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Electrochemical behaviors and hydration properties of multi-wall carbon nanotube coated electrodes in water

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Abstract

Vertically aligned and randomly oriented multi-wall carbon nanotube coated silicon substrates were used as electrochemical electrodes. The effects of anodization processes and cathodic treatments in deionized water on carbon nanotubes were studied by means of DC experiments as well as cyclic voltammetric (CV) measurements. Anodization processes modified as-grown and hydrophobic carbon nanotubes and converted them to become hydrophilic. Cathodic processes caused etching of carbon nanotubes. The etching products made originally clear water change into black water. The black etching products left on top of carbon nanotubes after water vaporized made the carbon nanotube coated electrode less hydrophobic than that of as-grown carbon nanotubes but also less hydrophilic than that of anodized carbon nanotubes.

Keywords: Carbon nanotubes; Electrochemical electrodes; Hydrophilic; Cyclic voltammetry

1. Introduction

Carbon nanotubes have been studied extensively and found to be promising as a new nanoscale material for a variety of potential applications [1] because of their excellent electrical properties, mechanical strength, and high resistance to chemical attacks [2–4]. For as-grown carbon nanotubes, polar substances such as water cannot wet the surfaces of carbon nanotubes easily. A large number of carbon-nanotube applications are hampered by the hydrophobic properties of as-grown carbon nanotubes. It is desirable to be able to modify the hydration properties of the surfaces of carbon nanotubes so that they become hydrophilic. Hydration properties of carbon nanotubes have been reported to be modified by oxidation and plasma activation processes [5–8]. In this study, behaviors and effects of anodic and cathodic treatments of carbon nanotubes in deionized water on hydration properties are reported and discussed [9–11].

2. Experimental details

A thermal chemical vapor deposition process was used for the growth of carbon nanotubes on silicon substrates [12]. The growth process was carried out in a vacuum quartz furnace with a flow of the gas mixture of argon and acetylene. Iron catalyst thin films were sputtered onto silicon substrates by a RF magnetron sputtering process and pre-treated to form nanopaticles before the growth of carbon nanotubes started. The deposition working pressure was 75 torr, and the typical growth time was 20 min at 700 °C. Both randomly oriented carbon nanotubes and vertically aligned carbon nanotubes with an average length of 20 μm were obtained by changing the catalyst deposition and treatment conditions.

3. Results and discussion

3.1. Electrochemical anodization

A randomly oriented carbon nanotube coated silicon substrate and a copper wire was immersed in deionized water. The experimental setup is shown in Fig. 1. The top half of the carbon nanotube coated electrode, which was in the air above water, shown in Fig. 1 appears black while the bottom half of the carbon nanotube coated electrode, which was immersed in water, shows the total reflection of light from the water–air interface above the hydrophobic carbon nanotubes. If carbon

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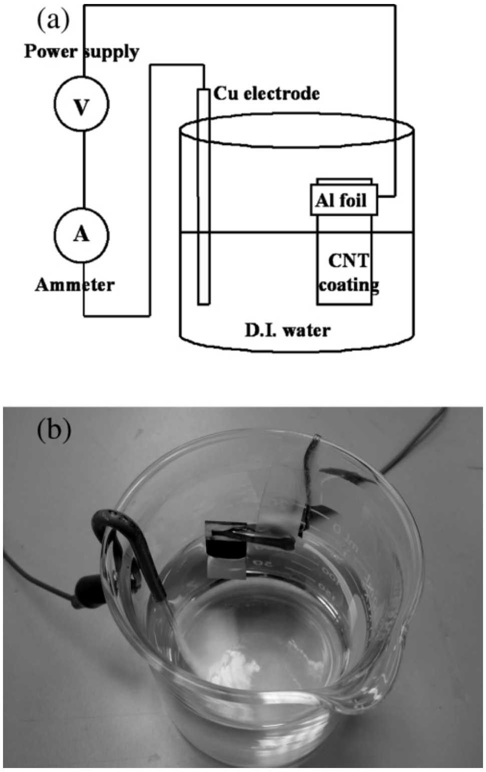

Fig. 1. (a) Schematic diagram for electrochemical anodization by immersing carbon nanotubes into deionized water. (b) Experimental setup for (a).

nanotubes are hydrophilic, the carbon nanotube coated electrode that is immersed in water will be wet by water and appears black similar to the way it appears in air.

