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ORIGINAL PAPER

Effects of capacitance and resistance of MWNT-film coated electrodes on voltammetric detection of acetaminophen

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Abstract The active electrode area, capacitances, and resistances of MWNT-film coated glassy carbon electrodes with different amount of MWNTs have been characterized by cyclic voltammetry and chronoamperometry. They are varied by controlling the amount of MWNTs dispersed on the electrode surface and affect the voltammetric responses of analytes in liquids. The redox current of acetaminophen is enhanced on the MWNT-film coated electrodes due to the enlarged active electrode area. The oxidation of acetaminophen occurs at 0.34 V and the reduction occurs at 0.27. Two electrons and two protons participate in the reversible redox reaction. The diffusion-controlled anodic peak current is proportional to the concentration of acetaminophen from 5.0 to 0.1 mM with a detection limit of 2.4 μM. The determination of acetaminophen in pharmaceutical formulations was also conducted.

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1 Introduction

Carbon nanotubes (CNT) are one novel form of carbon material [1, 2] and have been recognized as one of the quintessential nano-materials due to their physicochemical features, e.g., large surface area, high chemical stability, outstanding bio-compatibility, high conductance, good tensile strength, high catalytic capability and fast electron transfer rate [3–6]. They have been employed widely in the design of effective, low-cost, and environment-friendly electrochemical sensors and biosensors [5–12]. These CNT-based sensors/biosensors show high efficiencies for the detection of various analytes, e.g., large sized biomolecules (such as DNA, enzymes etc.) or smaller ones (such as ascorbic acid), and toxic metal ions in the environment. The big advantage of adopting CNTs for the construction of sensors/biosensors is the enhancement of active electrode area, which is controlled easily by the amount of CNT dispersed/immobilized on the electrode. Unfortunately, the capacitances and the resistances of CNT-film modified electrodes are also increased. It has been known that the capacitances of electrodes in liquids vary proportionally with electrode active area and subsequently affect the voltammetric behavior of analytes in liquid considerably [5–13]. However, few reports focus on the estimation of the capacitance and the resistance of CNT-film coated electrodes.

The purpose of this work is to measure the active electrode area of CNT-film coated electrodes as well as to evaluate their capacitances and resistances by the use of

$Fe(CN)_6^{3-}$ and acetaminophen as probe molecules. We followed the simplest way to fabricate CNT-film modified electrodes [14, 15] by directly dispersing a suspension of commercially available multi-walled carbon nano-tubes (MWNTs) on glassy carbon electrodes. Different volumes of CNT suspension were used for the fabrication of the modified electrodes. The reactivity, capacitances and surface areas of the resultant electrodes were examined and compared by means of voltammetry and chronoamperometry, instead of relatively complicated impedance spectroscopy.

Acetaminophen (paracetamol, *N*-acetyl-*p*-aminophenol), a widely used analgesic anti-pyretic drug, is a suitable alternative for patients who are sensitive to aspirin [16]. On the other hand, it has been known that overdoses of acetaminophen result in liver and kidney damage [17]. Attempted suicide by use of market available acetaminophen has also been reported. Therefore, various routines including titrimetry, spectrophotometry, liquid chromatography (LC) [18–20] and voltammetry have been developed for the determination of acetaminophen in pharmaceutical formulations and biological fluids. Among these methods, titrimetric and spectrophotometric methods always involve a tedious extraction process prior to detection, whereas the LC methods are time-consuming and expensive. Due to low cost, fast response, simple instrumentations, high sensitivity, facile miniaturization and low power requirements, electrochemical detection of acetaminophen has received extensive attention [21–30]. Various electrodes such as boron-doped diamond [20, 21], conductive polymer-film coated electrodes [22–29], and single wall carbon nanotube-film coated electrodes [30] have been used for the voltammetric detection of acetaminophen.

2 Experimental

2.1 Chemicals and apparatus

MWNTs were purchased from Shenzhen Nanotech Port (Shenzhen, China) and acetaminophen was bought from Sigma (NJ, USA). Other commercially available chemicals were bought from Shanghai 1st Chem. Factory (Shanghai, China) and were of analytical grade.

