determination of ascorbic acid (AA) was developed. The modified electrode showed excellent electrocatalytic activity towards the oxidation of AA. The oxidation potential of AA shifted negatively by as much as 460 mV to -18 mV (vs. SCE) at the modified electrode. Experimental variables were investigated and optimized. Amperometric tests of AA were performed at -10 mV. A linear response was obtained in the range of 5.0×10^{-6} to 4.0×10^{-3} M with a detection limit of 2.0×10^{-6} M. Interference studies indicated that the modified electrode is highly selective to AA in a mixture of AA, uric acid and dopamine. The proposed procedure was applied to the determination of AA in pharmaceutical and food samples with little or no sample pretreatment.

Keywords: Carbon nanotube, voltammetry, amperometry, electrode, ascorbic acid

INTRODUCTION

There has been much interest in the research of carbon nanotubes since their discovery.¹ Carbon nanotubes are molecular-scale wires with high electrical conductivity, good chemical stability and excellent mechanical strength and modulus.² Utilization of these properties has found applications of carbon nanotubes in scanning probes, nanoelectronic devices, batteries, potential hydrogen storage material and chemical sensors.² Generally, carbon nanotubes consist two categories: single-wall carbon nanotubes (SWNTs) and multi-wall carbon nanotubes (MWNTs). The subtle electronic behavior of carbon nanotubes reveal that they have the ability to promote electron-transfer when used as electrode material in electrochemical reactions.^{3,4,5} Since they are insoluble in most solvents, attaching carbon nanotubes to an electric circuit in a controllable manner is still a technical challenge. The MWNTs have been used to fabricate carbon nanotube modified electrodes by mixing them with binders such as bromoform, mineral oil or liquid paraffin. The resulting electrodes have been used in the electrochemical

oxidation of dopamine,³ electrocatalysis of O_2 ⁴ and electrochemistry of protein.⁵ SWNTs have been dispersed into DMF and cast on carbon electrodes to form carbon nanotube films. These films exhibit stable electrochemical behavior and are used to catalyze electrochemical oxidations of some biomolecules, such as dopamine, epinephrine, ascorbic acid (AA), and cytochrome *c*.⁶ The evaporation of DMF is very slow, and therefore the formation of carbon nanotubes films requires a long waiting time or heating of the electrode surface. Moreover the resulting films are brittle.

It is well known that AA exists extensively in fruits and is involved in many biological reactions. Recently, there has been a considerable effort in the development of voltammetric procedures for the determination of AA selectively and sensitively in biological systems and foodstuff. It is generally believed that direct electrooxidation of AA at bare electrodes is irreversible and requires high overpotentials. Furthermore, direct oxidations of uric acid (UA) and dopamine (DA) take place at potentials similar to that of AA. Electrochemical determination of AA therefore often suffers from interferences from these species. To differentiate voltammetric responses of these species and accurately determine each of them in a mixture, Gao *et al.* fabricated an ultrathin polypyrrole-teradecyl sulfate film modified gold electrode for simultaneous voltammetric determinations of UA, DA and AA.⁷ It was observed that all three species were resolved and determined voltammetrically at the modified electrode.

In this work the voltammetric response of AA at the MWNT film modified GCE was investigated. MWNTs were easily dispersed into water in the presence of an anionic surfactant, dihexadecyl hydrogen phosphate (DHP). The stable suspension of MWNTs was cast on GCE to form a carbon nanotube film after the solvent was evaporated. The electrochemical behavior of AA at SWNT modified electrodes has been previously reported.⁶ The oxidation peak potential of AA was observed at about 0.16 V (vs. SCE), which overlaps with that of DA (0.18 V). Compared to the SWNT film modified electrode, the MWNT film modified electrode not only exhibited stronger catalytic activity toward the oxidation of AA, but also resolved the overlapping voltammetric responses of UA, DA, and AA into three independent voltammetric peaks. Thus, a sensitive and selective procedure based on the MWNT film

modified electrode for the amperometric detection of AA was developed.

