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ORIGINAL PAPER

Functionalization of multi-walled carbon nanotube for electrocatalytic oxidation of nitric oxide

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Abstract The multi-walled carbon nanotube (MWCNT) was functionalized with hydroxyl, carboxyl and amido groups on the surface. Electrocatalytic oxidation of nitric oxide (NO) at the MWCNT modified electrodes was investigated. It was found that the MWCNT modified electrode could speed up greatly the electron transfer rate compared with the glass carbon electrode, and there was an adsorptive step for the oxidation of NO at the MWCNT modified electrode. The activation energy of NO electro-oxidation reaction at modified electrode of MWCNT treated by alkali and mixed acids (MWCNT-OH–COOH) decreased, and current density was almost two times that of the electrode modified with alkali treated MWCNT. The modified electrodes of MWCNT amidated with the aliphatic amines decreased the activation energy of NO oxidation compared with MWCNT modified electrode, but the reaction rate of amidated MWCNT electrodes decreased because of the steric effect. The results demonstrated that MWCNT-OH–COOH modified electrode is the best for NO electrocatalytic oxidation.

Keywords Multi-walled carbon nanotube · Modified electrode · Nitric oxide · Electrocatalytic oxidation · Cyclic voltammetry

1 Introduction

Since the report of carbon microtubules which is known as carbon nanotube (CNT) in 1991 by Iijima [1], there has been enormous interest on exploring and developing the unique mechanical, chemical and electrical properties of CNT, such as extremely high mechanical strength, high chemical stability and high electrical conductivity [2]. Although CNT is considered chemically inert, owing to their atomic structure, CNT behaves electrically as a metal or as a semiconductor. The subtle electronic properties suggest that CNT has the ability to promote electron transfer [3, 4]. The pentagonal defects and extra dimensional curvature present at the tips can enhance electron transfer rate when used as electrodes in some chemical reactions [5]. The electrodes based on CNT have been proved to have excellent electrochemical properties, such as wide potential window and small background current. The electrodes modified with CNT showed well-behaved electrochemical response and electrocatalytic activities compared with traditional carbon electrodes. And the CNT modified electrodes showed very stable electrochemical behaviors, it could be used to catalyze the electrochemical reaction of some bio-molecules [6–15] and organic molecules [16–20]. The experimental results of CNT modified electrodes indicate that once the CNT is treated with nitric acid, carboxyl groups will be introduced onto the open ends of CNT and the electrode activity was enhanced [21].

Nitric oxide (NO) is a major atmospheric pollutant that has caused a detrimental environment. NO has been found to play many significant roles in physiological and pathological function [22]. As a result, elimination of NO in atmosphere and accurate measurements of NO in complex biological matrices are extremely necessary. Several methods have been used to measure NO both in aqueous

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solution and gas phase. Monitoring and measurement of NO with electrochemical methods are of great significance because of their convenient, simple and rapid operation. Many modified electrodes have been used to detect NO, such as nickel phthalocyanine complexes [23], iron porphyrin complexes [24] and some proteins [25–28]. Detection of NH_3, NO_2 and O_2 at CNT electrodes were reported [29–31]. But papers on investigation of NO at CNT electrodes were seldom published [32].

This paper emphasized on the functionalization of multi-walled carbon nanotube (MWCNT) treated with chemical methods and its application for NO electrocatalytic oxidation. After the MWCNT surface was hydroxylated, carboxylated and amidated, the reaction rate and activation energy were changed. We expect to establish a high sensitivity method to detect NO in aqueous solution.

2 Experimental

2.1 Reagents

The MWCNT was purchased from Chengdu Organic Chemicals Co. Ltd. Chinese Academy of Science with the diameter ranging from 10 to 20 nm and the length ranging from 10 to 30 μm. The purity is higher than 95%. All other chemicals were of analytical-reagent grade, and solutions were prepared using deionized water after doubly distilled. All electrochemical experiments were carried out at the room temperature.