A positive voltage of up to 5 V with respect to the copper electrode was applied to the carbon nanotube coated silicon substrate causing an electrical current to flow through water. The electrical current was small in the microampere range and increased slightly with time. While the carbon nanotubes were anodized, hydrogen bubbles appeared around the copper counter electrode. Carbon nanotubes that were immersed into deionized water and anodically treated turned from hydrophobic to hydrophilic gradually while water slowly wet the surfaces of carbon nanotubes and made the hydrophilic portion of the carbon nanotube coated electrode appear black instead of the appearance due to the total reflection of light under water by the water–air interface on top of the hydrophobic carbon nanotubes.

Fig. 2 shows a partially hydrophilic carbon nanotube coated electrode that is in the process of being anodized. Islands of black areas could be seen on the carbon nanotube coated silicon electrode that was immersed in water. The conversion process from hydrophobic to hydrophilic carbon nanotubes appeared to start from certain parts of the carbon nanotube coating on silicon instead of from everywhere simultaneously. These islands expanded in area while additional small islands were created. Black appearing and hydrophilic islands of carbon nanotubes eventually merged, and the carbon

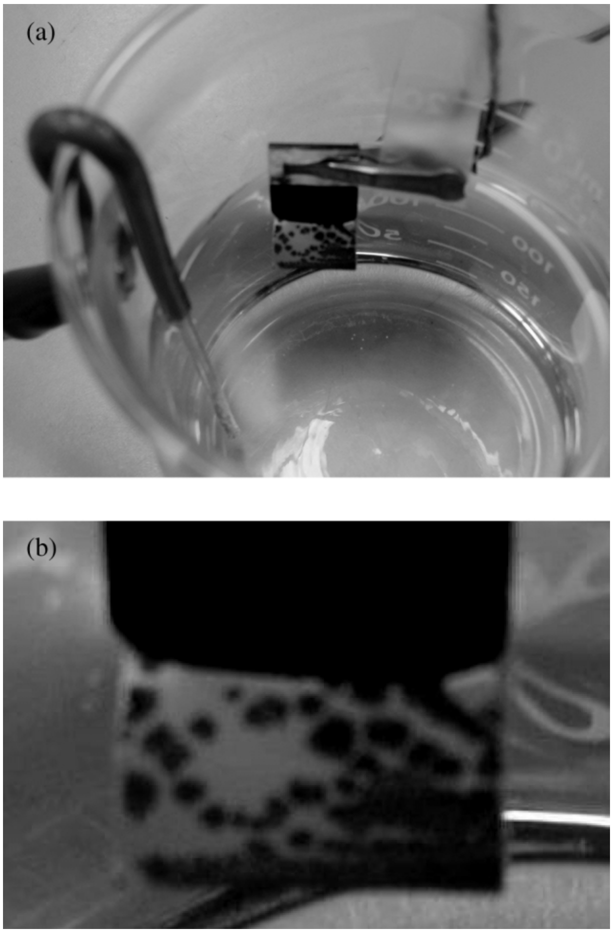

Fig. 2. Partially anodized carbon nanotubes in water. (a) Experimental set up with the bottom half of the carbon nanotube coated silicon electrode immersed in deionized water. A +5 V was applied to the carbon nanotube coated electrode for 2 min. (b) Enlarged view of the carbon nanotube coated electrode. The upper part was not immersed in water and, therefore, remained hydrophobic. Hydrophilic carbon nanotube islands were formed on the carbon nanotube coated electrode that was immersed in water.