Electrochemical measurements were performed on a CHI 760B electrochemical station (Chenhua Co. Ltd, Shanghai, China) at room temperature with a conventional three-electrode cell (5 mL). Either a bare glassy electrode (4 mm in diameter) or a MWNT-film coated electrode act as the working electrode. A saturated calomel electrode (SCE) was used as reference and a platinum foil electrode as the counter electrode. All potentials were determined against the SCE. The anodic current is positive and the cathodic negative. A 200-kV high-resolution transmission electron microscope (HRTEM, JEOL-2000) with a magnification of about 3 350 000 was used for the TEM images of MWNTs.

2.2 Fabrication of MWNT-film coated electrodes

Prior to fabricating MWNT-film modified electrodes, the purification and functionalization of the MWNTs was carried out. The purification was performed in a similar way as described in the literature [10, 13, 31]. Briefly, 500-mg of MWNTs were oxidized at 400 °C for 30 min to remove amorphous carbon particles. The oxidized MWNTs were dispersed in 60 mL of 6.0 M HCl for 4 h in an ultrasonic bath to eliminate metal oxide catalysts, rinsed in DI water until the pH of the solution was close to 7.0, and then dried in air at room temperature. In order to generate a carboxylic terminated (-COOH) MWNT surface [32, 33]: the purified MWNTs were further oxidized in a mixture of concentrated sulfuric and nitric acid (v/v = 3:1) with the aid of ultrasonication for 6 h at 50 ∼ 60 °C. The resulting solution was filtered by a poly (tetra Xuoroethylene) membrane with a 200-nm pore size. The filtrate was washed thoroughly with DI water to remove any remaining acid, followed by drying in an oven at 60 °C for 2 h. The functionalized MWNTs were then dissolved in alcohol and the suspension (1.0 mg mL^{-1}) was used for the fabrication of the MWNT-film coated electrodes.

Prior to casting the MWNT suspension on electrodes, the glassy carbon electrodes were polished with sand paper and alumina slurry, cleaned in an ultrasonic cleaner for 10 min and then thoroughly rinsed with distilled water. The required volume of MWNT suspension was distributed on the surface of the electrode. The electrode was dried in air at room temperature; thus the alcohol evaporated and we obtained the MWNT-film modified electrode. The volume of the suspension was changed to obtain different MWNT-film coated electrodes for voltammetric and chronoamperometric investigations.

3 Results and discussion

Figure 1 shows a typical TEM image of MWNTs after purification and functionalization. Long MWNTs about 5–15 μm are always observed; these are promising for electrode coating. The diameters of the MWNTs are around 10–20 nm. Other typical properties of MWNTs are listed as follows: purity $> 95\%$; concentration of amorphous carbon $< 3\%$; the concentration of ash (catalyst residue) $<0.2\%$; special surface area, 40–300 $m^2\ g^{-1}$; thermal conductivity, $\sim$2,000 W $m^{-1}\ K^{-1}$. These MWNTs are well suspended in alcohol. The resultant suspension was used as the stock solution and always stored in a refrigerator at 4 °C. Different MWNT-film coated electrodes were then fabricated with different volumes of the suspension. When the volume of the suspension was less than 20 μL, the MWNTs stuck to electrode surface very well since the voltammetric response of the analytes as discussed in the next sections did not change for over 1 week. However, precipitation of MWNTs was observed (with optical microscopy) after long electrochemical measurements. The strong adsorption of MWNTs on glassy carbon may be due to the relatively rough electrode surface and charged MWNTs surface. More detailed investigation is in progress in our lab.

$Fe(CN)_6^{3-}$ was adopted as a molecular probe to check the reactivity and active electrode area of the MWNT-film coated electrodes. Figure 2 shows a cyclic voltammogram of $Fe(CN)_6^{3-}$ (dashed line). As a control experiment, a cyclic voltammogram on a bare glassy carbon electrode (solid line) was recorded. The anodic and cathodic peak potentials for the MWNT-film coated electrode are the same as those on a bare glassy carbon electrode, indicating that the modified electrode presents good electro-activity towards the redox species. However, the peak currents do not significantly increase on the MWNT-film coated electrode. This is probably because the capacitive current of the modified electrode is also enlarged when its electrode active area is enhanced.