EXPERIMENTAL SECTION

The multi-wall carbon nanotubes (obtained from the Institute of Nanomaterials, Central China Normal University, China) were synthesized by a catalytic pyrolysis method and purified with hot concentrated HNO_3 .⁸

2.5 mg of the purified MWNTs and 5.0 mg of DHP were mixed with a 5.0 ml of doubly distilled water. A homogeneous and stable suspension of MWNT-DHP was achieved with the aid of ultrasonic agitation. The GCE was coated by casting a 5.0 μl aliquot of the MWNT dispersion and dried under ambient conditions. The amount of MWNT on the GCE surface was about 0.036 mg cm^{-2} . The freshly prepared modified electrode was activated in a phosphate buffered saline (PBS) solution by repetitive potential cycling between -0.40 and 0.80 V .

Voltammetric measurements were performed with a model CHI 660A electrochemical workstation (CH Instruments, Austin, USA) at room temperature. All solutions were deoxygenated with high-purity nitrogen for at least 5 min prior to each experiment. Voltammograms of AA on the modified electrode were obtained by scanning the potential at a rate of 50 mV s^{-1} . Amperometric tests were carried out at a poised potential of -10 mV .

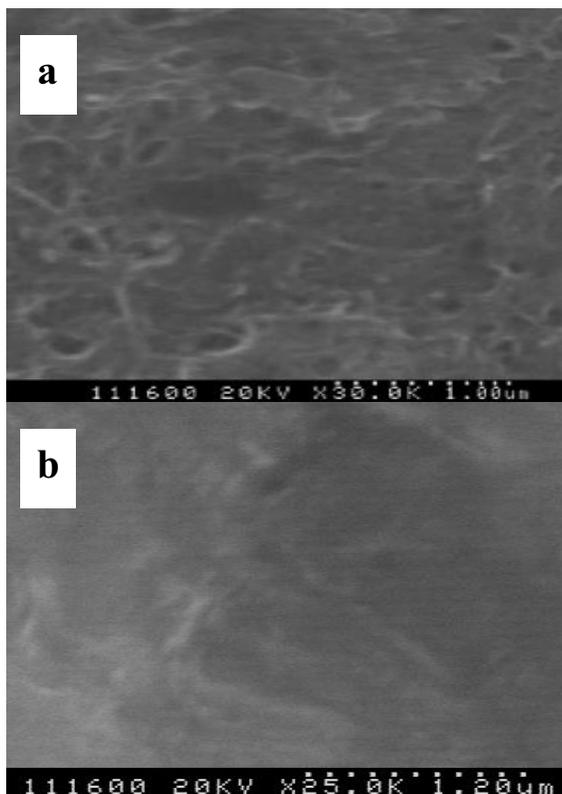


Fig. 1. (a) SEM image of a MWNT-DHP film and (b) a pure DHP film on GCE.

RESULTS AND DISCUSSION

The MWNT-DHP suspension was cast on the GCE and a SEM image of the film formed is shown in Fig. 1a. It can be seen that the GCE is completely and homogeneously coated by a thin MWNT-DHP film, with diameters of the MWNT bundles in the film spreading with a range from 20 - 40 nm. It can also be seen from this image that the MWNT-DHP film contained very small portion of amorphous carbon impurities. The SEM of a pure DHP film on a GCE is shown in Fig. 1b. As can be seen, a uniformed and compact DHP film readily forms on the GCE.