Take 0.1 mol L^{-1} KH_2PO_4–NaOH buffer solution (PBS) with pH 6.8 as a blank solution. The solution was bubbled for 30 min to remove oxygen with high purity nitrogen, and then bubbled with pure NO for 30 min to prepare a NO saturated solution.

2.2 MWCNT pretreatment with different methods

2.2.1 Alkali treatment of MWCNT

The mass ratio 10:1 of KOH to the MWCNT was mixed and grounded. The samples were heated from the room temperature to 1,073 K at a raising rate of 10 K min^{-1} under the nitrogen atmosphere (the flow rate 420 mL min^{-1}) in tubal furnace. The samples were kept 1,073 K for 2 h, cooled down in nitrogen, then washed with distilled water until the pH value is 7.0, dried at 383 K for 48 h; the MWCNT-OH sample was obtained.

2.2.2 Mixed acids treatment of MWCNT

The MWCNT or MWCNT-OH was added into the mixed solution with the volume ratio 3:1 of H_2SO_4 to HNO_3. The mixture was treated by ultrasonic for 10 min, stirred for 2 h, filtered, and washed until the pH of 7.0. The solid sample was dried for 24 h at 313 K in vacuum, then the MWCNT-COOH and MWCNT-OH–COOH samples were obtained.

2.2.3 Amines treatments of MWCNT

The MWCNT-OH–COOH was mixed with octadecylamine (ODA), hexadecylamine (HDA) and *n*-butylamine (BUA) with a mass ratio of 1:10, the sample and ODA refluxed at 393 K for 120 h; the sample and HDA refluxed at 343 K for 48 h; the sample and BUA refluxed at 353 K for 120 h. The products were cooled down to the room temperature, sonicated in ethanol, and filtrated. The solid samples were dried in vacuum.

2.3 Fourier transfer infrared spectra characterizations

In order to analyze and determine the functional groups of the modified MWCNT, Fourier transfer infrared (FTIR) spectra was used for characterization. The FTIR spectral measurements were carried out with FTIR Spectrometer (Perkin Elmer Spectrum one).

2.4 Electrochemistry characterizations

Before experiment, a glass carbon (GC) electrode (diameter 4 mm) was polished, sonicated in ethanol, acetone and deioned water. And then the electrode was dried at the room temperature. 2.5 mg MWCNT in 10 mL of acetone was dispersed with ultrasonic processing to get a suspension. The suspension of 10 μL was dropped on the surface of the GC electrode, and acetone was gradually evaporated under an infrared lamp, the MWCNT modified electrode was prepared.

Cyclic voltammetry (CV) measurements were performed with a conventional three-electrode cell by LK9805 electrochemical analyzer (Lanlik Instrument Co. Ltd., Tianjin, China). The working electrode is a GC electrode or MWCNT modified electrode, a platinum sheet was taken as the auxiliary electrode, Ag/AgCl electrode is used as the reference electrode. The scan rate was 50 mV s^{-1}.

Electrochemical impedance spectroscopy (EIS) measurements were performed by IM6e impedance measurement unit (ZAHNER Elektrik, Germany). The electrodes and reagents were the same as in the CV measurements. The AC voltage amplitude used was 10 mV in a frequency range from 10 mHz to 100 kHz and the data are processed with Zview2 software.