In order to determine the current enhancement of the analytes on the MWNT-film coated electrodes, we varied the amount of MWNT on the electrodes by changing the volumes of MWNT suspension during the fabrication process. Figure 3 shows cyclic voltammograms of $Fe(CN)_6^{3-}$ on the MWNT-film coated electrodes. The currents for $Fe(CN)_6^{3-}$ increase when larger volumes of suspension are used. The absolute value of anodic peak current varies from 0.25, to 0.26 and to 0.29 mA when 5 to 10, and 15 μL suspensions are dispersed, respectively. However, the anodic peak potentials shift positively when the larger volume of suspension is used. This may result from the increased electrode resistances [2, 5], which will be discussed in a later section.

In order to estimate the active electrode area of the MWNT-film modified electrode, we plotted the variation of anodic peak currents as a function of the concentration of $Fe(CN)_6^{3-}$ and of the square root of scan rate on both bare and MWNT-film coated glassy carbon electrodes in Fig. 4. A 10-μL MWNT suspension was used. The anodic peak currents are proportional to the concentration of $Fe(CN)_6^{3-}$ on a bare (full circles) as well as on the MWNT-film coated glassy carbon electrode (open circles). The anodic peak currents also increase proportionally to the square-roots of scan rate on both electrodes, indicating diffusion-controlled

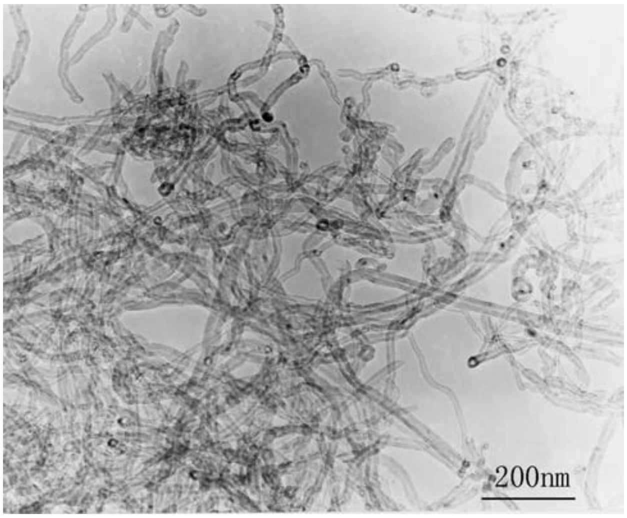

Fig. 1 Typical TEM image of multi-walled carbon nanotubes (MWNTs) used

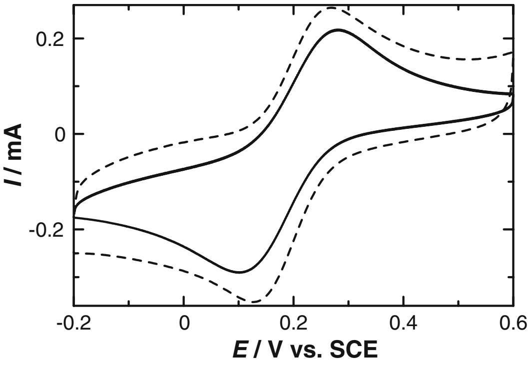

Fig. 2 Cyclic voltammograms of 10.0 mM $Fe(CN)_6^{3-}$ on a bare (solid line) and on the MWNT-film coated (dashed line) glassy carbon electrode at a scan rate of 50 mV s^{-1}. The concentration and the volume of MWNT suspension are 1.0 mg mL^{-1} and 10 μL, respectively

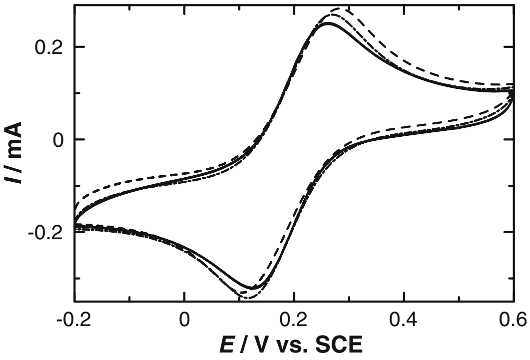

Fig. 3 Cyclic voltammograms of 10.0 mM $Fe(CN)_6^{3-}$ on the MWNT-film coated electrode at a scan rate of 50 mV s^{-1}. The concentration MWNTs suspension is 1.0 mg mL^{-1}. The volumes used are 5, 10, 15 μL from inside to outside, respectively