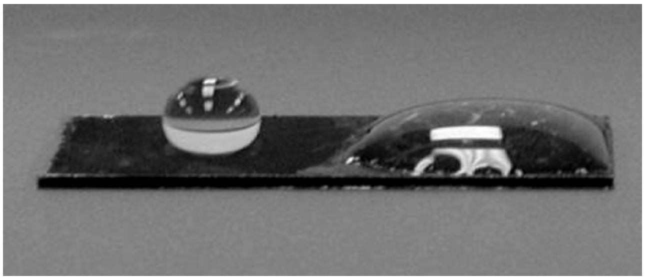

Fig. 3. A water drop on as-grown hydrophobic carbon nanotubes (left) and a water film on the electrochemically anodized hydrophilic carbon nanotubes (right).

nanotube coated electrode was converted from being hydrophobic to hydrophilic. Fig. 3 shows a water drop on the as-grown hydrophobic carbon nanotubes (left-hand side) and a water film on the electrochemically anodized hydrophilic carbon nanotubes (right-hand side). The photograph clearly shows that water does not wet the as-grown carbon nanotubes while it wets the electrochemically treated carbon nanotubes easily.

Silicon coated with vertically aligned carbon nanotubes was found to be more difficult to be anodized. When the same voltage as that applied to randomly oriented carbon nanotubes was applied to vertically aligned carbon nanotubes, little electrical current was allowed to flow in the circuit due to the lack of a conduction path between water and the electrode with a high number density of vertically aligned carbon nanotubes which were hydrophobic and did not allow water to wet them. The observation suggested that since tips and walls of randomly oriented carbon nanotubes were subjected to the wetting by water, there were more defective sites on the carbon nanotubes that allowed the initial wetting by water and; therefore, the better conduction of electrical current. This is believed to be the cause of the observed hydrophilic island formation in the anodization process for randomly oriented carbon nanotubes.

The current flow in the circuit for anodization of vertically aligned carbon nanotubes remained constant instead of increasing with time like it did for the anodization of randomly oriented carbon nanotube coated electrodes. The measured current likely flew through the backside of the silicon substrate instead of the hydrophobic carbon nanotubes that were not wet by water. To make sure all the electrical current flew through carbon nanotubes, the carbon nanotube coated electrode was not immersed in water. Instead, a drop of deionized water was placed on top of an as-grown vertically aligned carbon nanotube coated silicon substrate. A gold foil was attached on one end of the electrode to allow the application of voltage to the carbon nanotubes. A tungsten wire was inserted into the water drop as the counter electrode with an applied negative voltage with respect to the carbon-nanotube coated sample. Electrical current flew from carbon nanotubes under the water drop through the water drop to the tungsten wire counter electrode.

The experimental setup is shown in Fig. 4. A higher positive voltage of up to 10 V than that used for anodization of randomly oriented carbon nanotubes was needed to be applied to the nanotubes with respect to the tungsten wire causing an electrical current to flow through the water drop in the range of microamperes. Gas bubbles came out around the tungsten wire as soon as the voltage was applied and the water drop gradually decreased in size, and carbon nanotubes that were in contact with the water drop became hydrophilic. When a positive voltage of 10 V was applied, the flowing electrical current increased from a few microampere to 100 μA and then decreased down to 0 μA, i.e. forming an open circuit, within an hour or so when the water drop vaporized and disappeared. After this anodization process, water films could be formed on the anodized area, but water could not wet the remaining as-grown carbon nanotubes. Fig. 5 shows SEM photograph for the top view of an electrochemically anodized carbon nanotube coated silicon electrode. After the electrochemical anodization process, tips of vertically aligned carbon nanotubes became hydrophilic and joined with neighboring tips of carbon nanotubes to form a network instead of showing individual tips of carbon nanotubes. This surface carbon nanotube network is expected to have less electric field enhancement than vertically aligned carbon nanotubes with individual and separated carbon nanotubes. It indeed affected the electron field emission properties of anodized carbon nanotubes that will be discussed in the following section.