3 Results and discussion

3.1 FTIR spectra characterizations

The FTIR spectra of the MWCNT treated by alkali and mixed acids are depicted in Fig. 1. All spectra share a peak at about 3,131 cm^{-1} which is attributed to C–H stretching vibration in the MWCNT; and a peak at about 1,401 cm^{-1} which is assigned to O–H deformation vibration in C–OH groups [33]. The absorbance peak at 3,410 cm^{-1} for the curve (b) in Fig. 1 is assigned to the O–H stretching vibration [34], the peak intensity of MWCNT-OH increases compared with untreated MWCNT (as shown in Fig. 1a), the result indicates that there are a large number of hydroxyl groups on the surface of MWCNT treated by alkali. The curves (c) and (d) in Fig. 1 show the FTIR spectra of MWCNT-COOH and MWCNT-OH–COOH. The two curves share a broad absorbance peak at about 1,745 cm^{-1}, which is attributed to the carbonyl stretching vibration in the carboxyl groups [35]. The broad absorbance band about 1,300 cm^{-1} is due to O–H bending deformation in –COOH, the enhanced and broaden peak at 3,131 cm^{-1} is assigned to O–H stretching vibration in the carboxyl groups, which confirms that there are carboxyl groups on the MWCNT-COOH and MWCNT-OH–COOH surface.

The curves (a), (b) and (c) in Fig. 2 show the FTIR spectra of MWCNT-BUA, MWCNT-HDA and MWCNT-ODA. All spectra share a broad absorbance peak at about 1,612 cm^{-1}, which is attributed to the carbonyl stretching vibration in the amido groups. There are two peaks at 2,920 and 2,850 cm^{-1} in the FTIR spectra which are assigned to the asymmetric and symmetric stretching of C–H stretching. And the absorbance peak intensity of the curves (b) and (c) is stronger than that of curve (a) because the alkyl chain of BUA is the shortest. The peak at 3,340 cm^{-1} is assigned to the N–H stretching vibration, which confirms that there are amido groups on the MWCNT surface treated by amines [36].

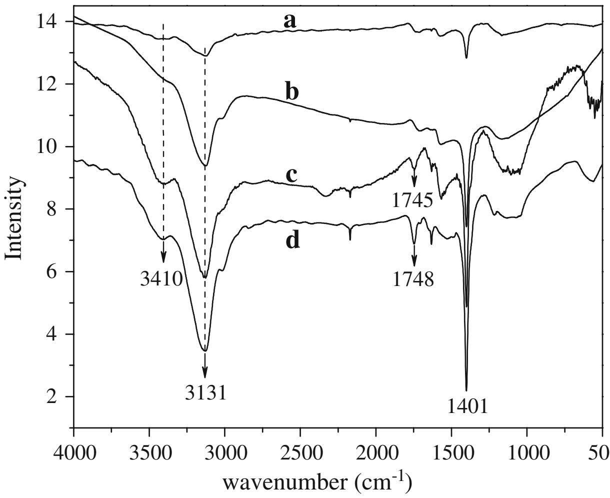

Fig. 1 FTIR spectra of MWCNT (*a*), MWCNT-OH (*b*), MWCNT-COOH (*c*) and MWCNT-OH–COOH (*d*)

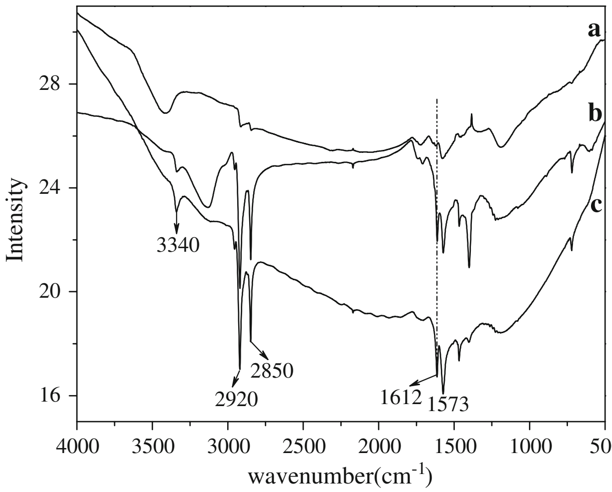

Fig. 2 FTIR spectra of MWCNT-BUA (*a*), MWCNT-HDA (*b*) and MWCNT-ODA (*c*)

3.2 NO electrooxidation at GC electrode and MWCNT modified electrodes

NO electrooxidation at bare GC electrode and MWCNT modified electrode are studied. The curves (a) and (b) in Fig. 3 show the cyclic voltammograms of the electrodes in the PBS without the existence of NO. No obvious redox peak is observed in the potential range from 300 to 1,500 mV. This indicates that they are inert in the blank solution.

