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ORIGINAL PAPER

Electrochemical oxidation of salicylic acid at well-aligned multiwalled carbon nanotube electrode and its detection

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Abstract In this paper, an electrochemical sensor for sensitive and convenient determination of salicylic acid (SA) was constructed using well-aligned multiwalled carbon nanotubes as electrode material. Compared to the glassy carbon electrode, the electro-oxidation of SA significantly enhanced at the multiwalled carbon nanotube (MWCNT) electrode. The MWCNT electrode shows a sensitivity of 59.25 μA mM^{-1}, a low detection limit of 0.8×10^{-6} M and a good response linear range with SA concentration from 2.0×10^{-6} to 3.0×10^{-3} M. In addition, acetylsalicylic acid was determined indirectly after hydrolysis to SA and acetic acid, which simplified the detection process. The mechanism of electrochemical oxidation of SA at the MWCNT electrode is also discussed.

Keywords Salicylic acid · Acetylsalicylic acid · Electroanalysis · Multiwall carbon nanotubes · Sensor

Introduction

Salicylic acid (SA) or 2-hydroxybenzoic acid, widely distributed in various plants, is physiologically active and vital for plants' survival and plays an important role in endogenetic growth in plants under normal conditions [1]. SA is an important chemical and curative raw material which has been widely used in cosmetics [2], lotions, and pharmaceuticals [3] due to its distinct exfoliating, antiseptic, antipyretic, analgesic, and anti-inflammatory properties. SA is also a primary hydrolysate of acetylsalicylic acid (ASA) which is commonly used as anti-inflammatory medicine. Therefore, effective and convenient determination of SA is very important.

Many analytical methods for SA determination have been described in literature. The most frequently used method is the Trinder test [4, 5], the basic principle of which is grounded on the formation of a purple composite of salicylate and Fe(III) ions that is monitored spectrophotometrically at 540 nm. Other methods developed for SA determination have been reported, namely spectrophotometry [6, 7], spectrofluorimetry [8, 9], colorimetry [10], chromatography [11], potentiometry [12], amperometry [13], voltammetry [14], and enzymatic methods [15, 16]. However, most of the above-mentioned methods need sample pretreatment and high cost, complicated operation or show poor efficiency. It is necessary to develop a simple, convenient, and accurate method for SA determination. In contrast, these problems can be well solved by using electroanalysis such as potentiometry, amperometry, or voltammetry.

Since the discovery of multiwalled carbon nanotubes (MWCNTs) by Iijima [17], carbon nanotubes (CNTs) have attracted extensive research interest due to their outstanding structural, electronic, and mechanical properties such as unique tubular structure like fullerene, high chemical and thermal stability, high electrical conductivity, high elasticity, and high mechanical strength. CNTs have also been considered with great prospect for electrochemical sensors

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and biosensors, depending on their special structure and properties such as high conductivity, excellent absorbability, large surface area, and modifiable sidewall. MWCNTs are regarded as metallic conductors with highly attractive properties for electrochemical determination. Moreover, the subtle structure of MWCNTs provides many active sites and enhances the sensitivity of electrochemical analysis. So far, it has been demonstrated that MWCNT-based electrochemical sensors exhibit outstanding electrochemical response to a variety of species such as hydroquinone and catechol [18], thiocholine [19], reserpine [20], lincomycin [21], quercetin [22, 23], etc.

To our knowledge, however, no work on the determination of SA has been reported by using MWCNT electrode. In this work, voltammetry and amperometry were used to determine SA, and the MWCNT-based sensor showed excellent electrocatalysis to SA. It is a convenient, simple, quick, inexpensive, and sensitive method for SA determination. In addition, the mechanism of electrochemical oxidation of SA at the MWCNT electrode is also studied.

Experimental

Chemicals and reagents

All reagents were of analytical grade and used without further purification. SA solution with different concentrations was prepared by dissolving SA (Chengdu Associated Chemical Engineering Reagents Institute) in 0.3 M NaOH for testing. High-quality deionized water (18.4 MΩ cm^{-1}) obtained from Millipore water system was used for preparation of all solutions. The electrochemical measurements were performed in 0.3 M NaOH solution.

