Low Potential Amperometric Determination of Ascorbic Acid at a Single-Wall Carbon Nanotubes-Dihexadecyl Hydrogen Phosphate Composite Film Modified Electrode

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A sensitive and selective electrochemical method was developed for the amperometric determination of ascorbic acid (AA) at a glassy carbon electrode (GCE) modified with single-wall carbon nanotubes-dihexadecyl hydrogen phosphate (SWNT-DHP) composite film. The SWNT-DHP composite film modified GCE was characterized with SEM. The SWNT-DHP composite film modified GCE exhibited excellent electrocatalytic behaviors toward the oxidation of AA. Compared with the bare GCE, the oxidation current of AA increased greatly and the oxidation peak potential of AA shifted negatively to about –0.018 V (vs. SCE) at the SWNT-DHP composite film modified GCE. The experimental parameters, which influence the oxidation current of AA, were optimized. Under the optimal conditions, the amperometric measurements were performed at a applied potential of –0.015 V and a linear response of AA was obtained in the range from 4×10^{-7} to 1×10^{-4} mol L^{-1} and with a limit of detect (LOD) of 1.5×10^{-7} mol L^{-1}. The interferences study showed that the SWNT-DHP composite film modified GCE exhibited good sensitivity and excellent selectivity in the presence of high concentration uric acid and dopamine. The proposed procedure was successfully applied to detect AA in human urine samples with satisfactory results.

Key Words : Amperometry, Ascorbic acid, Single-wall carbon nanotubes, Electrocatalysis

Introduction

It is well known that ascorbic acid (AA) exists extensively in fruit and joins in many biological reactions. Recently there has been a considerable effort in the development of the voltammetric procedures for the determination of AA selectively and sensitively in biological organization and food etc. It is generally believed that direct electrooxidation of AA at bare electrodes is irreversible and therefore requires high overpotential.[1] Moreover the direct redox reaction of uric acid (UA), dopamine (DA), and AA take place at very similar potentials and often suffer from a pronounced touling effect, which resulting in rather poor selectivity. Although various electrochemical methods, mainly based on the chemically modified electrodes, have been proposed[2-11] for determination of AA, seldom procedure could well resolve this problem by eliminating the interferes of high concentration DA and UA at the same time.

There has been much interest in the research of carbon nanotubes since their discovery.[12] Carbon nanotubes are molecular-scale wires with high electrical conductivity, high chemical stability, and extremely high mechanical strength and modulus.[13] Utilization of these properties has lead to application of carbon nanotubes as scanning probes,[14] electron field emission sources,[15] actuators,[16] nanoelectronic devices,[17] batteries,[18] nanotubes-reinforced materials,[19] potential hydrogen storage material[20] and chemical sensors.[21] The subtle electronic behaviors of carbon nanotubes reveal that they have the ability to promote electron-transfer reactions when used as an electrode material in electrochemical reactions. However, since carbon nanotubes have a large dimension and hydrophobic surface, the aqueous suspension of intact carbon nanotubes was usually unstable, which limited the applications of carbon nanotubes in electroanalytical chemistry. Carbon nanotubes consisting of cylindrical shells of graphitic sheets with nanometer diameter were found in two distinct types of structures: the single-wall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (MWNT). The multi-wall carbon nanotubes (MWNT) were firstly used to fabricate carbon nanotubes electrodes by mixing them with binders such as bromoform, mineral oil or liquid paraffin, which was applied in the oxidation of DA,[22] electrocatalysis of oxygen[23] and electrochemistry of protein.[24] Then MWNT was either treated with concentrated acids[25] or heated in the air[26] to produce hydroxyl, carboxyl and ketone groups at the terminus and dispersed in concentrated sulfuric acid[25] or organic solvents.[26] The resulting suspensions were then cast on the electrode surface and dried. However, these electrodes often suffered from the lack of stability or controllable dispersion on the electrode surfaces, i.e. attaching carbon nanotubes to an electric circuit in a controlled way is still a problem. Our previous work[27-29] reported that MWNT could be easily dispersed into water in the presence of dihexadecyl hydrogen phosphate (DHP). Based on the stable suspension of MWNT in the aqueous suspension of DHP, MWNT-DHP composite film modified GCEs have been developed. These electrode exhibited catalytic activity towards several biomolecules. Compared with other MWNT modified electrodes, MWNT-DHP composite film modified GCE has the advantages of easy fabrication, controllable dispersion, and high stability as well as reproducibility.