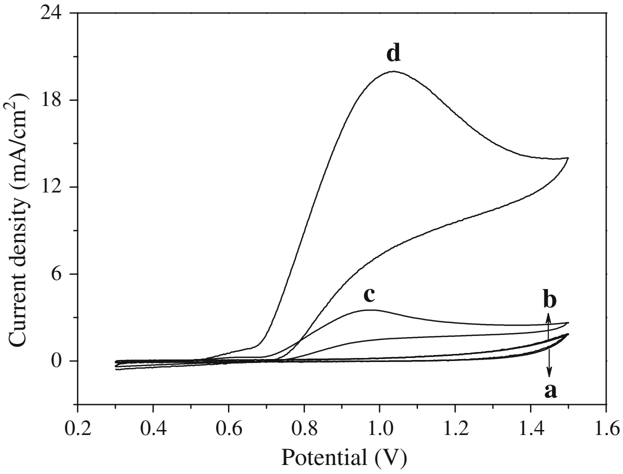

Fig. 3 Cyclic voltammograms of the GC electrode (*a*, *c*) and the MWCNT modified electrode (*b*, *d*). For (*a*) and (*b*), there is blank PBS; for (*c*) and (*d*), the PBS saturated with NO

The curves (c) and (d) in Fig. 3 show the cyclic voltammograms of NO electrooxidation at the bare GC electrode and the MWCNT modified electrode. As shown in the curve (c), a small NO electrooxidation peak is observed at the bare GC electrode in the potential range between 300 and 1,500 mV. The peak potential is 975 mV and the peak current density is 3.46 mA cm^{-2}. No reduction peak appears and this indicates the NO electrooxidation at the GC electrode is irreversible. Results show that NO is oxidized at the GC electrode and the oxidation reaction equation is likely to be $NO + 2OH^- \rightarrow HNO_3 + H^+ + 3e^-$ [37]. The effect of scan rate on the electrochemistry of NO at the GC electrode was investigated by cyclic voltammetry. As shown in Fig. 4, when the scan rate increased, the peak currents increased and the peak potentials shifted to more positive values. The oxidation peak currents of NO depend linearly on the square root of the potential scan rate in the range from 10 to 320 mV s^{-1} and the linear correlation coefficient of the curve is 0.996. Then it can be concluded that the anodic oxidation processes of NO at the GC modified electrode are controlled by diffusion of NO.

The curve (d) in Fig. 3 shows the cyclic voltammogram of NO at the MWCNT modified electrode. An obvious NO electrooxidation peak is observed and the peak potential is 1,036 mV. The peak current density is 19.72 mA cm^{-2} which is 5.7 times the value of the GC electrode. Moreover, the current density at the MWCNT modified electrode is always higher than that at the bare GC electrode. The fact indicates that MWCNT modified electrode, as a promoter, can enhance the reaction rate of NO electrooxidation. The high porosity and large surface area of the MWCNT contribute to the adsorption of gas molecules; the pentagonal defects and extra dimensional curvature presenting at the tips on the MWCNTs are favorable to electron transfer [5]. All of the above facts demonstrate that the MWCNT modified electrode has the better electrocatalytic activity for NO oxidation in comparison with the bare GC electrode.

The EIS is employed to investigate the NO electrooxidation. Figure 5 shows the Nyquist diagrams of the bare GC electrode (a) and the MWCNT modified electrode (b), the constant potential is 900 mV. The equivalent circuit compatible with the studied system is depicted in the inset. R_s is the solution resistance, constant-phase element (CPE) corresponds to the double-layer capacitance, and R_{ct} is the charge transfer resistance. The R_{ct} of the electrode reaction shows the rate of charge transfer during NO electrooxidation.