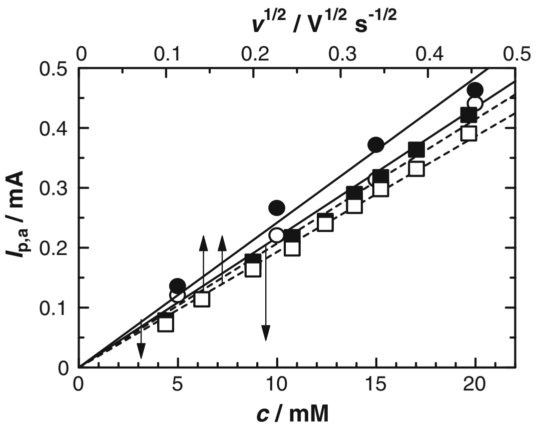

Fig. 4 Variation of anodic peak currents, $I_{p,a}$, with the concentration of $Fe(CN)_6^{3-}$, c, on the MWNT-film coated (full circles) and on a bare (open circles) glassy carbon electrode at a scan rate of 50 mV s^{-1}. $I_{p,a}$, as a function of the square root of scan rates, $v^{1/2}$, on the MWNT-film coated (full squares) and on a bare (open squares) glassy carbon electrode when the concentration of $Fe(CN)_6^{3-}$ is 10.0 mM. The concentration and the volume of MWNTs suspension are 1.0 mg mL^{-1} and 10 μL, respectively

anodic currents. For a diffusion-controlled electrode process, the peak current, I_p, can be expressed in the form [34]

$$I_p = 0.446nFcA(DvnF/RT)^{1/2} \quad (1)$$

where D is the diffusion coefficient of $Fe(CN)_6^{3-}$ (6.70×10^{-6} cm^2 s^{-1}), c is its molar concentration, n (=1) is the number of electrons participated in the redox reaction, A is the electrode active area, and the other variables have their conventional meanings. The electroactive area of two electrodes can be estimated by knowing the slope of I_p *vs.* c or I_p *vs.* $v^{1/2}$. In Fig. 4, the slopes of $I_{p,a}$ *vs.* c are 2.17, 2.42 (unit was not shown) and the slopes of $I_{p,a}$ *vs.* $v^{1/2}$ are 0.85 and 0.91 (unit not shown) for a bare and for the MWNT-film coated glassy carbon electrode, respectively. The ratio of the electroactive area of the MWNT-film coated electrode to that of a bare one is calculated to be 1.115 and 1.071 from the slopes of $I_{p,a}$ *vs.* c and $I_{p,a}$ *vs.* $v^{1/2}$, respectively. From Eq. (1), the real electroactive area of the MWNT-film coated electrode is calculated to be 0.14 cm^2. This result agrees with the reported increase in active electrode areas by CNTs [8–12]. If we assume that the average length of MWNT used is 12.5 μm and their diameters are around 15 nm, the surface area of one MWNT will be 5.89×10^{-9} cm^2. That is to say, when 10 μL of MWNT dispersion is dispersed on the electrode, the number of MWNTs on the electrode will be roughly 2.33×10^7 if the MWNTs are immobilized in the form of a mono-layered structure.

The capacitance of the MWNT-film coated electrode in pH 7.38 phosphate buffer solution was investigated by use of cyclic voltammetry and chronoamperometry. The currents in the cyclic voltammograms on bare and on MWNT-film coated glassy carbon electrode (not shown) in the window potential from 0.2 to 0.8 V increase proportionally to scan rate from 10 to 140 mV s^{-1}, indicative of capacitive currents. The slope of the variation of the current with scan rate on the MWNT-film coated electrode is 1.1-time larger than that of a bare glassy carbon electrode (not shown). If we assume that the capacitance of MWNTs is not so different from glassy carbon (because both are from carbon), the difference in the capacitance directly reflects the change in electrode active area (since the capacitance is proportional to the electrode area). This agrees with previous discussions about 1.1-time enhancement of active electrode area after casting MWNTs.