Compared with MWNTs, the SWNTs stand out as unique materials for fundamental research and emerging applications in terms of electronic properties, in particular, and their high aspect ratio. In the present work described here is to investigate the voltammetric responses of AA at the SWNT-DHP composite film modified GCE. The electrochemical behaviors of AA at the SWNT[30] and MWNT[31] modified electrode have been reported. However the oxidation peak potential of AA was observed at SWNT modified electrode about 0.16 V (*vs.* SCE), which overlaps with that of DA (0.18 V). Although ref[31] has separated oxidation peaks of DA and AA successfully, the effect of UA has not discussed. In this report, the SWNT-DHP composite film modified GCE not only exhibited strong electrocatalytic activity toward AA oxidation with a lowering of the overpotential by about 468 mV and a great increase in the magnitude of the oxidation peak current, but also resolved the overlapping voltammetric responses of UA, DA, and AA into three independent voltammetric peaks. The feature of the electrocatalysis that appears to be particularly promising is the relatively low potential (–0.018 V, *vs.* SCE) at which the AA oxidation takes place. And based on this, the SWNT-DHP composite film modified GCE allows amperometric detection at a significantly lower operating potential and hence yields improved selectivity and signal-to-noise. Thus, a sensitive and highly selective voltammetric method for amperometric detection of AA at SWNT-DHP composite film modified GCE was developed.

Experimental Section

Reagents and Apparatus. AA purchased from Chemical Reagent Company of Shanghai (Shanghai, China) was used without further purification. Solution of AA (2×10^{-3} mol L^{-1}) were prepared immediately by dissolving it into doubly distilled water deaerated with nitrogen at least for 5 min. Dihexadecyl phosphate (DHP) was purchased from Fluka Chemical Reagent Corporation. The phosphate-buffer saline solution (PBS, pH 7.0) was prepared from phosphate salts (0.02 mol L^{-1}) and sodium chloride (0.15 mol L^{-1}). All other chemicals were analytical grade reagents and all the solutions were prepared from doubly distilled water.

The single-wall carbon nanotubes (obtained from from the Chengdu Organic Chemicals Co., Ltd, CAS, China) were synthesized by a catalytic pyrolysis method and purified with concentrated HNO_3.[32]

All electrochemical measurements were performed with a computer controlled model 830B electrochemical analyzer (Shanghai Chenhua Co., China). A conventional three-electrode cell was employed with a platinum wire as counter electrode; a saturated calomel electrode (SCE) as reference electrode and a SWNT-DHP composite film modified GCE as working electrode. All potentials were quoted with respect to SCE.

Preparation of the SWNT-DHP Composite Film Modified Electrode. Glassy carbon electrodes of 3 mm diameter were used. These electrodes were sanded in ultrafine sand paper, polished with 0.3 μm and 0.05 μm alumia slurry (CH instrument, Inc., USA) in sequence and sonicated successively in 1 : 1 HNO_3-H_2O (v/v) and doubly distilled water between each polishing step.

2.5 mg purified SWNTs were added into 5 mL 0.5 mg mL^{-1} DHP suspension. A homogeneous and stable suspension of 0.5 mg mL^{-1} SWNT-DHP was achieved with the aid of ultrasonication agitation for about 30 min. The GCE was coated by casting 5 μL suspension of SWNT-DHP and dried in the air. The amount of SWNTs on the GCE surface was about 0.036 mg cm^{-2}. The freshly prepared SWNT-DHP composite film modified GCEs were activated in 0.02 mol L^{-1} PBS (pH 7.0) by using successive cyclic scans from –0.4 V to 0.8 V until the stable voltammograms were obtained.

Procedure. Voltammetric measurements were performed at room temperature (~25 °C). All the supporting solutions were deaerated with nitrogen at least 5 minutes to remove oxygen prior to the beginning of a series of experiments. The amperometric determinations were carried out in a well-stirred solution. A measured amount of human urine samples were directly spiked into the supporting electrolyte and measured by the standard addition method, by spiking a very small volume of relatively concentrated standard solution, so that the dilution effect could be neglected in the calculation.