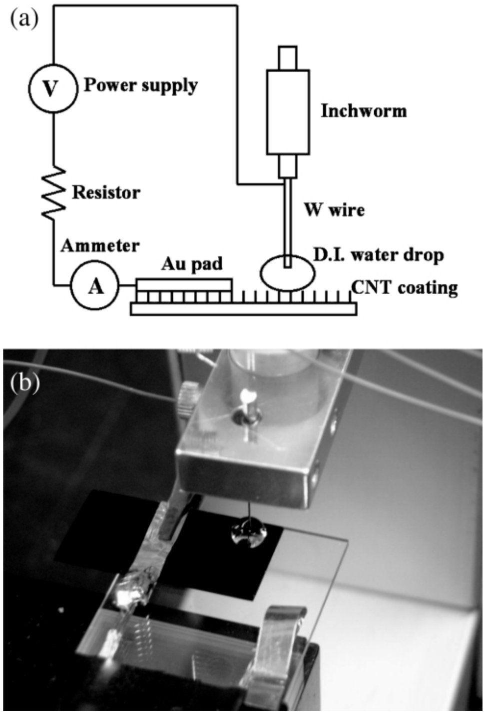

Fig. 4. (a) Schematic diagram for electrochemical anodization by placing a deionized water drop on carbon nanotubes. (b) Experimental setup for (a).

3.2. Cathodic treatments

Similar experiments were carried out with a negative voltage being applied to the carbon nanotubes with respect to the counter electrode. A randomly oriented carbon nanotube coated silicon electrode was immersed into deionized water with a negative voltage up to −5

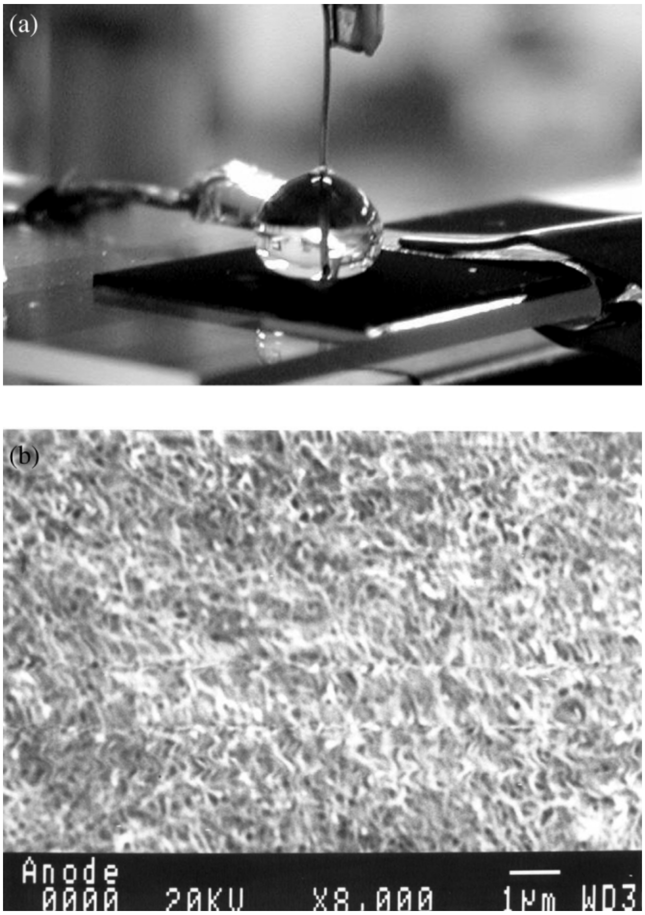

Fig. 5. (a) The contact area between a water drop and the carbon nanotube coated electrode increased during the electrochemical anodization process. (b) SEM photograph of the electrochemically anodized carbon nanotubes.