Potential step experiments were then carried out on a bare and a MWNT-film coated glassy carbon electrode from 0.2 to 0.4 V in pH 7.38 phosphate buffer solution to estimate the capacitances and resistances. Figure 5 shows the corresponding chronoamperometric curves. The currents decay exponentially on both the MWNT-film coated and bare glassy carbon electrode. For a potential step with a magnitude of E, the variation of the current, i, with time, t, is expressed as [34]

$$i = \frac{E}{R_s} e^{-t/R_s C_d} \quad (2)$$

where R_s represents the electrode resistance and C_d stands for the capacitance. If we take natural logarithm on both sides of Eq. (2), we obtain

$$\ln i = \ln \frac{E}{R_s} - \frac{t}{R_s C_d} \quad (3)$$

From the linearity of ln$i$ *vs.* t, we can obtain the values of R_s and C_d. The calculated capacitances are 5.34×10^{-4} and 5.67×10^{-4} F for the bare and the MWNT-film coated glassy carbon electrodes, respectively. If we take their active electrode surface into account, we get similar values

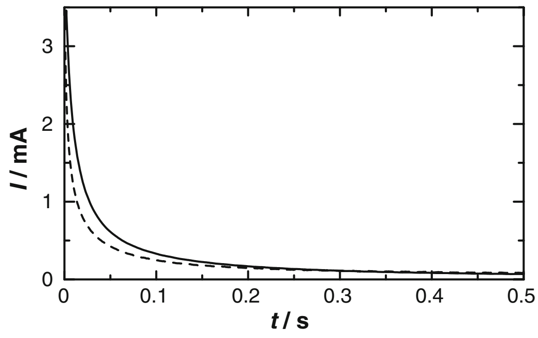

Fig. 5 Chronoamperometric curves of the MWNT-film coated (solid line) and a bare (dashed line) glassy carbon electrode in the pH 7.38 phosphate buffer solution. The potential is set at 0.2 V for 5 s and then step to 0.4 V. The concentration and the volume of MWNT suspension are 1.0 mg mL^{-1} and 10 μL, respectively

of normalized capacitance for the bare glassy carbon electrode and the MWNT-film coated electrode. This is reasonable since both originate from carbon. The calculated values of R_s are 323 and 455 Ω for the bare and the MWNT-film coated glassy carbon electrodes, respectively. The increased resistance of the MWNT-film coated electrodes results in the positive shift of anodic peak potentials of $Fe(CN)_6^{3-}$ observed in Fig. 3.

The voltammetric behavior of acetaminophen on the MWNT-film coated electrode (dashed line) was then studied and is presented in Fig. 6, which shows a sharp anodic peak at 0.36 V with a diffusion tail and a well-defined cathodic wave at 0.27 V. The absolute value of the anodic peak current is almost equal to the cathodic one. The cyclic voltammogram of the MWNT-film coated electrode in pH 7.38 phosphate buffer solution (solid line) only shows a capacitive current. At the bare glassy carbon electrode (dotted-dashed line), acetaminophen is oxidized irreversibly with an oxidative peak at 0.36 V and a broad cathodic reductive peak from 0.36 to 0.16 V. The anodic current is more pronounced than the cathodic one. These facts suggest that the voltammetric response of acetaminophen is significantly improved at the MWNT-film coated electrode, in agreement with the literature [5–12].

The effect of pH of the buffer solution, scan rate, the volume used for the fabrication of modified electrode, and the interference on the redox current of acetaminophen were then inspected. When the pH of the phosphate buffer solution is changed from 4.4 to 8.3, the anodic peak potential shifts negatively and shows a linear relationship with pH slope -0.057 mV pH^{-1}, indicating that the same numbers of electrons and protons accompany the oxidation of acetaminophen. It has been known that the number of electrons transferred during the oxidation of acetaminophen is 2 [35]. Therefore, two electrons and two protons participate in the oxidation of acetaminophen. The anodic wave at 0.37 V probably results from the oxidation of acetaminophen into the oxidized imidogenquinone, while the cathodic one at 0.27 V is due to the reduction of imidogenquinone to acetaminophen. The maximum anodic peak current is obtained at pH 7.38. Therefore, pH 7.38 phosphate buffer solution was adopted for the voltammetric measurements of acetaminophen in the next sections.

The anodic peak current, $I_{p,a}$, increases with square root of scan rate, $v^{1/2}$, on the MWNT-film coated electrode, as shown by the full circles in Fig. 7, indicating a diffusion-controlled electrode process. As a control experiment, $I_{p,a}$ as a function of $v^{1/2}$ on a bare glassy carbon (open circles) is plotted in Fig. 7, showing proportionality. The slope of $I_{p,a}$ *vs.* $v^{1/2}$ of the MWNT-film coated electrode is 1.1-times larger than that of the bare glassy carbon electrode. This difference is due to the increased active area by MWNTs, as discussed in the previous sections.