Result and Discussion

SEM Characterization. The suspension of SWNT-DHP was cast on a pretreated glassy carbon disk and the SEM image of the film formed is shown in Figure 1b. From this figure, it can be found that the glassy carbon disk surface is completely and homogeneously coated by an SWNT-DHP composite film, with diameters of SWNTs bundles spreading with a range from 15-30 nm. It also can be seen from this image that the SWNT-DHP composite film contained very small portion of amorphous carbon impurities. The SEM of the pure DHP film on the glassy carbon disk surface is also shown and a compact film can be seen (Fig. 1a).

Electrochemical Behavior of the SWNT-DHP Composite Film. Firstly, the voltammetric behavior of DHP film was investigated using cyclic voltammetry between –0.50 and 0.50 V at a scan rate of 50 mV s^{-1} and the results showed that no reduction/reoxidation wave were observed (Fig. 2 dashed line). When the SWNT-DHP composite film modified GCE was immersed into 0.02 M PBS (pH 7.0), a pair of broad reduction/reoxidation waves was observed and the cathodic and anodic peak potentials were around –0.121 and –0.049 V at a scan rate of 50 mV s^{-1}, respectively (Fig. 2, solid line). Meanwhile, a large background current of the SWNT-DHP composite film modified GCE was also observed, which might be due to the catalytically active surface.[22] Figure 2 also demonstrates the effect of scan rate

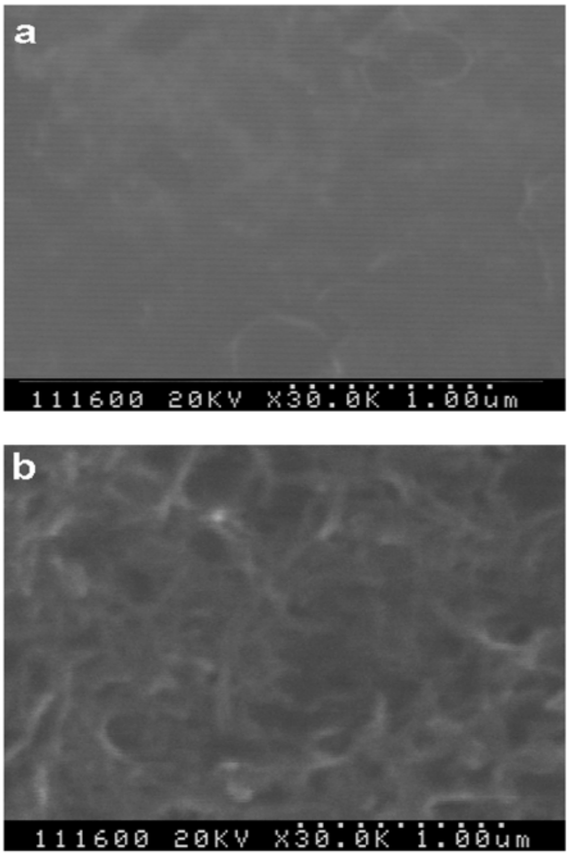

Figure 1. SEM images (30,000 ×) of a DHP film (a) and an SWNT-DHP composite film (b) over glassy carbon disk.

on the voltammetric responses of the SWNT-DHP composite film was studied by varying the scan rate from 50 mV s^{-1} to 1000 mV s^{-1}. It can be seen, with the scan rates increasing, both the anodic and cathodic peak currents increase linearly and the separations between the reduction and the oxidation peak potentials have little change even while the scan rate up to 1000 mV s^{-1}, indicating the fast charge transfer properties of the SWNT-DHP film. It was also found that both the cathodic and anodic peak potentials shifted linearly to lower potential with the increasing pH, which shows that protons are involving in the redox reaction of the SWNT-DHP film. Similarly to the other SWMT film,[30] the pair of surface waves at the SWNT-DHP composite film might be due to the redox of carboxylic functionalities introduced on the SWNT-DHP composite film due to the pretreatment of SWNTs purification by using concentrated nitric acid.

The impedance responses of $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1 : 1) were also studied and the experiment results were simialr to our previous work,[33] which clearly showed that the SWNT can greatly increase the electron transfer rate.