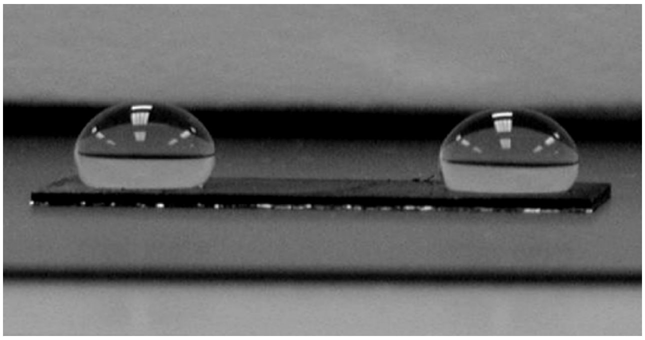

Fig. 6. A water drop on as-grown carbon nanotubes (left: hydrophobic) and a water drop on carbon nanotubes after 25 min of cathodic treatment in deionized water with -5 V applied to the carbon nanotubes with respect to a copper counter electrode in water (right: hydrophobic).

V applied to the electrode. Fewer bubbles in the cathodic process were observed than the anodization experiments. The detected electrical current increased within a range of microamperes from 6.7 to 7.6 μA in 25 min of operating. After 25 min of cathodic treatment, water films still could not be formed on carbon nanotubes that were immersed into deionized water and served as the cathode indicating that carbon nanotubes were not converted from hydrophobic to hydrophilic. Fig. 6 shows water drops on both as-grown carbon nanotubes and carbon nanotubes that were subjected to 25 min of cathodic treatment in deionized water with -5 V applied voltage to carbon nanotubes with respect to the copper counter electrode.

For vertically aligned carbon nanotubes, a negative voltage of -10 V, was applied to the carbon nanotube coating, on which a drop of water was placed and a tungsten wire was inserted into water as the counter electrode. The detected electrical current started from tens of microamperes and increased to more than 2 mA after 1 min or so experiment. The treated area became slightly hydrophilic but a water film still could not be formed completely on the cathodically treated area of the carbon nanotube coated silicon. The applied voltage was reduced to -2 V in order to monitor the current change at a different site on the same carbon nanotube coated silicon electrode used for the previous experiment. As soon as the voltage was applied, an electrical current of 16 μA started to flow and then increased in magnitude. It increased and exceeded 2 mA in approximately 5 min. During this process, the color of the water drop changed gradually from clear to black. The black water drop was removed and placed on a molybdenum plate. After water vaporized, the remaining black reaction products could be seen in Fig. 7. Fig. 8a shows carbon nanotube coating after the cathodic treatments through a water drop placed on the top of a carbon nanotube coated electrode using -10 V applied voltage. Water vaporized before the photograph was taken. Fig. 8b and c show carbon nanotube coating after a cathodic treatment, in which a water drop was placed on carbon nanotubes and -2 V was applied to the carbon nano-

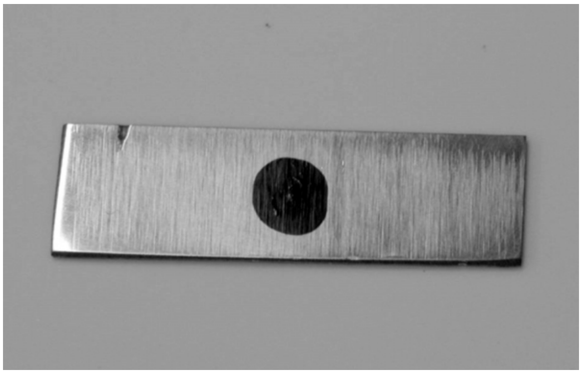

Fig. 7. The black water generated during the cathodic processing was placed on a molybdenum substrate. After water vaporized, black reaction products were left on the surface of the molybdenum substrate.