Preparation of the MWCNT electrode

A detailed process for the synthesis of well-aligned MWCNTs with Ta-plate as a substrate was reported previously [24–27]. In brief, Ta-plates were first coated with thin cobalt (Co) layer of 8–50 nm as catalyst by magnetron sputtering. Under a flow of N_2, the Ta-plates were put into the middle of the quartz tube reactor, which was heated to 800–900 °C. After purging by N_2 (500 sccm) for a few minutes, ethylenediamine was introduced by bubbling N_2 through ethylenediamine liquid in a glass bottle. After reacting for 5–45 min, the reactor was cooled to room temperature in N_2 ambient. The carbon nanotubes have diameters ranging from 80 to 120 nm and a length of about 10 μM. The well-aligned MWCNTs on Ta-plate were connected to the copper electrode as working electrode. The freshly prepared MWCNT electrodes were placed in PBS solution for specified time intervals and then transferred to electrochemical cell for measurement.

Instruments and apparatus

Electrochemical measurements were performed using CHI 660C electrochemical workstation (Shanghai Chenhua, China) in a three-electrode system, including a working electrode (MWCNT electrode, glassy carbon electrode (GCE)), a platinum counter electrode, and an Ag/AgCl (3 M KCl) reference electrode. All potentials were referred to Ag/AgCl (3 M KCl) electrode, and all experiments were performed at room temperature (about 25 °C).

Results and discussion

Electrochemical characterization of the MWCNT electrode using potassium ferricyanide

Potassium ferricyanide ($K_3[Fe(CN)_6]$) shows very good performance as an electronic conducting medium. Here, $K_3[Fe(CN)_6]$ is used as a probe to evaluate the conducting property and calculate the effective surface area of the MWCNTs. Cyclic voltammetry (CV) of 5 mM $K_3[Fe(CN)_6]$ with 1 M KCl as supporting electrolyte at the MWCNT electrode was implemented at various scan rates (Fig. 1). With scan rates from 20 to 1,000 mV s^{-1}, both the oxidation peak potential (E_{pa}) and reduction peak potential (E_{pc}) of $K_3[Fe(CN)_6]$ remain approximately constant around +0.28 and +0.22 V, respectively. $\Delta E_p \left(\Delta E_p = E_{pc} - E_{pa}\right)$ between oxidation and reduction peak potentials is around 59 mV. Thus, $K_3[Fe(CN)_6]$ exhibits a reversible redox reaction at the MWCNTs surface with the slopes of the straight lines of I_{pa} (R=0.9987), I_{pc} (R=0.9986) vs $\upsilon^{1/2}$ are 4.93×10^{-4} and 4.81×10^{-4} A $s^{1/2}$ $V^{-1/2}$, respectively. Being a reversible

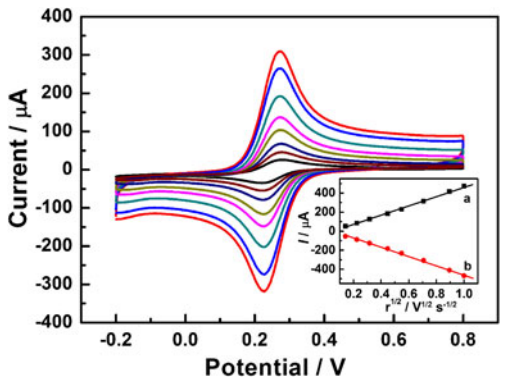

Fig. 1 CVs of the MWCNT electrode in 5 mM $K_3[Fe(CN)_6]$ with 1.0 M KCl as the supporting electrolyte at different scan rates (20–1,000 mV s^{-1}). *Inset* shows the plots of oxidative and reductive peak currents with square root of scan rate

reaction at the electrode, the effective surface area of the MWCNT electrode was calculated to be 1.1×10^{-1} cm^2 according to the Randles–Sevcik equation (Eq. 1) [28].