Figure 8 shows cyclic voltammograms of acetaminophen on the MWNT-film coated glassy carbon electrodes with different amount of MWNT used. The current response increases when more MWNTs are dispersed on the electrode although the capacitive current increases significantly. Experimentally, too large an amount of MWNT (larger than 20 μL) is not helpful for the fabrication of modified electrodes because part of the MWNTs on the electrodes is lost when the electrode touches the solutions.

Possible interferences for the detection of acetaminophen at the MWNT film coated electrode were examined. Various ions were added to 50 μM acetaminophen solutions and then the voltammetric behavior was investigated. The volume used for the fabrication of the MWNT-film coated electrode was 10 μL and the concentration of MWNTs

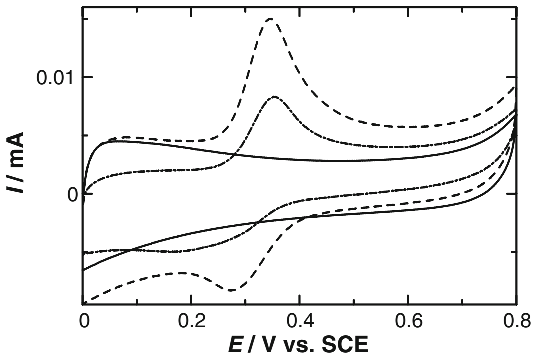

Fig. 6 Cyclic voltammograms of 0.1 mM acetaminophen on the MWNT-film coated (dashed line) and on a bare (dashed-dotted line) glassy electrode in pH 7.38 phosphate buffer solution. The solid line is the cyclic voltammogram of the MWNT-film coated electrode in pH 7.38 phosphate buffer solution without acetaminophen. The scan rate is 40 mV s^{-1}. The concentration and the volume of MWNTs suspension used are 1.0 mg mL^{-1} and 10 μL, respectively

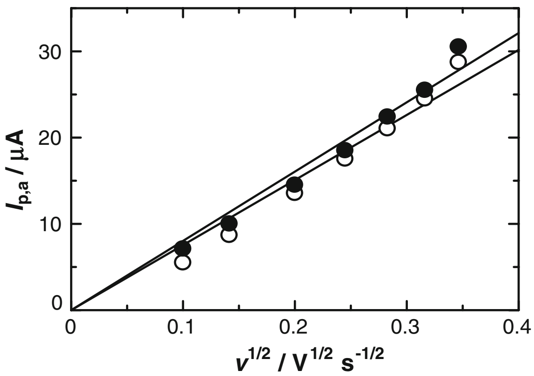

Fig. 7 Variation of the anodic peak currents, $I_{p,a}$, with the square-root of scan rate, $v^{1/2}$ on the MWNT-film coated (full circles) and on the bare (open circles) glassy carbon electrode. The concentration and the volume of MWNTs suspension used are 1.0 mg mL^{-1} and 10 μL, respectively. The concentration of acetaminophen is 0.1 mM

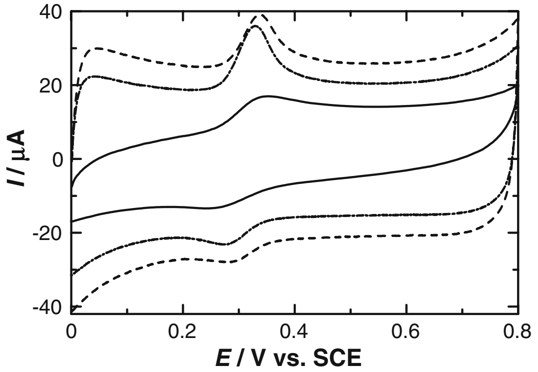

Fig. 8 Cyclic voltammograms of 0.1 mM acetaminophen on the MWNT-film coated glassy electrodes in pH 7.38 phosphate buffer solution at a scan rate of 50 mV s^{-1}. The concentration of MWNTs suspension used for the fabrication of electrode is 1.0 mg mL^{-1}. The volumes used are 5 (solid line), 10 (dotted-dashed line), 15 (dashed line) μL