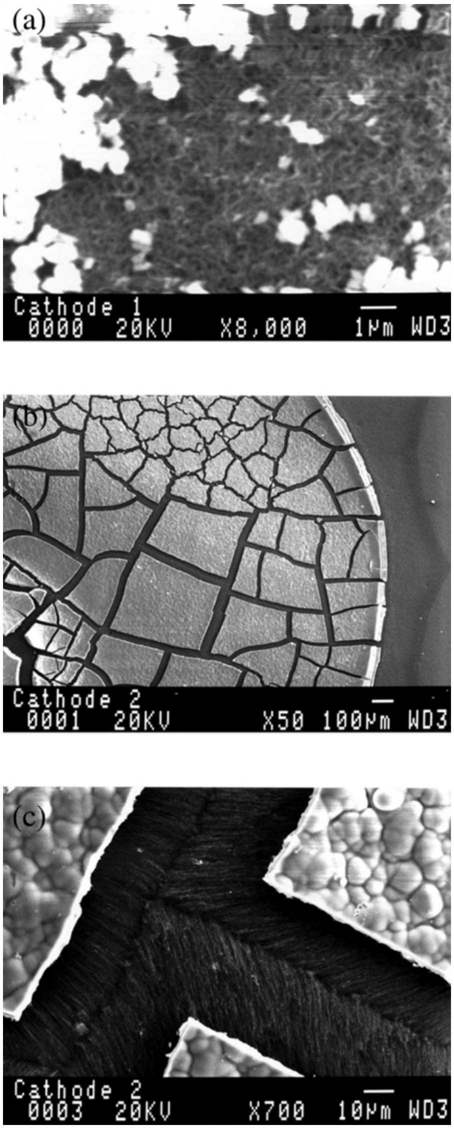

Fig. 8. (a) CNT coating after cathodic treatments with −10 V applied voltage and after the water drop was removed. (b) and (c) CNT coating with −2 V applied voltage and after the black water drop was removed.

tubes. A residual coating by the black cathodic reaction products can clearly be seen in these photographs.

3.3. Cyclic voltammetry (CV) of aligned multi-wall carbon nanotubes

A deionized (DI) water drop was placed on the surface of an aligned carbon nanotube coated electrode and a cyclic voltammetric (CV) experiment was performed in the potential ranging from −0.4 to 1.0 V (vs. Ag). The experiment was conducted by using a platinum wire as the anode, a silver wire as the reference electrode. As expected, CVs obtained from MWNT by using DI-water showed only a featureless voltammogram as shown in Fig. 9.

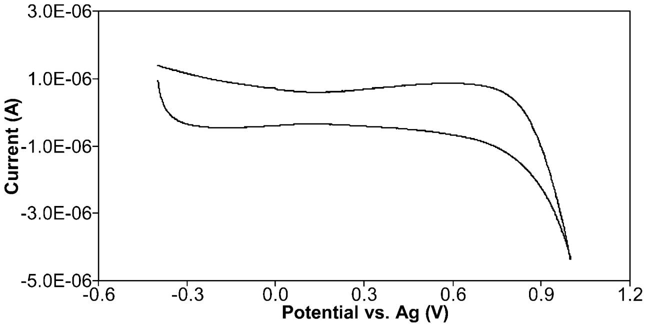

Fig. 9. Cyclic voltammogram of hydrophobic MWNT electrode in deionized water. The scan rate is 100 mV/s.

However, after running a number of cycles the first obvious cathodic and anodic peaks were observed at −0.31 and −0.26 V, respectively. Moreover, the peak current increased gradually as shown in Fig. 10. Both cathodic and anodic peaks indicate the reactions at the MWNT electrode surface since the applied potential and oxygen ions from DI-water could oxidize the MWNT and change it from hydrophobic to hydrophilic state as stated in a previous section. The black colloid particles suspended in the droplet on the MWNT electrode surface were observed. These suspended colloids were products of the etching of the carbon nanotubes as the voltage applied and might be one of the factors, which increased the electrical conductivity of the DI-water and caused the redox reactions.