$$I_p = 2.69 \times 10^5 n^{2/3} A D^{1/2} \upsilon^{1/2} C_0 \quad (1)$$

In Eq. 1, I_p, n, A, D, C_0, and υ denote the redox peak current (ampere), the number of electrons per molecule transferred, the electrode effective surface area (square centimeter), the diffusion coefficient of $K_3[Fe(CN)_6]$ in 1 M KCl, the concentration of redox species (moles per cubic centimeter), and the scan rate (volts per second), respectively. For 5 mM $K_3[Fe(CN)_6]$, n=1, $D = 0.76 \times 10^{-5} cms^{-2}$.

Voltammetry of SA at the MWCNT electrode

Electrocatalytic behaviors of the MWCNT electrode and GCE toward SA were investigated using CVs in the potential range of 0 to 0.80 V at a scan rate of 100 mV s^{-1}. Figure 2 shows CVs of the MWCNT electrode and GCE in the absence and presence of 5 mM salicylic acid in 0.30 M NaOH solution. As shown in Fig. 2, no obvious redox peak was observed both at the MWCNT electrode and GCE in 0.30 M NaOH blank solution. Upon addition of 5 mM SA, the oxidation process of SA at the GCE occurs at +0.4 V with a small current of SA oxidation, whereas when the MWCNT electrode was employed, an obvious negative shift (about 100 mV) of the oxidation potential appeared, and sharp rising of current response was observed. More interestingly, at the MWCNT electrode, SA only gives an irreversible anodic peak I_a in the first anodic scan (curve in Fig. 2), with peak potential at around 0.50 V, depending mainly on the pH value and slightly on scan rates. This anodic peak I_a is commonly used for direct electrochemical determination of SA [29–31] on glassy carbon electrode. On the reverse scan, no complementary reduction peak is observed for I_a, which is a typical behavior for a fast irreversible chemical reaction related to the charge transfer [32–34]. At potential around 0.15 V, a new couple (peaks II_c and II_a) are defined, which correspond to the reduction–oxidation of a product resulting from the chemical reaction. The product might be the soluble compound of carboxyl-para-benzoquinone [35] which can be expected to undergo the reversible redox reaction at this potential [36]. These results are in good agreement with previous report [37]. Compared to GCE, the MWCNT electrode, due to large surface area, strong absorption ability, and excellent electronic conductivity, exhibits higher electrocatalytic activity and stronger electron transfer ability toward the electrochemical oxidation of SA. In addition, the MWCNT electrode also shows higher stability and reproducibility in the determination of SA with a relative standard deviation about 7.44% in 12 times.

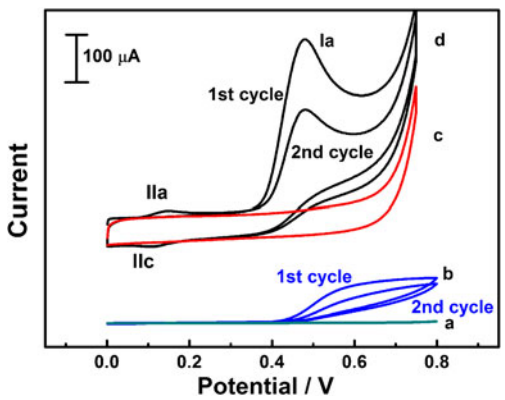

Fig. 2 CVs of GCE (**a** and **b**) and MWCNT electrode (**c** and **d**) in the absence (**a** and **c**) and presence (**b** and **d**) of 5.0 mM SA in 0.30 M NaOH solution. Scan rate 100 mV s^{-1}

The CV responses of SA at different scan rates from 20 to 200 mV s^{-1} (Fig. 3) were further examined at the MWCNT electrode. The primary oxidation peak current of SA (inset) increased linearly with the scan rates in the range of 20–200 mV s^{-1} with a correlation coefficient of 0.9988, which suggests that the process of electrode reaction was controlled by adsorption. In addition, it was found from continuous CVs that the oxidation peak current of SA decreased during the second cyclic potential sweep and tended to be stable after the third cyclic potential sweep at both GCE and MWCNTs, which also revealed the fact that the adsorptive process of SA is the controlling step for the electrode reaction.