Electrochemical Oxidation of AA at the SWNT-DHP Composite Film Modified Electrode. To investigate the electrocatalytic activity of the SWNT-DHP composite film modified GCE toward the oxidation of AA, the electrochemical behaviors of AA were studied in different electrodes by cyclic voltammetry in 0.02 M PBS (pH 7.0) at a rate of 25 mV s^{-1}, as shown in Figure 3. Figure 3a shows that the cyclic voltammogram of SWNT-DHP composite film in the absence of AA only presents a pair of broad redox waves, which are corresponding to the redox of carboxylic functionalities introduced on the SWNT-DHP composite film. Figure 3b shows the voltammetric response of AA at bare GCE and a broad anodic peak of AA is irreproducible observed at about 0.45 V with $E_p - E_{p/2} \approx 0.25$ V. Compared with the bare GCE, the oxidation peak current of AA increase significantly at the SWNT-DHP composite film modified GCE and the oxidation peak potential shifted negatively to –0.018 V with $E_p - E_{p/2} \approx 0.038$ V (Fig. 3d). The obviously increased peak current and the decrease in the anodic overpotential of 468 mV for AA demonstrate an efficient catalytic reaction between the SWNT-DHP com-

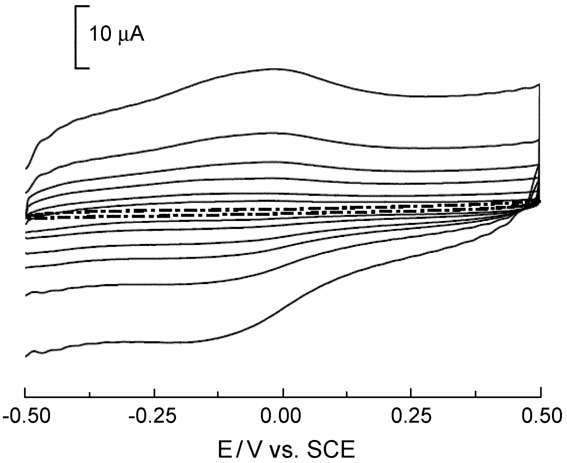

Figure 2. Cyclic voltammograms of SWNT-DHP composite film at different scan rates in blank supporting electrolyte. Scan rates from the innermost to the outermost waves: 50, 100, 200, 300, 500, 1000 mV s^{-1}. Dashed line: Cyclic voltammograms of DHP film at a scan rate of 50 mV s^{-1}.

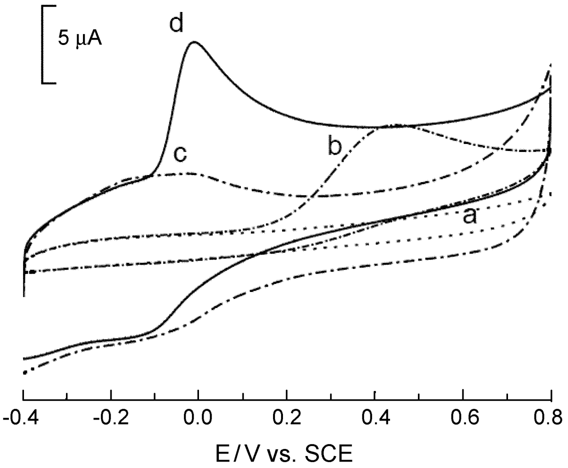

Figure 3. (a) Cyclic voltammograms of SWNT-DHP composite film in the absence of AA. Cyclic voltammograms of 1 × 10^{-5} mol L^{-1} AA in 0.02 M PBS at (b) a bare GCE; (c) a DHP film modified GCE; and (d) an SWNT-DHP composite film modified GCE; Scan rate: 25 mV s^{-1}.

posite film modified electrode and AA in the solution. Since the AA oxidation takes places at the redox potentials of carboxylic functionalities, these functionalities may mediate the charge transfer and improve the reversibility of the electron transfer processes, hence greatly increases the rate of electron transfer from AA to the electrode.[33] Additionally, the high aspect ratios of the nanotubes may present a steric effect for more efficient oxidation reaction of AA.[22] It is general known that the oxidation of AA proceeds *via* two consecutive one-electron processes, involving a predissociation of proton to give the monoanionic species followed by a one-electron, one-proton oxidation of the monoanionic species to form a radical anion, which then undergoes a second one-electron oxidation to dehydroAA.[33,34] The latter is rapidly protonated and then dehydrated to form the final electroinactive product of 2,3-diketogulonic acid. Therefore only the anodic anion peak of AA can be observed and the cathodic peak cannot be observed even at high scan rate, which is in agreement with the results obtained by Wehmeyer and Wightman.[36] The electrochemical behavior of AA at the pure DHP modified electrode was also examined. As it can be seen from Figure 3c, the oxidation peak of AA disappeared totally at the DHP film modified electrode and this may be due to the DHP film prohibited the electron exchange between AA and the electrode.