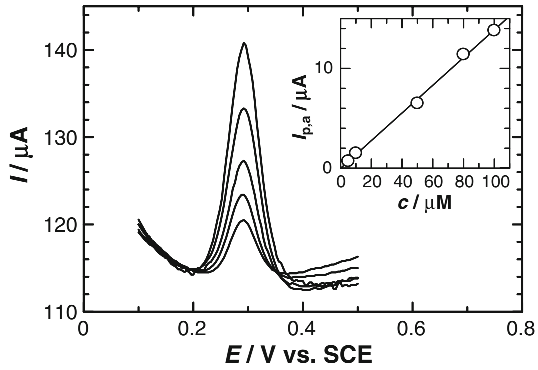

Fig. 9 Differential pulse voltammograms of acetaminophen on the MWNT-film coated glassy electrode at a scan rate of 50 mV s^{-1}. The pulse voltage is 10 mV and the amplitude is 2.5 mV. The concentrations of acetaminophen are 5.0, 10, 50, 80, 100 μM from inside to outside, respectively. The insert is the proportionality of the anodic peak currents from differential pulse voltammograms, $I_{p,a}$, to the concentration of acetaminophen, *c*. The concentration and the volume of MWNTs suspension used are 1.0 mg mL^{-1} and 10 μL, respectively

was 1.0 mg mL^{-1}. Most of common ions like Na^+, K^+, Fe^{3+}, Cu^{2+}, Al^{3+}, Cl^-, NO^{3-}, $CO_3{}^{2-}$, and $SO_4{}^{2-}$ show no interference to acetaminophen detection. The common interferences in biological samples, like lysine, ascorbic acid, tyrosine, cysteine and vitamin $B_{6,}$ show interference up to a 30-fold concentration of acetaminophen.

Since a large capacitive current is noticed on the MWNT-film coated electrode, differential pulse voltammetry was applied for the detection of acetaminophen. Figure 9 shows differential pulse voltammograms of acetaminophen with different concentrations when the 10-μL suspension was used for the fabrication of the modified electrode. The anodic peak current, $I_{p,a}$, is proportional to the concentration of acetaminophen, *c*, in the concentration range 5.0 μM to 0.1 mM. The linear regression equation is inserted into Fig. 9 and is expressed as $I_{p,a}$ (μA) = 0.14*c* (μM) (*R* = 0.9989). The detection limit is 2.4 μM when the signal/noise ratio is 3. When 5- or 15-μL suspension is used, the linear equations are $I_{p,a}$ (μA) = 0.07*c* (μM) (*R* = 0.9989) and $I_{p,a}$ (μA) = 0.09*c* (μM) (*R* = 0.9987), respectively. Unfortunately, the MWNT-film coated electrodes do not show lower detection limits than those using single-walled carbon nanotube-film coated glassy carbon electrodes [30]. The possible reasons may be the types of functional groups used on the CNTs, the immobilization methods of CNTs on the electrodes, and the detection method used. We are currently working on this topic and will report results in the future.

The MWNT-film coated electrode using different amounts of MWNT was applied to determine the amount of acetaminophen in composite chlorzoxazone tablets (Shiguibao Pharmaceutical Group Corporation, Shanghai, China). The powdered tablets were dissolved in approximately 125 mL distilled water. The suspension was stirred and centrifuged at 3,500 rpm for 10 min. The 5-mL supernatant was diluted into 250 mL with phosphate buffer saline. A 10-mL resulting solution was then taken out and used as the sample for the concentration detection of acetaminophen. The concentration of acetaminophen was calculated using the standard addition method. The analytical results obtained are listed in Table 1. When the volumes of MWNT suspension (1.0 mg mL^{-1}) used for the fabrication of modified electrodes are 5. 10, 15 μL, the relative standard deviations of each sample for five time parallel detections are in the ranges 2.05 to 7.8, 1.97 to 7.94, and 1.95 to 8.06%, respectively. The recoveries are in

Table 1 Determination of acetaminophen in tablets by the MWNT-film coated electrodes

Volume[a]/ μL	Content/ 0.1 μM	Added/ 0.1 μM	Found/ 0.1 μM	Recovery/ %
5	1	1	2.05	105
		2	3.09	109
	4	2	5.98	99.5
		4	7.8	95
10	1	1	1.97	97
		2	2.97	97
	4	2	6.03	100.8
		4	7.94	98.5
15	1	1	1.95	95
		2	3.08	108
	4	2	6.24	106
		4	8.06	101.5

[a] The volume of the suspension (1.0 mg mL^{-1}) of MWNTs used for the fabrication of electrodes

the ranges 95 to 105, 97 to 100.8, 95 to 108%, respectively. These results indicate the MWNT film coated electrodes are effective and sensitive for the detection of acetaminophen in tablets.