It is well known that the reaction of para-benzoquinone can be easily reduced to hydroquinone, which is a reversible reaction of hydroquinone being oxidized to para-benzoquinone, so para-benzoquinone and hydroquinone constitute an electrochemical reversible redox system (Fig. 4). The redox reaction of SA can easily occur on the surface of the MWCNT electrode. According to references [38, 39], the possible mechanism of electrochemical oxidation of SA at the MWCNT electrode is indicated in Fig. 4. SA was first adsorbed on the surface of MWCNTs, and then it transferred the electron to the electrode; thus, SA was oxidized to carboxyl-hydroquinone, which is the main product of SA oxidation [38]. In the electro-oxidation process, a fast irreversible chemical reaction occurred, and then the carboxyl-hydroquinone was further oxidized to carboxyl-para-benzoquinone. On the reverse scan, carboxyl-para-benzoquinone was reduced to carboxyl-hydroquinone and diffused into solution. During the electro-oxidation process of SA at the surface of the MWCNT electrode, OH^- also served as reactive species. Hence, NaOH solution not only acts as supporting electrolyte but also facilitates the oxidization of SA. When the electrochemical experiment lasted for several minutes, the color of the solution changed

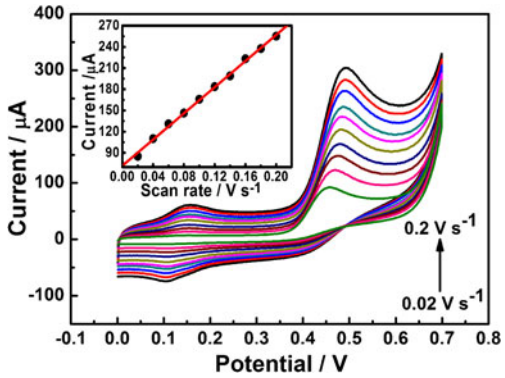

Fig. 3 CVs of the MWCNT electrode in 5.0 mM SA and 0.30 M NaOH solution at different scan rates (20 – 200 mV s^{-1}). Inset is the plot of oxidative peak current of SA with scan rate

from colorless to yellow, which is the color of para-benzoquinone. In general, depending on their property, substituting groups on benzene exert influence on the reduction of para-benzoquinone. For instance, electron-withdrawing groups such as carboxyl and chloro facilitate reduction of para-benzoquinone and increase the reduction potential of para-benzoquinone. At 25 °C, the standard reduction potential of para-benzoquinone is 0.699 V, while in NaOH solution (pH=13), according to the Nernst equation, the reduction potential of para-benzoquinone is −0.07 V. In contrast, the reduction potential of carboxyl-para-benzoquinone at pH 13 at the MWCNT electrode is +0.101 V, which is a positive shift due to the strong electron-withdrawing effect of the carboxyl group.

Optimization conditions for the MWCNT electrode

As we all know, ASA can be immediately hydrolyzed to SA and acetic acid in alkaline solution, and the content of SA is proportional to the ASA concentration in the sample, but in neutral and acid solutions (pH 4–8), the hydrolysis rate of ASA is slow, and it is very stable at pH 2–3 [40]. So, in order to determine ASA quantitatively, NaOH solution was selected as supporting electrolyte. When the concentration of NaOH solution was changed from 0.01 to 1.0 M, the peak potential of SA oxidation decreased sharply until the concentration of NaOH reached 0.30 M, and then it became virtually constant. On the other hand, the peak current of 5.0 mM SA gradually increased until the concentration of NaOH reached 0.30 M, and then it also kept stable with the further increase of the concentration of NaOH (Fig. 5a). Thus, 0.30 M NaOH solution was selected as the supporting electrolyte. The reason for this phenomenon may be the two dissociable protons of SA (pKa_1=2.97; pKa_2=13.4 [41]). When the concentration of NaOH solution increased to 0.3 M, its pH is near pKa_2=13.4, in which SA exists mainly in the form of $^{-}$OOC-SA-O^{-}. NaOH solution is favorable for the oxidation process [42].