Since DHP film can prohibit the electron exchange between AA and the electrode, the concentration of DHP in the DHP-SWNTs suspension solution should be kept as low as possible. However, the lower concentration of DHP leads to a poor dispersion characterization and hence affects the casting of SWNT-DHP composite film. In present case the DHP concentration of 0.5 mg mL^{-1} is suitable. The relationship between the amount of SWNTs on the GCE and the oxidation current of AA has been examined and the results are illustrated in Figure 4. The oxidation current increases gradually with the increasing the amount of the SWNTs over the electrode surface at firstly. When the amount of SWNT exceeds 0.036 mg cm^{-2}, no obvious change in the peak current is observed, which suggests that the SWNT-DHP composite film has genuine catalytic function towards the oxidation of AA and that the diffusion of electron transfer processes within the film and at the film-solution interface are sufficiently fast and not the rate-controlled steps. Thus the thickness of film does not affect the catalytic oxidation of AA. However, the charging current increased with the amount of the SWNTs on the electrode surface, thus preventing from determining AA at low concentration level. Then the amount of SWNTs on the GCE surface is chose for 0.036 mg cm^{-2}.

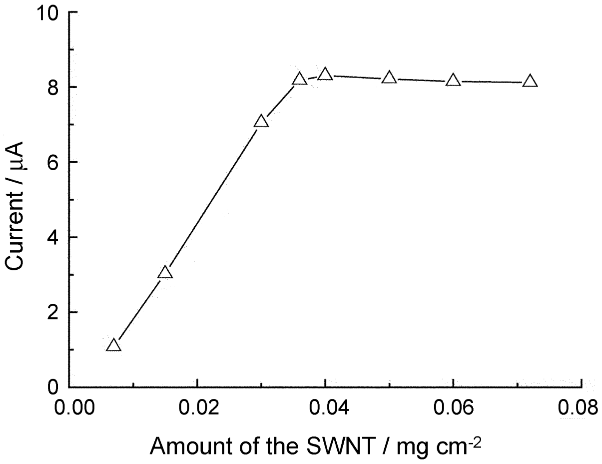

Figure 4. Effect of amount of the SWNT on the GCE on the oxidation current of 1 × 10^{-5} mol L^{-1} AA. Scan rate: 25 mV s^{-1}.

The pH of the supporting electrolyte has a significant influence on the AA electrooxidation at the SWNT-DHP composite film modified GCE, by altering both peak currents and peak potential. Figure 5 illustrates the dependences of the peak current and peak potential of AA on the pH of 0.02 M PBS. As shows in Figure 5a, when the pH of the solution is lower than 6.3, the oxidation peak current of AA increases with the increasing pH and no obvious change in the peak current is observed over the pH range from 6.3 to 7.2. At the pH higher than 7.2, the peak current of AA decreases quickly with increasing pH. This can be explained as follows: with the increase in pH, those carboxylic functional groups at the SWNT-DHP composite film may become deprotonated and possessed negative charges. Electrostatic repulsion between the analyte (HA^-) and the