4 Conclusions

The electrode area and the redox current of analytes in liquids are enhanced by CNT coated on glassy carbon electrodes. However, the capacitance and the resistance of electrodes are increased due to the enlarged surface area of the nano-sized materials. Therefore, the first thing that should be taken into consideration before the detection of analytes in solutions by use of nano-sized materials is to optimize the amount of nano-sized material on the electrodes, although these MWNT-film coated electrodes are still efficient and sensitive for the electrochemical detection of analytes in liquids and are promising for the analysis of pharmaceutical formulations.

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References

1. Iijima S (1991) Nature 354:56
2. Ajayan PM (1999) Chem Rev 99:1787
3. Tasis D, Tagmatarchis N, Bianco A, Prato M (2006) Chem Rev 106:1105
4. Serp P, Corrias M, Kalck P (2003) Appl Catal A: Gen 253:337
5. Davis JJ, Coles RJ, Allen H, Hill O (1997) Electroanal Chem 440:279
6. Rivas GA, Rubianes MD, Rodríguez MC, Ferreyra NF, Luque GL, Pedano ML, Miscoria SA, Parrado C (2007) Talanta 74:291
7. Wang J, Musameh M (2003) Anal Chem 75:2075
8. Moore RR, Banks CE, Compton RG (2004) Anal Chem 76:2677
9. Chen RS, Huang WH, Tong H, Wang ZL, Cheng JK (2003) Anal Chem 75:6341
10. Gong KP, Zhang MN, Yan YM, Su L, Mao LQ, Xiong SX, Chen Y (2004) Anal Chem 76:6500
11. Hrapovic S, Liu Y, Male KB, Luong JHT (2004) Anal Chem 76:1083
12. Zhang MG, Smith A, Gorski W (2004) Anal Chem 76:5045
13. Valentini F, Amine A, Orlanducci S, Terranova ML, Palleschi G (2003) Anal Chem 75:5413
14. Luo H, Shi Z, Li N, Gu Z, Zhuang Q (2001) Anal Chem 73:915
15. Guo M, Chen J, Nie L, Yao S (2004) Electrochim Acta 49:2637
16. Wade A (ed) (1979) Martindale, the extra pharmacopoeia, 27th edn. The Pharmaceutical Press, London
17. Clayton BD, Stock YN (2001) Basic pharmacology for nurses. Mosby Inc., Harcourt Health Sciences Company, St. Louis
18. Li S, Berger J, Hartland S (1990) Anal Chim Acta 232:409
19. Garrigues S, Gallignani M, de la Guardia M (1993) Talanta 40:1799
20. Schreiber-Deturmeny E, Bruguerolle B (1996) J Chromatogr B 677:305
21. Waterston K, Wang JW, Bejan D, Bunce NJ (2006) J Appl Electrochem 36:227
22. Wangfuenkanagul N, Chailapakul O (2002) J Pharm Biomed Anal 28:841
23. Wang C, Li C, Wei L, Wang C (2007) Microchim Acta 158:307
24. Li HM, Ge RL, Wang EK (1994) Anal Chim Acta 292:107
25. Zen JM, Ting YS (1997) Anal Chim Acta 342:175
26. Shi GY, Xue F, Jin LT (1999) Electroanalysis 11:432
27. Huang SS, Tang H, Li BF (1998) Microchim Acta 128:37
28. He FY, Liu AL, Xia XH (2004) Anal Bioanal Chem 379:1062
29. Boopathi M, Won MS, Shim YB (2004) Anal Chim Acta 512:191
30. Sun D, Zhang H (2007) Microchim Acta 158:131
31. Zhang MN, Yan YM, Gong KP, Mao LQ, Guo ZX, Chen Y (2004) Langmuir 20:8781
32. Liu Z, Shen Z, Zhu T, Hou S, Ying L, Shi Z, Gu Z (2000) Langmuir 16:3569
33. Jang SR, Vittal R, Kim KJ (2004) Langmuir 20:9807
34. Bard AJ, Faulkner LR (2000) Electrochemical methods, 2nd edn. Wiley, New York
35. Wangfuengkanagul N, Chailapakul O (2002) Pharm Biomed Anal 28:841