In addition, the influence of applied potential on the response current of the sensor was also investigated, as illustrated in Fig. 5b. The maximum response current was observed at +0.55 V. Therefore, +0.55 V was used for the subsequent experiments.

Amperometric detection of SA at the MWCNT electrode

For amperometric detection, in general, electrodes can be appraised by measuring current response at a fixed potential via adding analyte. Figure 6 compares the amperometric response (at +0.55 V) of (a) GCE and (b) MWCNT electrode to successive addition of 0.20 mM SA in 0.30 M NaOH solution. As expected, the GCE showed weak current response to these concentration changes. The MWCNT electrode, in contrast, responded favorably to all additions and showed an obvious increasing current response with SA injections, producing steady-state signals within 3–4 s (Fig. 6a). The obvious signals were accompanied with a low noise and permit convenient quantitative measurement of these millimole concentration changes. In addition, response current of the MWCNT electrode exhibited a good linear range on SA concentration from 2.0×10^{-6} to 3.0×10^{-3} M with a low detection limit of 0.8×10^{-6} M (signal/noise=3). The sensitivity of the MWCNT

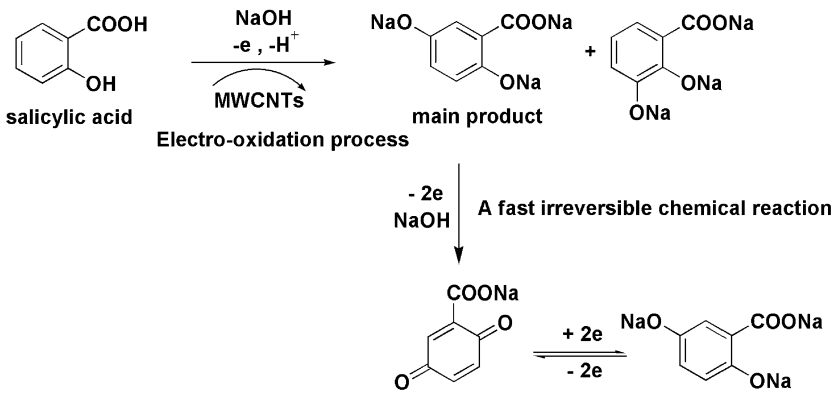

Fig. 4 Mechanism of SA electrochemical oxidation at the MWCNT electrode

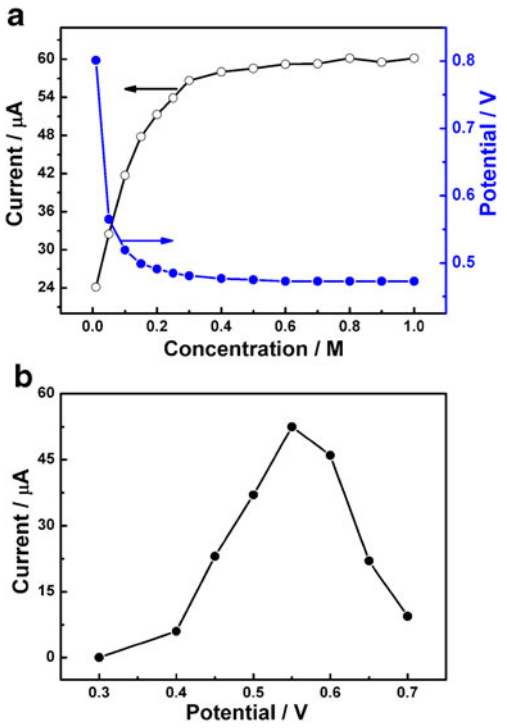

Fig. 5 **a** The effect of NaOH concentration on peak current and potential to 1.0 mM SA at the MWCNT electrode. **b** The effect of applied potential on the response current to 1.0 mM SA in 0.30 M NaOH solution