There is a capacitive semicircle at the bare GC electrode. The capacitive semicircle of MWCNT modified electrode is smaller than that of the GC electrode, which

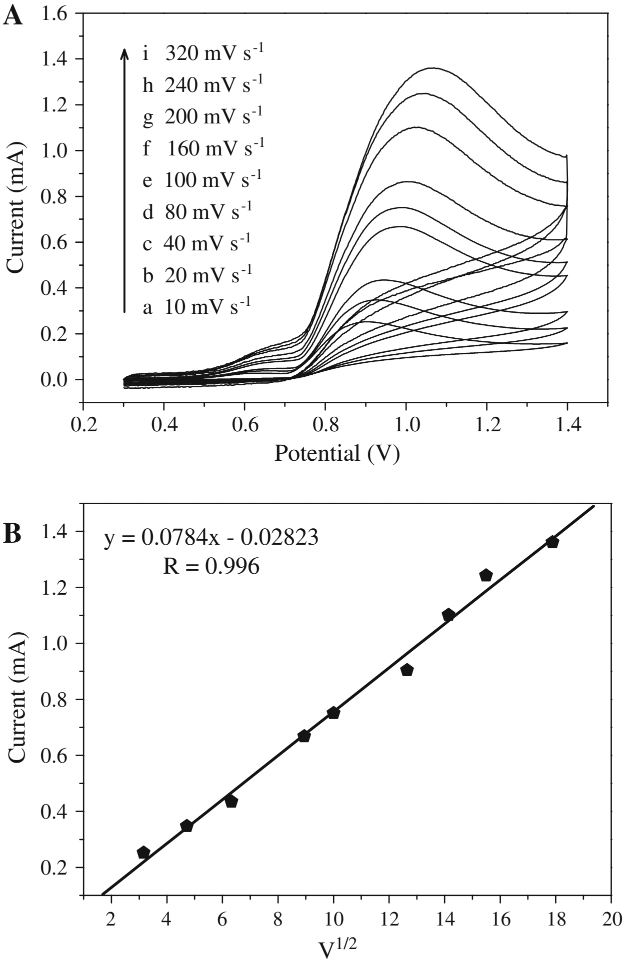

Fig. 4 **a** Cyclic voltammograms of GC electrode in different scan rate. Potential sweep rates from (*a*) to (*h*) are: 10, 20, 40, 80, 10, 160, 200, 240 and 320 mV s^{-1}. **b** Dependency of peak currents on the corresponding square root of the scan rate

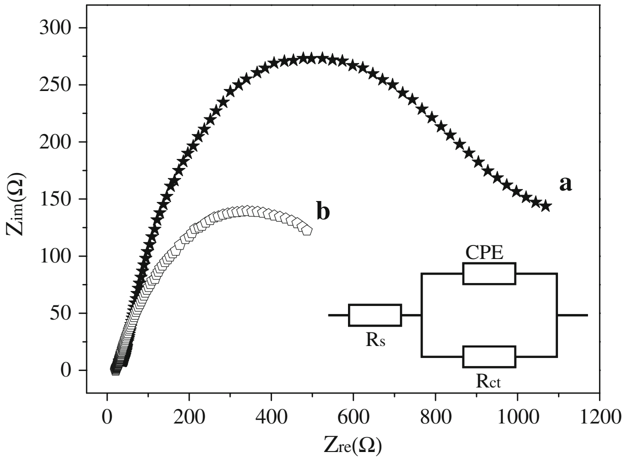

Fig. 5 Nyquist diagram of GC electrode (*a*) and MWCNT modified electrode (*b*) in the PBS saturated NO. The inset is the equivalent circuit compatible with the studied system (the constant potential was 900 mV)

suggests that the modified electrode can increase the charge transfer rate. The resistance values of charge transfer is calculated by Zview2 software. The resistance value of the bare GC (958 Ω) is higher than that of the MWCNT modified electrode (364 Ω); the results are consistent with the CV results.