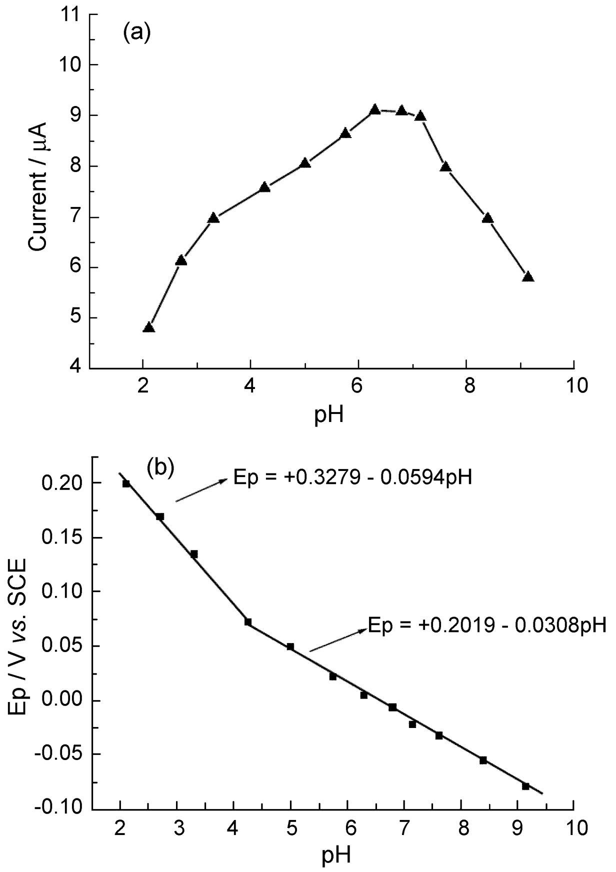

Figure 5. Dependences of peak current (a) and peak potential (b) of 1 × 10^{-5} mol L^{-1} AA on pH at an SWNT-DHP composite film modified electrode. Scan rate: 25 mV s^{-1}.

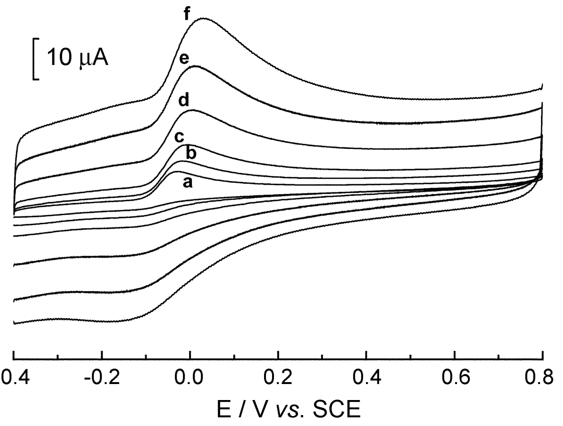

Figure 6. Dependence of cyclic voltammetric responses of 1 × 10^{-5} mol L^{-1} AA on scan rate at an SWNT-DHP composite film modified GCE. Scan rate: (a) 10; (b) 25; (c) 50; (d) 100; (e) 150; (f) 300 mV s^{-1}.

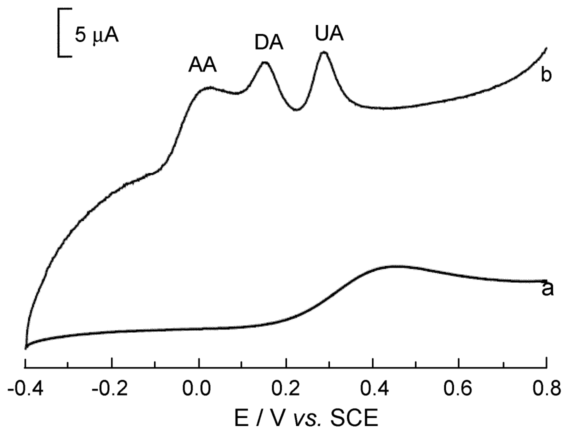

Figure 7. Linear scan voltammograms of 1 × 10^{-5} mol L^{-1} AA, DA, and UA at a bare GCE (a) and an SWNT-DHP composite film modified GCE (b).

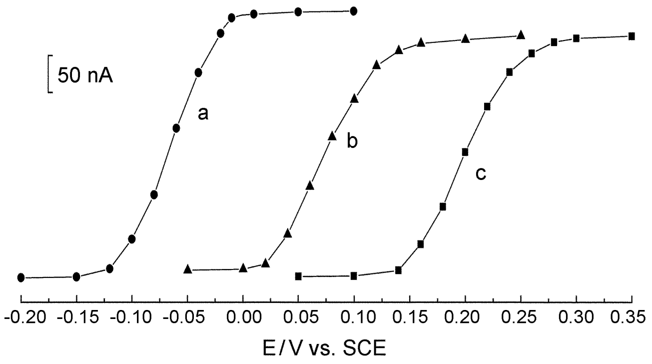

Figure 8. Hydrodynamic voltammograms of AA (a), DA (b), and UA (c) at an SWNT-DHP composite film modified GCE.

electrode might be the reason for the fast decrease of the oxidation current of AA at higher pH.

The pH effects on peak potentials (*Epa*) for the oxidations of AA on the SWNTs modified electrode is shown in Figure 5b. The E_{pa} of AA shift to lower potential with increase in pH and the calculated $[\partial Epa/\partial pH]$ is –59.4 mV pH^{-1} between pH 2.1 to 4.2, indicating a two-electron, two-proton oxidation process, whereas at higher pH values the calculated $[\partial Epa/\partial pH]$ decreased to –30.8 mV pH^{-1}, suggesting a two-electron, one-proton oxidation process. The break point was corresponding to the pK_{a1} of 4.20 for AA.