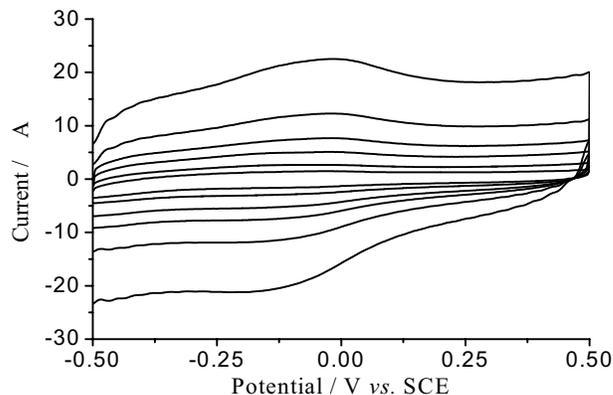


Fig. 2. Cyclic voltammograms of the MWNT film modified electrode. Scan rates from the innermost to the outermost: 50, 100, 200, 300, 500 and 1000 mV s^{-1} .

As shown in Fig. 2, when the modified electrode was immersed in PBS, a pair of reduction and oxidation waves were observed and the reduction and oxidation peak potentials were centered at 0.12 and -0.049 V , respectively. Similar to the case of MWNT microelectrodes,³⁻⁵ the reduction and oxidation waves of the MWNT film were very broad. Meanwhile, a large charging current of the modified electrode was observed, which might be due to the ultrahigh surface area of the MWNT film. Voltammetric experiments also demonstrated that the electrochemical response of the MWNT film remained very stable after numerous successive potential scans and after exposing the MWNT film to air under ambient conditions for several days. The effect of potential scan rate on the voltammetric response of the MWNT film was studied by varying the scan rate from 50 to 1000 mV s^{-1} . With increasing scan rate, both the reduction and oxidation peak currents increased linearly and the difference between the reduction and oxidation peak potentials remained unchanged even at a scan rate of 1000 mV s^{-1} , suggesting a very fast charge transfer process of the MWNT film. Voltammetric experiments at various pH showed that both the reduction and oxidation peak potentials shifted negatively with increasing pH, implying that protons are probably involved in the redox reaction of the MWNT film.

Fig. 3 shows cyclic voltammetric responses of AA at different electrodes. At a bare GCE, a broad oxidation peak was observed at 0.45 V with $E_p - E_{p/2} = 0.25$ V (Fig. 3 trace a). Compared to the bare GCE, the oxidation peak current of AA increased significantly at the modified electrode and the oxidation peak potential shifted negatively to -0.18 mV with $E_p - E_{p/2} = 0.045$ V (Fig. 3 trace c). The obvious increase in the oxidation current and the decrease in overpotential of about 468 mV for AA demonstrated unambiguously the existence of an efficient catalytic reaction between the MWNT film and AA in solution. The shift in the overpotential is due to kinetic effect, or in other words, the increase in charge transfer rate of AA, which results in the improvement of the reversibility of the electron transfer processes and the increase in oxidation current.⁹ The electrochemical behavior of AA at the pure DHP film coated electrode was also examined. As shown in Fig. 3 trace b, the oxidation of AA disappeared completely at the DHP film modified electrode. Since pK_{a1} of AA is 4.20, AA is anionic in PBS. Considering that DHP is anionic and forms a compact film on the GCE, the disappearance of the oxidation peak of AA is obviously due to the impermeable nature of the anionic DHP film to anionic AA.

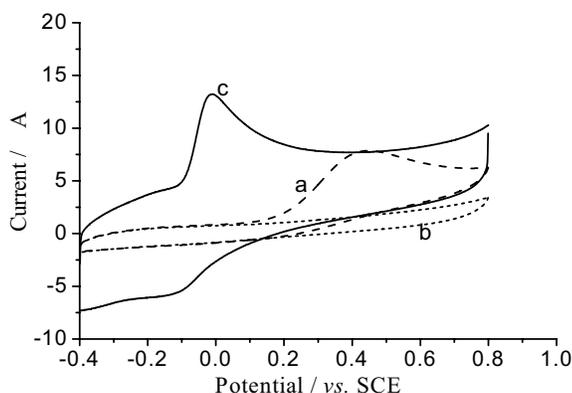


Fig. 3. Voltammograms of 5.0×10^{-4} M AA in PBS at (a) a bare GCE, (b) the DHP modified and (c) the MWNT film modified GCE. Potential scan rate: 50 mVs^{-1} .