3.3 NO electrooxidation at different electrodes

Figure 6c shows cyclic voltammograms at the MWCNT-OH modified electrode in the PBS saturated with NO. The current density decreases dramatically and is only a half of the current density at the MWCNT-COOH modified electrode; it is also lower than the current density of the MWCNT modified electrode. The reasons are as follows: On the one hand, there are a lot of hydroxyl groups on the surface of MWCNT-OH and the oxygen and hydrogen in the hydroxyl groups have already formed a covalent bond. The oxygen atoms in the hydroxyl groups can not adsorb NO in solution; On the other hand, the active sites on the MWCNT-OH surface are much less than the crude MWCNT surface because of the occupation of hydroxyl groups. Therefore the probability of NO in solution contacting with MWCNT-OH modified electrode surface is decreased.

The curve (d) in Fig. 6 shows cyclic voltammograms at the MWCNT-OH–COOH modified electrode in the PBS saturated with NO. Its peak current density is almost equal to that at the MWCNT-COOH modified electrode, however, its peak potential shifts 175 mV toward negative direction compared with the latter. The fact indicates that synergistic action of MWCNT treated by alkali and mixed acids enhanced the electrocatalytic ability of the MWCNT-OH–COOH modified electrode for NO electrooxidation. The alkali treatment shortened the length of MWCNT. The area of open end augmented and the defect sites also increased [38, 39]. Moreover, after treated by mixed acids, the hydroxyl groups on MWCNT-OH surface were replaced by carboxyl groups. The NO electrooxidation occurred at lower potential since the activation energy was decreased. Therefore, the MWCNT-OH–COOH is an excellent electrode material for NO electrooxidation.

The MWCNT-OH–COOH was further treated by ODA, HDA and BUA. The curves (a), (b) and (c) in Fig. 7 show cyclic voltammograms of the MWCNT-ODA, MWCNT-HDA and MWCNT-BUA modified electrodes in the PBS saturated with NO. Their peak potentials shift toward negative direction compared with the peak potential on MWCNT modified electrode; Their peak current density depends on the fatty chain length of amines. The peak current density of MWCNT-BUA modified electrode is the biggest among MWCNT-BUA, MWCNT-ODA, MWCNT-HDA modified electrodes. When the MWCNT-OH–COOH is treated by amines, the amino groups of aliphatic amines react with carboxyl groups on the MWCNT surface and the amido groups are formed (as shown in Fig. 1). The steric hindrance effect of the alkyl groups in aliphatic chain float outside the electrode surface inhibited the diffusion and contact of NO to the electrode surface. The longer the chain is, the larger the steric effect is. The steric hindrance effect decreases the reaction rate of NO electrooxidation, i.e. decreases the current density of NO electrooxidation.

It is found from the comparison of the curve (c) in Fig. 7 and the curve (b) in Fig. 6 that the current density at the MWCNT-COOH modified electrode is greater than that at the MWCNT-BUA modified electrode, but the peak

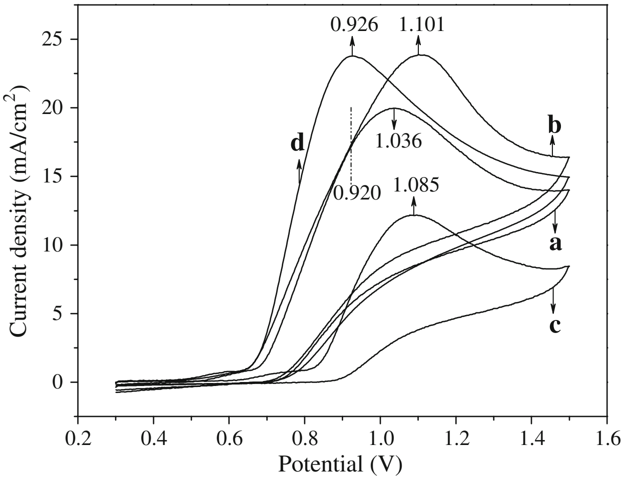

Fig. 6 Cyclic voltammograms of MWCNT (*a*), MWCNT-COOH (*b*), MWCNT-OH (*c*), and MWCNT-OH–COOH (*d*) modified electrodes in the PBS saturated with NO