The influence of scan rate on AA oxidation at the SWNT-DHP composite film was examined by cyclic voltammetry varying the scan rate from 10 to 300 mV s^{-1}, as is shown in Figure 6. The peak current of AA is proportional to the square root of scan rate, indicating a diffusion-controlled electrode process. As stated earlier, the oxidation of AA proceeds via two consecutive one-electron processes and the rate-determining step for the oxidation of AA can be determined by evaluating the apparent transfer coefficient.[35] The oxidation peak potential of AA depends linearly on the logarithm of scan rate according to following equation: E_p (V) = 0.01 + 0.0215 log ν, R^2 = 0.9987. The apparent transfer coefficient, calculated from the slope of the plot of 0.0215, is 1.4, which indicates the second one-electron oxidation step is the rate-determining step for the oxidation of AA.

Interferences. As discussed earlier, the electrochemical determination of AA is often affected by the oxidation of DA and UA. So it is necessary to solve the problem of the separations of the electrochemical responses of AA, DA, and UA. Figure 7a shows that AA, DA, and UA exhibit a broad anodic peak at 0.42 V at bare GCE. While at the SWNT-DHP composite film modified GCE, AA, DA, and UA were oxidized at the potentials of –0.018, 0.17 and 0.31 V, respectively (Fig. 7b). The separations between the peak of AA and the peaks of DA and UA are large enough to allow the amperometric determination of AA in the presence of high concentration UA and DA. In order to obtained an optimal working potential for amperometric detection of AA, the hydrodynamic voltammograms of AA, DA, and UA at the SWNT-DHP composite film modified GCE are presented (Fig. 8). It can be seen, the oxidation current of AA starts at about –0.16 V and increases with increasing potential, and it finally reaches a steady response at about –0.015 V. However, the onset of the oxidation current of DA and UA occurs at 0.02 V and 0.14 V, respectively. These results further manifested the possibility for detecting AA in the presence of DA and UA. The optimum applied potential of –0.015 V for AA detection at the SWNT-DHP composite film modified electrode is significant lower than that at most reported electrodes, which is typically more than 0.15 V. This is a considerable advantage since the number of interferences in electrochemical detection increases exponentially with increasing extremes of potential and most interferences are not expected to oxidized at the potential of –0.015 V. Further experiment showed that addition of 1 × 10^{-4} mol L^{-1} DA and 1 × 10^{-4} mol L^{-1} UA had no effect to the amperometric response of 5 × 10^{-6} mol L^{-1} AA. Further experimental results showed that at least 50-fold of xanthine, hypoxanthine, glucose, serine, adenine, epinephrine, guanine,

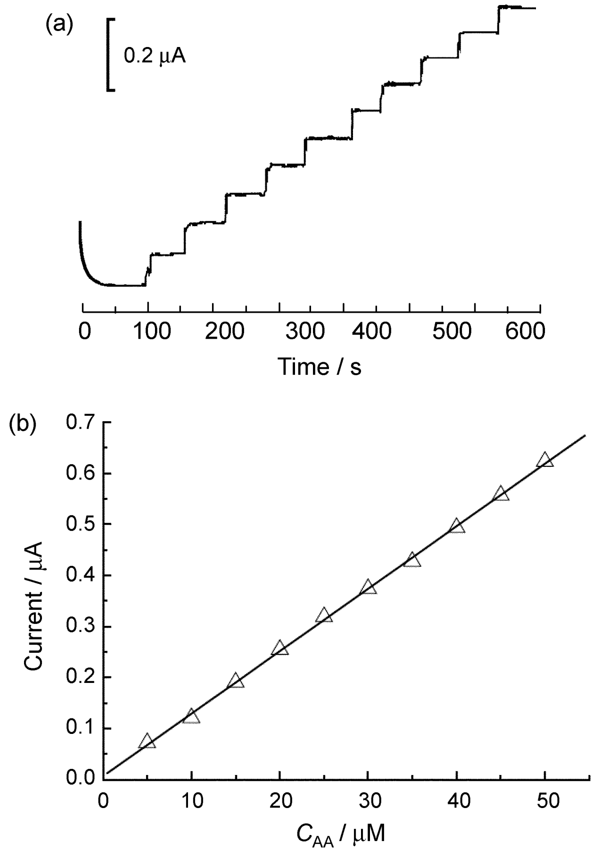

Figure 9. (a) Amperometric responses to the ten sequential additions of AA (each 5×10^{-6} mol L^{-1}) at an SWNT-DHP composite film modified GCE with held potential at –0.015 V. (b) Calibration plot of steady-state current *vs.* AA concentration.

progesterone, purine, urea, theophylline, estradiol, estrone, and estriol have no effect on the amperometric current of AA.