The relationship between the amount of MWNT on GCE and the oxidation peak current of AA was studied. It was found that the oxidation peak current increases gradually with increasing the amount of MWNT and starts to level off at 0.036 mg cm^{-2} . However, the charging current increased semi-linearly with increasing the amount of the MWNT on the electrode surface. Therefore large amounts of MWNT prevent from determining AA at low concentrations. In this report, the amount of MWNT on the GCE surface was controlled at 0.036 mg cm^{-2} .

The pH of the supporting electrolyte had significant influence on the oxidation of AA at the modified electrode, altering both the oxidation peak current and potential. For examples, the oxidation peak current of AA increased with

increasing pH from 2 to 6.3, reached maximum over the pH range from 6.3 to 7.2 and decreased quickly with further increase in pH beyond 7.2

The study of the effect of pH on the oxidation peak potential (E_{pa}) of AA at the modified electrode showed a negative shift in E_{pa} with increasing pH (Fig. 4). An estimated $[E_{pa}/pH]$ of -59.4 mV pH^{-1} was obtained between pH 2.0 and 4.2, indicating that the total number of electrons and protons involved in the electrochemical oxidation of AA is the same in this pH range, whereas at higher pH the $[E_{pa}/pH]$ decreased to 30.8 mV pH^{-1} , suggesting a $2e^-/1H^+$ oxidation process.

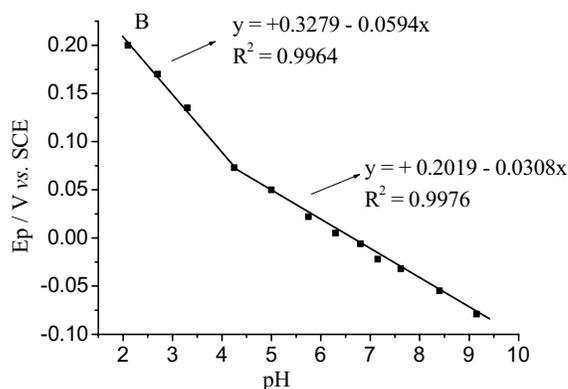


Fig. 4. Dependence of E_{pa} on pH. 5.0×10^{-4} M AA in PBS, potential scan rate: 50 mVs^{-1} .

The influence of potential scan rate on AA oxidation at the modified electrode was examined by cyclic voltammetry from 10 to 300 mVs^{-1} . It was found that the peak current of AA is proportional to the square root of the scan rate indicating that AA is undergoing a diffusion-controlled process. The oxidation peak potential of AA depended linearly on the logarithm of the scan rate according to the following equation $E_p(\text{V}) = -0.0777 + 0.0363 \log v$, $R^2 = 0.997$. From the slope of the plot, 0.0363, the value of an , where α is transfer coefficient of the oxidation of AA and n is the number of electrons transferred during the oxidation of AA, was estimated to be 0.82. As the oxidation of AA is generally known to occur via a two-electron transfer process, thus α is 0.41.

Usually, poor reproducibility (fouling) is encountered when unmodified electrodes are employed in the determination of biomolecules. Our experimental results showed that no fouling effect was observed for the determination of AA and this might be due to that AA cannot penetrate into the highly compact and conductive MWNT film and cannot adsorb on the anionic MWNT film neither. Therefore, good reproducibility is expected. For example, for a series of 10 repetitive determinations of AA, carried out in a 2.0×10^{-4} M AA solution in PBS, a RSD of 2.2% was obtained. The modified electrode also showed high stability. The voltammetric response decreased by only 3.5 % after 4 h of continuous tests.