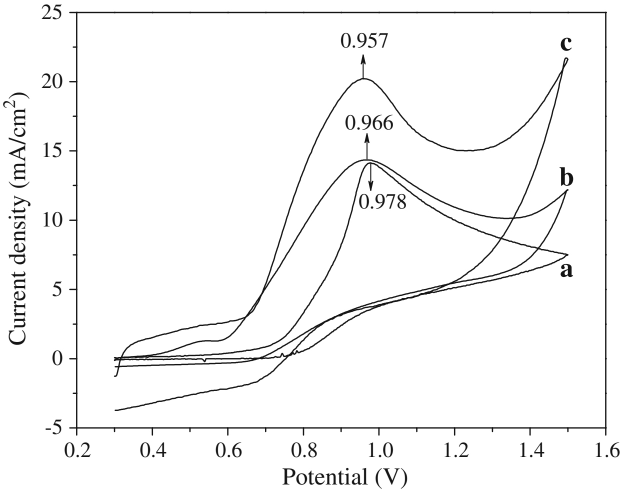

Fig. 7 Cyclic voltammograms of the MWCNT-ODA (*a*), the MWCNT-HDA (*b*) and the MWCNT-BUA (*c*) modified electrodes in the PBS with NO

potential of the latter is lower than that of the former. The NO electrooxidation process includes its diffusion, adsorption and electron transfer. And the adsorption of NO is in favor of its electron transfer. The carbonyl group in carboxyl groups or in the amido groups reacts with NO in solution to form a covalent adsorption. But the electronegativity of nitrogen in amido groups is less than that of oxygen in carboxyl groups of MWCNT-COOH and the attraction to electron of the former is less than the latter. Then the oxygen in amido groups possesses more negative charge compared with that at carbonyl groups in carboxyl groups. It has the stronger adsorptive ability to NO and the activation energy of NO electrooxidation at MWCNT-BUA modified electrode decreases. The electrooxidation potential of MWCNT-BUA modified electrode shifted toward negative direction compared with that of the MWCNT-COOH modified electrode. The lower current density resulted from the steric effect of long aliphatic chain in BUA.

4 Conclusions

The MWCNT modified electrode has a higher electrocatalytic activity to the NO oxidation compared with the GC electrode. Electron transfer is the control step in NO electrooxidation at the GC electrode; while NO electrooxidation at the MWCNT modified electrode is controlled by the mass transfer process of NO and the oxidation rate is influenced by adsorption of NO at the same time.

After the MWCNT was chemically treated by mixed acids and amines, the electrocatalytic activity of the modified electrode was enhanced and that of alkali treated MWCNT was reduced. The current density (the reaction rate of NO electrooxidation) and the peak potential (the activation energy of NO electrooxidation) were also changed. The reaction rate of NO electrooxidation at the MWCNT-COOH modified electrode increased apparently, but it decreased at the MWCNT-OH modified electrode. For the MWCNT-OH–COOH modified electrode, the reaction rate and the activation energy of NO electrooxidation increased, i.e. the peak potential decreased apparently. It is the best electrode material for NO oxidation in all experimental electrodes.

As to the modified electrodes of MWCNT amidated with the aliphatic amines, the activation energy of NO electrooxidation decreased. The modified electrodes did not enhance the reaction rate of NO oxidation because of the steric effect; the effect of the MWCNT-BUA modified electrode was the best one due to its shortest chain in all the amidated electrodes. However, the reaction rate of NO electrooxidation at MWCNT-BUA modified electrode was lower than that at MWCNT-OH–COOH modified electrode.

According to all of above results, it can be concluded that chemical modification of the MWCNT is one of the most powerful mediums to enhance the adsorption ability of the modified electrodes to NO, and that also increases the sensitivity of the modified electrodes to NO electrooxidation.

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