Amperometric Response of AA at SWNT-DHP Composite Film Modified Electrode. Amperometric determinations of AA were carried out in a well-stirred solution and the results demonstrated that the SWNT-DHP composite film modified electrode has a good response for ten sequential additions of 5 μM AA (Fig. 9a). Keeping the SWNT-DHP composite film modified electrode at –0.015 V, after spiking the AA solution, the oxidation current increased and reached the steady-state fast, within 5 seconds, indicating a fast electrocatalytic response. Figure 9b further shows that steady-state current increased linearly with the AA concentration. Amperometric responses to the sequential additions of 5 μM AA in the presence of 1×10^{-4} mol L^{-1} DA and 1×10^{-4} mol L^{-1} UA were also investiged and similar result was obtained, indicating the presence of DA and UA had little effect on the AA determination. The linear range was from 4×10^{-7} mol L^{-1} to 1×10^{-4} mol L^{-1} with a sensitivity of 35.0 *n*A (μ mol $L^{-1})^{-1}$ and an intercept of 4.6 *nA* with a correlation coefficient, *r*, of 0.9992. The limit of detection (LOD), defined as a signal-to-noise ratio of 3 : 1, was found to be 1.5×10^{-7} mol L^{-1}.

Table 1. Results of Determination of Ascorbic Acid in Human Urine Samples and Recoveries

Sample No	Original (μg mL^{-1})	Added μmol L^{-1}	Expected μmol L^{-1}	Found μmol L^{-1}	RSD (%)	Recoveries (%)
1	50.90	–	–	5.78	3.23	–
1		5	10.78	11.01	3.42	102.1
2	56.79	–	–	6.45	2.19	–
2		10	16.45	16.17	2.70	98.3
3	53.10	–	–	6.03	3.18	–
3		15	21.03	21.07	2.37	100.2

[a] Average of four replicate determination. [b] Original value is obtained by multiplying the detected value by the dilution factor of 50

The precision was estimated from two series of 15 successive measurements of 5 and 50 μM AA solutions. The relative standard deviations (RSD) were obtained to be 2.3% and 2.7%, respectively. The inter-electrode reproducibility was also investigated and the RSD of 5.6% was obtained for n=10. These results suggest that the SWNT-DHP composite film modified electrodes fabricated by using recommended method exhibit good precision for the determination of AA.

Stability and Sample Analysis. The stability tests were carried out in room temperature. The current response decreased only by around 2.1% of its initial response after a week exposing the electrode in air, which shows the SWNT-DHP composite film modified GCE has good long-time stability for determination of AA.

In order to confirm the sensitivity and generality of the proposed method, we have used the method for the determination of AA in human urine, which the concentration of UA was about 25 μmol L^{-1}. A 2 mL portion of human urine samples were transferred to a 100 mL volumetric flask and diluted to the volume with water. The concentration of AA in volumetric flask were evaluated by the standard addition method, and then the origal values in human urine samples are obtained by multiplying the concentration of AA in volumetric flask by the dilution factor of 50 and transformed the unit to μg mL^{-1}. The results are listed in Table 1. The recoveries obtained was found to be 98.3-102.1%, which indicates that this method exhibits good accuracy and selectivity for practical application.

Conclusion

An easy prepared SWNT-DHP composite film modified GCE was performed to investigate the oxidation of AA in detail. In near physiological solution conditions, the modified electrode reduced the overpotential of AA oxidation greatly and increased the oxidation current significantly, which clearly demonstrates the excellent electrocatalytic activity of the SWNT-DHP composite film toward the oxidation of AA. Since the lower applied working potential in the amperometric detection of AA, most interferents including DA and UA cannot oxidize at this potential. Thus a sensitive and highly selectively amperometric method was developed for determination of AA in real samples. Its sound results showed that the method is quite valuable and seems to be of great utility for further sensor development.

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