As discussed earlier, the electrochemical determination of AA, particularly amperometric, is often affected by the oxidations of DA and UA. It is necessary to solve the problem of resolving the electrochemical oxidation processes of these species. Since the overpotential of AA oxidation was significantly reduced at the modified electrode, it is highly possible that selective determination of AA can be achieved through a careful selection of poise potential. The overall facility of the modified electrode for selective determination of AA was demonstrated in Fig. 5. As shown in Fig. 5, the presence of the MWNT film at the electrode surface resolved the mixed voltammetric response of UA, DA and AA into three well-defined voltammetric peaks at potentials of 0.29, 0.15 and -0.018 V, corresponding to the oxidations of UA, DA and AA, respectively. It was found that an applied potential of -10 mV is sufficient for amperometric determinations of AA, which is significantly lower than those using other modified electrodes. This is a considerable advantage since the number of interferences in the amperometric determination increases drastically with increasing poise potential and most interferences are expected not to be oxidized at -10 mV. Our experiments showed that additions of 5.0×10^{-4} M DA and 1.0×10^{-3} M UA have no obvious effect on the amperometric response of 1.0×10^{-5} M AA.

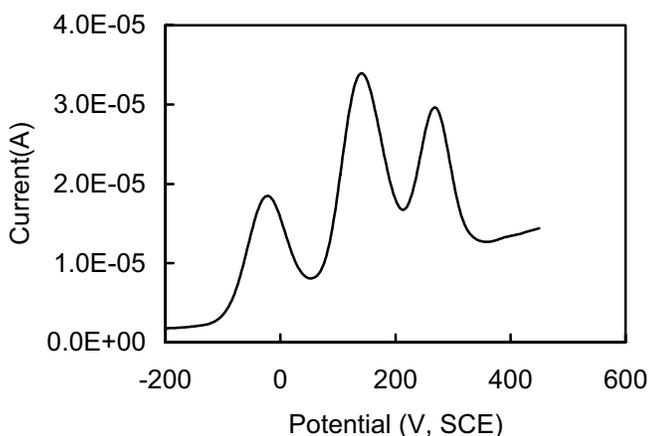


Fig. 5. Differential pulse voltammogram of 5.0×10^{-4} M UA, DA and AA the modified electrode. Potential scan rate: 10 mV s^{-1} , pulse amplitude: 50 mV .

Amperometric determinations of AA were carried out in PBS with the poise potential of -10 mV. Under optimal conditions, the amperometric response was linearly related to the AA concentration over the range of 5.0×10^{-6} to 4.0×10^{-3} M with a sensitivity of $14.2 \text{ nA}/\mu\text{M}$, an intercept of 67.3 nA and a correlation coefficient, r , of 0.998 . The limit of detection, defined as a signal-to-noise ratio of 3:1, was found to be 2.0×10^{-6} M.

To confirm the applicability of the proposed method, we have employed it to determine AA in tomato juice and multi-vitamin tablets without any sample pretreatment For the multi-vitamin tablet analysis, three tablets of 100 mg

each were finely powdered, dissolved in double distilled water and then made up to 100 ml . An aliquot of the sample solution was subsequently added to PBS and analyzed amperometrically. The results agreed well with the indicated vitamin C contents and the recoveries were found to be $97.5 \sim 101.9 \%$. Since the proposed amperometric method is very sensitive, a small aliquot of the tomato juice was adequate for the determination of AA and the average AA concentration in the tomato juice was found to be 9.85 mg ml^{-1} and the recoveries obtained were found to be $96.3 \sim 103.7\%$.

CONCLUSIONS

An MWNT film modified electrode was fabricated and used to investigate the electrochemical oxidation of AA in detail. In PBS, the modified electrode reduced the overpotential of AA oxidation and increased the oxidation current significantly, which clearly demonstrated the excellent electrocatalytic activity of the MWNT film toward the oxidation of AA. Due to a much less positive poise potential in the amperometric determination of AA, most interfering species, including DA and UA, cannot be oxidized at this potential. Thus a sensitive and highly selective amperometric procedure was developed for the determination of AA in real world samples with little sample pretreatment. Its sound results showed that the method is quite valuable and seems to be of great utility for further development.

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