Fig. 10 shows the redox peaks corresponded to the reduction and oxidation of the surface of MWNT caused by the presence of the etching products. This result showed the presence of ions (etching products) in the DI-water besides MWNT alone (Fig. 9), which could be carbon black, graphite, or other existing carbon ions. At the electrode, the obvious cathodic (C) peak was observed at −0.31 V and the peak current increased and shifted toward positive direction after a few cycles. The anodic (A) peak was observed at −0.26 V and the peak current increased and shifted toward positive direc-

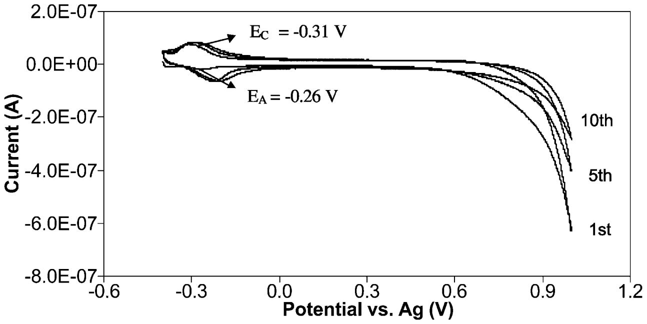

Fig. 10. Cyclic voltammograms of hydrophobic MWNT electrode in deionized water. The scan rate is 100 mV/s.

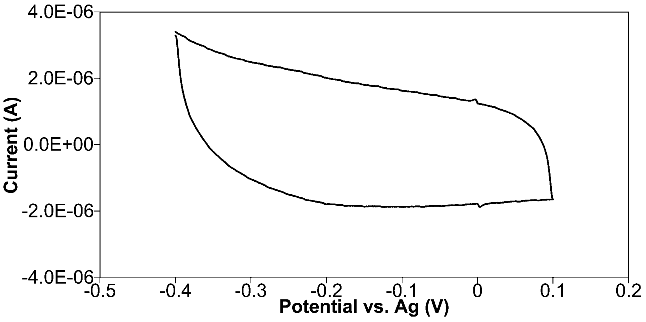

Fig. 11. Cyclic voltammograms of hydrophilic MWNT electrode in deionized water. The scan rate is 100 mV/s.

tion after a few cycles as well. These suggested that MWNT increased the surface area of the electrode and caused the background current of electrode to become stronger than that of the first cycle.

In this experiment, the hydrophilic MWNT was investigated as well. By thermal oxidation in the ambient air, the MWNT changed from hydrophobic to hydrophilic state [6]. The cyclic voltammetry was utilized to observe this hydrophilic MWNT in the potential range of -0.4 to 0.1 V. The experiment was conducted by using a platinum wire as the anode, a silver wire as the reference electrode. CVs obtained from hydrophilic MWNT showed featureless voltammogram as shown in Fig. 11.

Based on the CVs obtained from both hydrophobic and hydrophilic MWNT the background current of the hydrophilic MWNT was higher. This might be the case since the hydrophobic MWNT has little contacting area (only a few hydrophilic spots might have existed in the imperfect carbon nanotube coated electrode) compared with that of hydrophilic one, which allows not only the tip, but also the walls of the tubes as electrical contacts.

4. Conclusions

Electrochemical behaviors of multi-wall carbon nanotubes have been studied. Electrochemical anodization was applied to convert both vertically aligned and randomly oriented carbon nanotubes from the hydrophobic state to the hydrophilic state. Electrochemical cathodic reactions resulted in the etching of multi-wall carbon nanotubes and the production of black colloidal particles suspended in the water droplet on the carbon nanotube coated electrode surface. These colloidal particles increased the conductivity of the water droplet by several orders of magnitude depending on its concentration.

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