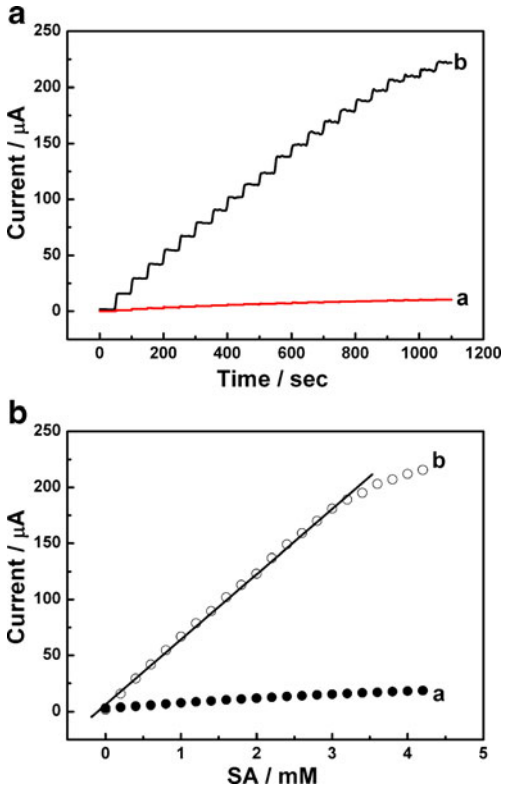

Fig. 6 **a** Amperometric response obtained at the GCE (*a*) and MWCNT electrode (*b*) to successive addition of 0.20 mM SA into 0.30 M NaOH. **b** Calibration plots for SA obtained at the GCE (*a*) and MWCNT electrode (*b*). Working potential +0.55 V

electrode is 59.25 μA mM^{-1} with a correlation coefficient of 0.9995, as depicted in Fig. 6b. When the concentration of SA is higher than 3.0×10^{-3} M, the response current began to decline due to the formation of polymer films on the electrode surface [43]. As a result, the calibration curve would be leveling off at higher concentration levels. In summary, the prepared MWCNT electrode exhibited an excellent electrocatalytic activity toward the oxidation of SA leading to a marked improvement in response current as compared to GCE. A highly stable amperometric response, with no apparent sensitivity loss, was observed for amperometric detection over a continuous 120-min period.

Real pharmaceutical samples measurement

The MWCNT electrode was applied to the determination of ASA in real pharmaceutical samples (aspirin). Ten tablets were powdered, and a certain amount of the samples was dissolved in 100.00 ml of 0.30 M NaOH solution. The current response was recorded at +0.55 V. Table 1 displays the determination result of these real samples. The result obtained by amperometry is almost consistent with that obtained by traditional titrimetry [44], which indicates that the MWCNT electrode is promising for practical application in drug testing.

Conclusion

In this work, we demonstrated the measurement of SA by using well-aligned MWCNTs on Ta-plate as an electrode. Our results indicated that the MWCNT electrode provided a stable, high response, and sensitive amperometric detection of SA. Compared to the GCE, the MWCNT electrode displayed high electrocatalytic activity toward the oxidation of SA, showing a sensitivity of 59.25 μA mM^{-1}, a low detection limit of 0.8×10^{-6} M, and a large response linear

Table 1 Determination of acetylsalicylic acid in commercial pharmaceutical samples using the amperometry and titrimetry

Samples	Amperometry				Titrimetry
	Testing value (mg/tablet)	RSD (%)	Added (mM)	Recovery (%)	
1	48.67	4.86	0.10	96.79	48.25
2	48.80	2.21	0.10	97.49	49.10
3	48.76	3.01	0.10	95.12	48.72

range with SA concentration from 2.0×10^{-6} to 3×10^{-3} M. In addition, we also discussed the mechanism of electro-oxidation of SA at the MWCNT electrode. To sum up, the electrode based on well-aligned MWCNTs shows potential of being fabricated as electrochemical sensors for SA quantitative detection.

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